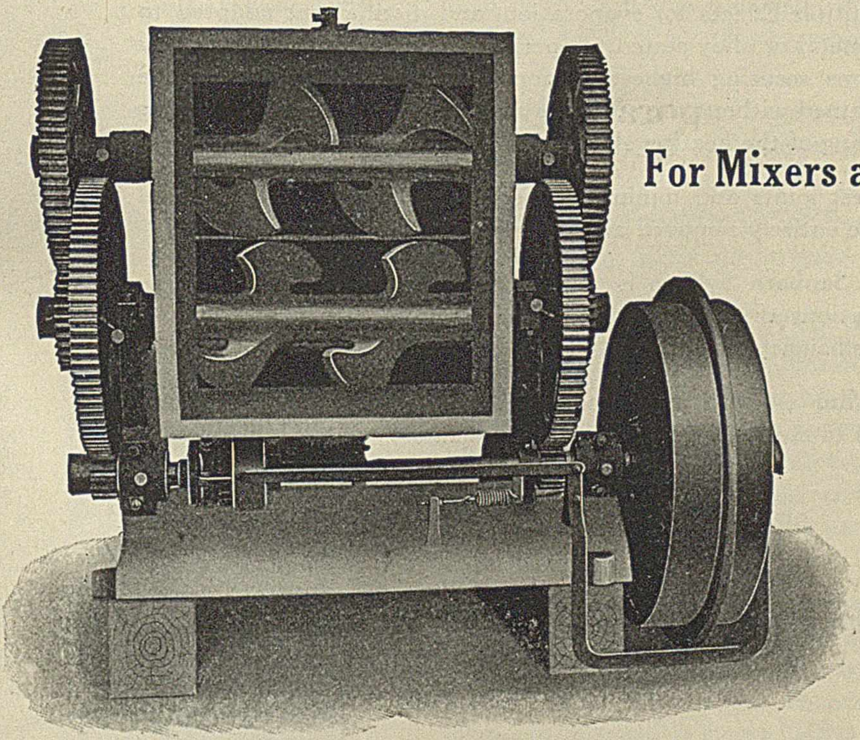
Some of the Materials with which the "Universal" Kneading and Mixing Machines have been Successful

Accumulator Mass
Aniline
Asphalt
Blacking
Blasting Powders
Bone Fat
Butter
Calcium Carbide
Celluloid
Cheese
Chocolate
Cocoa
Colours, Dry and Wet
Compositions of all kinds
Core Sand and Loam
Cordite
Crucible Paste
Dextrine
Dog Biscuits
Doughs of every description
Drugs
Electrode Mass
Electric Carbons
Emery Wheel Compositions
Enamel
Explosives
Face Powder
Felt (Artificial)
Glass
Gum (Chewing)
Gun Cotton
Gunpowder
Gutta Percha
Horn (Artificial)
India Rubber and Gutta Percha
Indigo Doughs and Solutions
Insulating Material
Ivory (Artificial)
Lacquers of every description
Lead Pencil Composition
Leather (Artificial)
Linoleum
Macaroni, Vermicelli, etc.
Margarine
Milk (Condensed)
Modeling Clay
Molasses
Paper Cellulose
Paper Pulp
Papier Mache
Paint
Pulp
Putty
Rubber and Rubber Solutions
Silk (Artificial)
Starch
Viscose
Vulcanite
Wall Paper
Yeast



Mixer for Stiff Mass. Power Tilting Arrangement.

For Mixers and Kneaders, Vacuum Kneaders, Presses, Masticators, Rapid Dissolvers and Solution Making Machines

Inquiries Solicited
Demonstrations Arranged

WERNER & PFLEIDERER COMPANY

"The Best is the Cheapest"

MAIN OFFICE AND FACTORY
SAGINAW, W. S., MICHIGAN

NEW YORK, 41 Park Row SAN FRANCISCO, Pacific Building PHILADELPHIA, Drexel Building

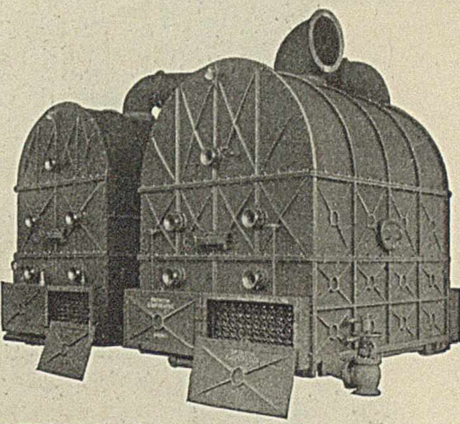
Cannstatt-Stuttgart, Wuerttemburg, Berlin, Cologne, Hamburg, Frankfort, Dresden, Vienna, London, Peterborough, Paris, Zurich, Hague, Milan, Moscow, Buenos Ayres

EVAPORATORS

ANY CAPACITY **ANY LIQUOR**

Single and Multiple effects designed to meet conditions as we find them.

Start the new year by planning a campaign to reduce your cost of manufacture (saving coal, labor, repairs, etc.) by the installation of modern equipment designed for your work by evaporation engineers who have the experience necessary to warrant your confidence.



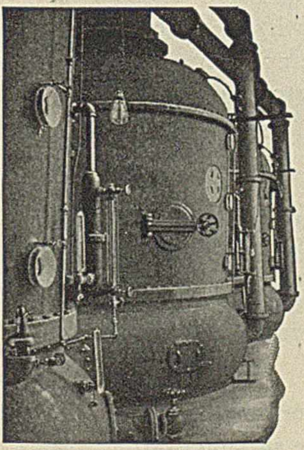
STANDARD SWENSON EVAPORATORS for straight concentration. Hundreds of installations have proved the merit of this design.

PATENTED SECO BASKET TYPE EVAPORATORS for crystallizing solutions. Also used where scale is apt to form on heating surface. Maximum circulation of **both** steam and liquor. Easily cleaned. For salt caustic, calcium chloride, glycerine, distilled water, etc.

STANDARD VERTICAL TUBE PANS for large installations, equipped for crystallizing solutions, also for straight work. All pans fitted with our patented vapor and steam controlling device, giving a perfect and uniform distribution of vapor to **all** the tubes, thereby increasing the amount of work possible with a given tube area.

SPECIAL LEAD EVAPORATORS (patent granted) for acid concentration. A design which is durable and efficient. Not lined or coated, but a substantial lead pan built for hard and continuous service.

EVAPORATORS FOR SPECIAL SOLUTIONS made of bronze, copper, aluminum, steel, cast iron, etc. Any of our standard type pans can be lined with brick, tile, cement or metal—a proven success for a good many years.



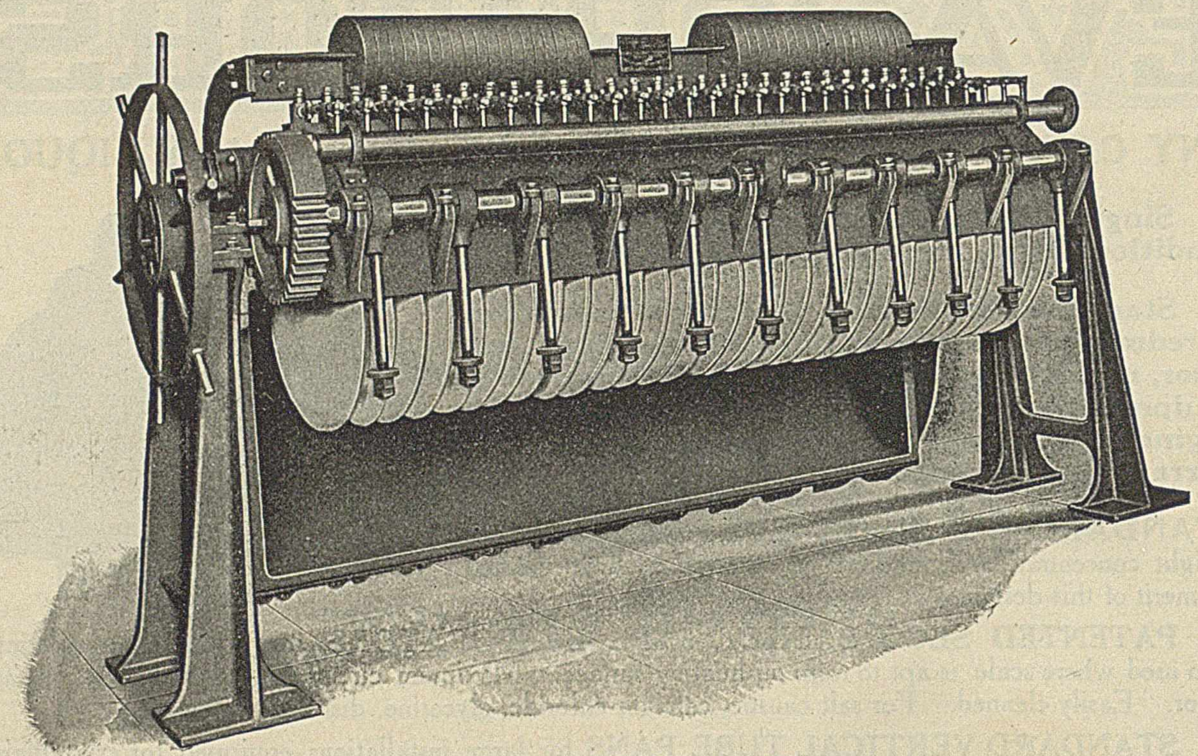
A NEW EVAPORATOR FOR HIGH DENSITY WORK —our latest and most important improvement. With this apparatus you can economically concentrate solutions (whether crystallizing or not) much heavier than is possible in any commercial equipment previously offered. We have successfully and continuously boiled down in this equipment calcium chloride to a 68 per cent solution with steam. Simple operation, easy cleaning, uniform results and small repairs make this an ideal design for high density work.

Economy, durability, accessibility, low repairs, easy operation and maximum simplicity in design (consistent with the attaining of these results) characterize Swenson Service. We can refer to more than 600 installations—fully half of which have been "repeat" orders. Assistance given in processes utilizing waste solutions or new chemical products.

Let us send one of our engineers to look over your conditions to determine the type best suited to your requirements

SWENSON EVAPORATOR CO.

945 Monadnock Bldg. **CHICAGO, ILL.**



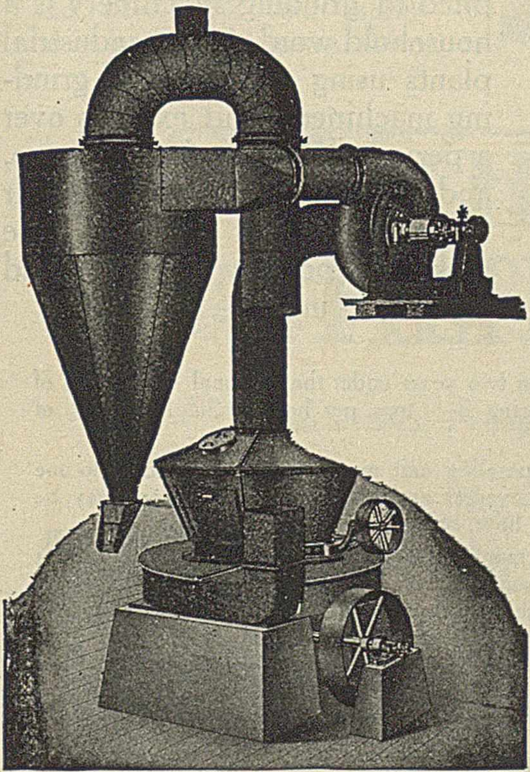
The Economy of Pulverizing Materials by the

RAYMOND PULVERIZING AIR-SEPARATING **SYSTEM**

has been proven by 400 plants which are reducing more than 100 materials of widely varying character

MANY of these concerns who were originally in doubt as to the adaptability of the Raymond System to their special grinding problem have, after a thorough trial, been unconditionally convinced of the economies produced by this system in their grinding departments.

The Raymond System produces these economies in many and various ways, the most striking of which is the elimination of expensive screening, elevating and conveying machinery. This is accomplished by using air-separation instead of screens to produce the fineness; at the same time, without any extra power, this air delivers the finished product direct to the next point of operation or storage.



This reduces the amount of labor and repairs required with other methods of grinding and at the same time produces a greater capacity per horse-power and a finer, more uniform product than any other method.

Wouldn't it be worth your while to investigate the possibilities of the Raymond System in your grinding department?

——THE COUPON IS FOR YOUR CONVENIENCE——

We design special machinery and methods for Pulverizing, Grinding, Separating and Conveying all powdered products. We manufacture Automatic Pulverizers, Roller Mills, Vacuum Air Separators, Crushers, Special Exhaust Fans and Dust Collectors.

Send for our Book

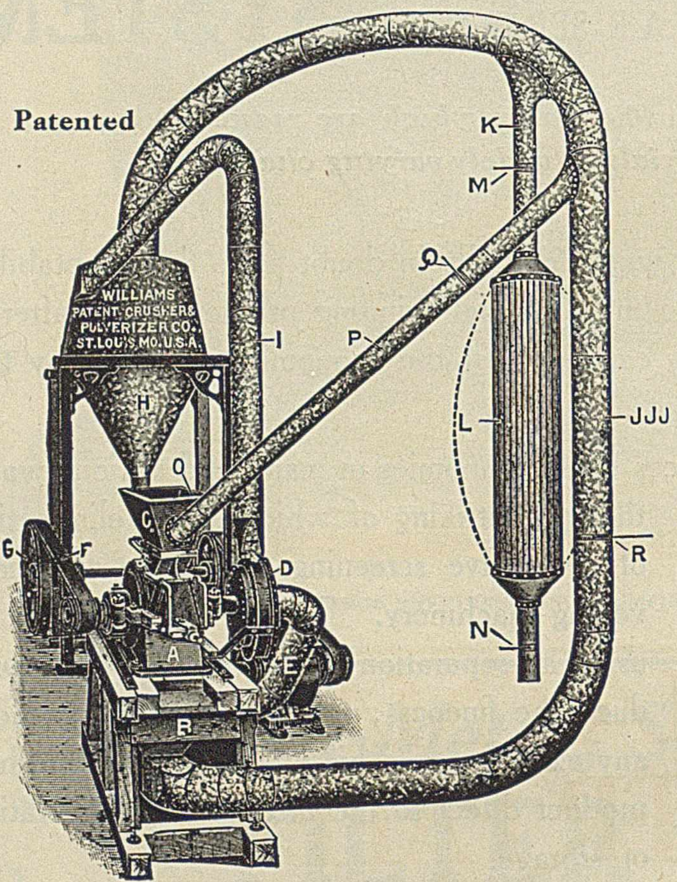
RAYMOND BROS. IMPACT
PULVERIZER COMPANY
1308 No. Branch Street, CHICAGO, ILL.

Please send us your literature.

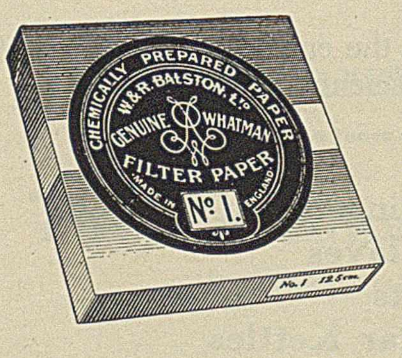
NAME..

STREET..

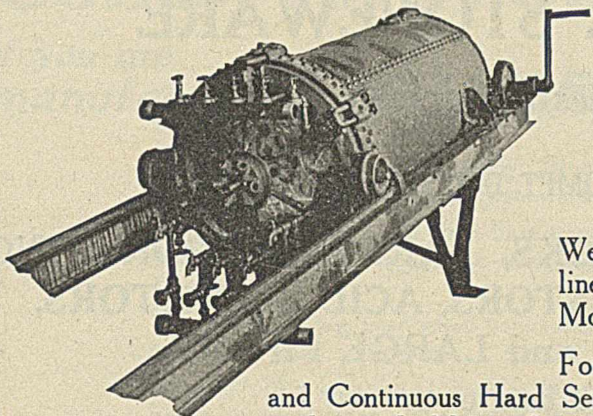
CITY............STATE..


Patented
K
M
Q
P
I
WILLIAMS
PATENT CRUSHER &
PULVERIZER CO.
ST. LOUIS, MO. U.S.A.
H
O
C
G
F
D
A
E
B
L
JJJ
R
N


CHEMICALLY PREPARED PAPER
W.&R. BALSTON, Ltd
GENUINE WHATMAN
FILTER PAPER
No. 1


CHEMICALLY PREPARED PAPER
W.&R. BALSTON, Ltd
GENUINE WHATMAN
FILTER PAPER
MADE IN ENGLAND
No. 1.
No. 1 12.5 cm.

KELLY FILTER PRESS PATENTED



Used in the following industries: Mines, Chemical Works, Paper Mills, Oil Refineries, Sugar Houses, Soap and Soda Works, Sewerage Disposal Plants, Color Works, Water Works, Tanneries, etc.

We furnish these presses, Copper, Lead and Nickel lined, and cast of Brass, Copper, Phosphor Bronze and Monel Metal. Also jacketed to keep presses hot or cold.

For Dry Cakes, Complete Wash, Minimum Labor Costs and Continuous Hard Service, buy **"The Kelly."** *We are prepared to make quick delivery from stock.*

FILTER PLATES—THE DAVIS PATENT: Made of heavy metal, indestructible, filtering as fast and clean as cloth.

FILTCHAR: A new decolorizing carbon of exceptional efficiency, and economical in price. Available in various grades of fineness to meet all requirements. Free of sulphur and arsenic. Regular supplies guaranteed.

For information, catalogs, blueprints, etc., apply to the nearest agency

New York: **EMIL E. LUNGWITZ, 30 CHURCH STREET**

KELLY FILTER PRESS COMPANY, ***Salt Lake City, Utah*** ***Berlin:*** **A. L. GENTER, FREDERICHSTR. 60**

EVAPORATORS

OF ANY SIZE—FOR ANY SERVICE

The Zaremba Patent Evaporator

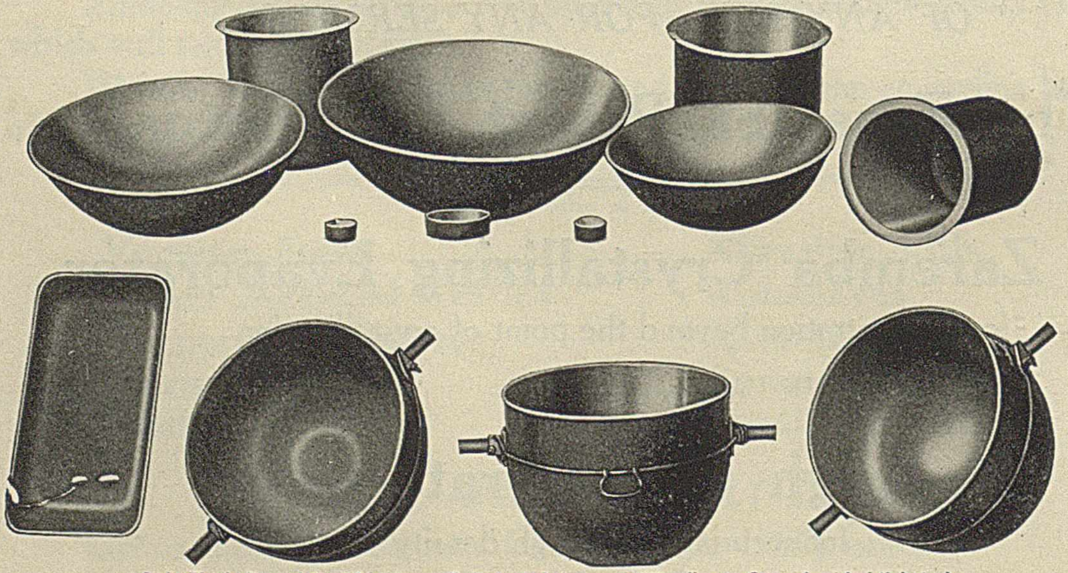
The Zaremba Crystallizing Evaporator

for concentration beyond the point of crystallization

High Concentrators

for securing extra high density

ZAREMBA CO. D. S. MORGAN BUILDING **BUFFALO, N. Y.**



Come to Woodbridge, N. J.,

if you are manufacturing **Stoneware Products**

Geologically and geographically, Woodbridge, New Jersey, constitutes an ideal locality for the manufacture of Stoneware Products.

Not only is this section in immediate touch with the greatly increased market demand in the East, but in Woodbridge there is a great variety of Clays of pure and adaptable quality.

Woodbridge enjoys unequalled transit facilities. Good industrial sites are readily acquired and labor is plentiful.

Situated within eighteen (18) miles from the City Hall of New York City, Woodbridge is within reach of more than 10,000,000 people who represent every sort of industrial activity and manufacture.

We want live, energetic manufacturers who can make the most of the excellent possibilities which Woodbridge offers for the manufacture of Stoneware Products.

We will furnish samples of Woodbridge Clay for your inspection and test, and will also give any further details desired.

Woodbridge Industrial and Development Co.

CHARLES L. STEUERWALD, *Manager*

Post Office Bldg. WOODBRIDGE (Middlesex Co.), N. J.

Our Guarantee

Royal Guernsey Porcelain, Casserole with Porcelain Handles, Glazed Inside and Outside

Trade GUERNSEY Mark.

Guernseyware for your Laboratory

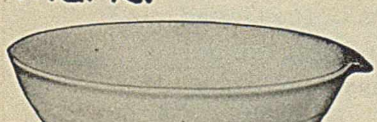
When you see this Trade Mark on Chemical Porcelainware, you know that it has been thoroughly tested and is the equal of any Laboratory Porcelain made. We stand back of every piece of GUERNSEYWARE, with our guarantee of Quality and Service, the equal of any Standard Porcelain made anywhere in the world. A piece of GUERNSEYWARE that does not give as satisfactory service, we will replace to you with your following shipment. *No Charge.* All we ask, is the same treatment in usage.

Write now for March 1, 1916, Catalog "B" and prices, before you place your next order

The Guernsey Earthenware Company

41 East End Street

Cambridge, Ohio U. S. A.



Royal Guernsey Porcelain Evaporating Dish with Lip

Royal Guernsey Porcelain Covered Crucible

CHEMICAL APPARATUS

1841

We are the only concern in the United States with the expert engineering knowledge, plant and experience necessary to furnish much of the special equipment required by the chemical industry at the present time. A knowledge of this has meant thousands of dollars to many concerns under special conditions now existing.

1915

Recent installations and orders include:

Stills—
- Vacuum
- Pressure
- Badger-Barbet

Continuous, Discontinuous for:
- Toluol
- Benzol
- Xylol
- Acetone
- Ether
- Methyl Alcohol
- Ethyl Alcohol
- Ammonia
- Carbon Tetrachloride
- Phenol
- Ethyl Nitrite
- Ketone Oils
- Wood Oil
- Rum
- Acetic Acid, in crude form, refined form, mixtures

- Iron Autoclaves
- Copper Autoclaves
- Lead-lined Autoclaves
- Silver-lined Autoclaves
- Iron and Copper Multiple Effect Evaporators
- Mixing Tanks
- Mixing Stills
- Dissolving Tanks
- Crystallizing Tanks
- Retorts
- Copper and Iron Tanks
- Nitrators
- Condensers
- Absorption Columns
- Steam-jacketed Copper and Iron Kettles
- Piping
- Pyrometer Systems

COMPLETE PLANTS

BENZOL RECOVERY
BENZOL REFINING
ALCOHOL PRODUCTION
PHENOL MANUFACTURE
WOOD DISTILLATION
ACETONE PRODUCTION
ETHER MANUFACTURE
SOLVENT RECOVERY

Our Line and Service

Apparatus

We construct any type of standard or special apparatus for chemical industries, including stills, dryers, evaporators, extraction and absorption equipment, etc.

Plants

We contract for the erection of complete plants, involving our special apparatus or systems.

Research

We investigate conditions under which apparatus must work; make tests on materials to be handled, and advise on process, design of apparatus, arrangement of plant, etc.

Why You Should Come to Us

Engineering

We have in our Engineering Department and in consulting capacity, experts of recognized highest authority.

Design

Our standard and special equipment represents absolutely the latest developments in its line.

Workmanship

We construct practically all apparatus furnished by us in our own shops; have skilled workers in lead, silver, copper and iron.

Deliveries

We specialize in quick deliveries and make them as promised.

Our customers include practically all of the largest chemical concerns in the United States, and in many cases we are exclusive constructors for them of apparatus in our line. We have proved that they cannot obtain elsewhere such service as we give them.

E. B. Badger & Sons Company, Boston, Mass.

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY
AT EASTON, PA.

Volume VIII MARCH, 1916 No. 3

Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly.
Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.
Entered as second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City
Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

Eschenbach Printing Company, Easton, Pa.

TABLE OF CONTENTS

EDITORIALS

SPRING MEETING OF AMERICAN CHEMICAL SOCIETY

The Fifty-Second Meeting of the American Chemical Society will be held at the University of Illinois, Urbana-Champaign, from Tuesday, April 18th, to Friday, April 21st, inclusive. The Beardsley Hotel, Champaign, has been chosen as headquarters; all meetings will be held at the University of Illinois.

The provisional program, printed elsewhere in this issue, includes as a special feature the dedication of the new chemistry building University of Illinois, when addresses will be made by Governor Edward J. Dunne of Illinois, President Edmund J. James, University of Illinois, W. R. Whitney of the U. S. Naval Board, and Professor Alexander Smith of Columbia University. The public lectures will be on the "Production and Use of Radium," by C. L. Parsons of the U. S. Bureau of Mines, and Dr. C. F. Burnham of Baltimore. A special excursion has been arranged to Danville, Illinois, where the following will be visited: Hegeler Brothers' Zinc Smelter and Sulfuric Acid Plant, Western Brick Company's Kilns, Three Rivers Coal Company's Strip Coal Mine.

COÖPERATION IN FOREIGN TRADE

An address by Joseph E. Davies, Chairman of the Federal Trade Commission, before the National Foreign Trade Council, at New Orleans, discusses the epochal opportunities that now confront American business in foreign trade, which has suddenly become a large factor in our national outlook.

Mr. Davies summarizes the general problems connected with the development of foreign trade as follows: production, shipping, banking and credit facilities, creation of markets and meeting of international competition.

Eighty-five per cent of the thousands of replies that the Trade Commission has received from a questionnaire directed to the business men of the United States disclose a demand for permission to coöperate in foreign trade, under Federal regulation.

Conditions of foreign competition which existed in the world's markets prior to the war are illustrated by typical examples of the effectiveness and comprehensive character of foreign methods:

> "A combination of non-competing manufacturing plants of Great Britain, for instance, are equipped to establish, and have established, joint selling agencies, with branch offices and warehouses, and with such effective organizations that they are equipped to handle any kind of service within their lines, from the sale of a handsaw to the building of a railroad.
>
> "Much of the oriental business of Germany, is alleged to have been acquired through so-called rings, * * * * The markets are scientifically studied and assiduously cultivated. In one of these rings, 48 different German manufacturers participated. Its organization with the local bank and home bank connections was complete. It had within its organization facilities for selling to a Chinaman a five cent file, or for planning, financing, and completing the industrial development of an entire province, opening harbors, building railways and telegraph lines, sinking mines, erecting factories, installing light and power plants, and even to clothing the people and marketing of products. * * * * * *
>
> "Prior to the war, in Germany, approximately 600 cartels or manufacturing and selling syndicates, of a high degree of integration in industry and capacity, were projecting their activities into foreign markets. It is generally recognized that at the same time there were approximately 130 international cartels of a similar character; and it may occasion surprise to know that the control of a smelting and refining plant in Colorado was owned by such a little known international organization.
>
> "At the University of Kiel there has existed, and does now exist, an institute for the study of world trade, subsidized by the Imperial Government of Germany, and organized with a corps of highly trained economists. In Turkey, during the last several years, a German trade paper has been published daily in both French and German.
>
> "The Imperial Government of Japan has projected its enterprise into foreign countries, with its government monopolies of salt, camphor, and tobacco. In Chosen, which is a new name for Korea, it is significant that there has been established an institute for the development of native Japanese chemical and industrial engineers. It is generally recognized that exporting and marketing Japanese firms threaten the complete domination of the Chinese trade.
>
> "These manifestations of activity in Europe and in the Orient are indicative of the kind and character of competition that will be met in foreign trade in the future. Subsequent to the war these conditions will be emphasized and activities will be intensified by the spur of economic necessity in some of the nations of Europe. Under conditions such as these, the embarkation of American enterprise into foreign trade and the maintenance of its rightful place there, will require the strongest initiative and the highest order of business intelligence."

Two-thirds of our exports consist of foodstuffs and materials to be used in manufacture abroad; these practically sell themselves, so that here our main problem is that of conserving these natural resources.

> "The remaining one-third of our exports are manufactured articles, and consist generally of two classes—specialties and staples. Here demand must be created; and foreign competition must be met. In specialties, the demand is largely created and the competition met through the popular character of the product. In staples, which constitute the large bulk of international trade in manufactured goods, the condition differs. The development of the demand is difficult, and the competition to be met most severe. * * * * * *
>
> "Relatively few of the larger organizations of the country manifest a desire to enter into extensive coöperation in foreign trade. They do not seem to feel the need of coöperative effort, because of their ability and capacity to project their own enterprises. In that connection it may be said, with some reservation, that a very substantial part of our foreign trade has been developed through large organizations of this character. This development of our foreign trade is characterized by the fact that the ownership and management of plants reside in a single corporation, and is in distinct contrast in the manner in which the foreign trade of some European countries has been developed, where similar results have been obtained through the syndicated relations of smaller manufacturers who retain the individual ownership and individual control of their respective plants."

The demand for coöperation comes especially from the manufacturer of staples. In many lines of manufacture it is impossible for a small concern to engage directly in foreign enterprise: cost is prohibitive, risk is too great, warehousing and credit facilities are individually impossible.

The census taken by the Federal Trade Commission discloses that misapprehension as to the application of the anti-trust laws to foreign commerce, and doubt as to the legality of such enterprise in the foreign fields amounted in many instances to a prohibition of any action in the foreign market.

> "It is the opinion of the Federal Trade Commission that enterprise in foreign trade should not be impeded by conditions of this kind. In the absence of injury to any American interest a greater degree of coöperation in export trade than is allowed in domestic trade may be beneficial to the country. If this is not now permitted by law, new legislation, to that end, properly safeguarding the public interest, should be enacted."

ORIGINAL PAPERS

RESEARCH ON THE CORROSION RESISTANCE OF COPPER STEEL

By D. M. Buck[1] and J. O. Handy[2]

Received January 22, 1916

In order to obtain further definite information relative to the influence of varying amounts of copper and other elements when alloyed with steel, an extended series of service tests was undertaken by the authors in the spring of 1914.

Following work which had been done by one of us,[3] we continued the practice of conducting the tests on full size, uncoated sheets, under exact service conditions, extreme care being taken so to plan the work that those differences found in the various grades of steel used could be safely ascribed to the influence of the particular element which had been added.

In addition to repeating work which had already been done on the effect of the addition of approximately 0.25 per cent copper, we have included in this test steels with a copper content as low as 0.04 per cent, as well as steels with higher amounts up to and including 2 per cent copper.

As will be seen from Tables I to III, we also made additions of phosphorus, silicon, aluminum, sulfur, roll scale, and, following a suggestion by a colleague[4] that the addition of cold steel to the middle ingots of the heat would cause them to outlast the first poured ingots, a similar amount of cold steel turnings was added to one of the ingots in exactly the same manner in which the copper had been added to the others.

Some work has also been done on the influence of annealing temperatures higher than the average practice, and we have kept careful records of inside and outside sheets of the pack,[5] and of the presence or absence of mill scale on the surface of the sheets at the time of exposure, to determine whether or not these differences in initial protection affected the ultimate time of failure of the sheets.

STEELS USED IN TESTS

Several heats of open-hearth and Bessemer steel were used in the tests. Table I gives the additions as they were made: the grade numbers given here are those used throughout this paper. It will be noted that in one instance ten ingots were used from a single heat, and that they differed one from the other only in the amount and kind of element which was added. In Tables II and III appear the final analyses of the sheets rolled from these ingots.

In the manufacture of basic open-hearth heat No. 7750, an effort was made to produce a wild, oxidized heat. The steel was melted "hot;" ore was fed faster than usual and continued even after carbon had been reduced to 0.12 per cent. Silica sand was added instead of dolomite. The heat had a very wild appearance, rose strongly in the moulds, and in addition, we had a running stopper in the ladle giving a divided stream, which of course favored oxidation. Analyses of the sheets from this heat by the Ledebuhr method showed an oxygen content averaging only 0.03 per cent, which is no higher than that in normal open-hearth steel.

Basic open-hearth heat No. 8857 was made without the addition of manganese or other deoxidizer at any stage.

Table I—Steels Used in Tests and Additions Made to Modify Them

Basic Open-Hearth Heat

Heat No. 6807 Grade	Heat No. 8805(*a*) Grade	Ingot No.	Additions Material	Additions Amount
..	..	1	None	....
2	2	2	Copper	0.25%(*d*)
3	3	3	Copper	0.50%(*d*)
4	4	4	Copper	1.00%(*d*)
5	5	5	Copper	2.00%(*d*)
6	6	6	None	....
7	7	7	Phosphorus	0.100%(*d*)
8	8	8	Silicon	0.300%(*d*)
9	9	9	Aluminum	8 ozs.
10	10	10	Sulfur	0.100%(*d*)
11	11	11	Cold steel	6 lbs.
Heat No. 8815 Grade	Heat No. 7699(*b*) Grade	Ingot No.		
12	12X	2	Copper to ladle	0.25%(*d*)
13	13X	2	Copper to mould	0.25%(*d*)
14	14X	3	None	....
Heat No. 7750 Grade		Ingot No.		
19		4	Copper	0.25%(*d*)
20		6	Copper Roll scale	0.25%(*d*) 20 lbs.
21		7	Roll scale	20 lbs.
22		8	Silicon	0.10%(*d*)
23		9	Phosphorus	0.10%(*d*)
24		3	None	....
Heat No. 8857 Grade		Ingot No.		
25		2	None	....
26		3	Copper	0.35%(*d*)
High Sulfur Bessemer Heat [Residual (Not Added) Sulfur]				
Grade		Ingot No.		
15		(*c*)	Copper	0.25%(*d*)
16		(*c*)	None	....
Normal Bessemer Heat				
Grade		Ingot No.		
17		(*c*)	Copper	0.25%(*d*)
18		(*c*)	None	....

(*a*) About 0.04 per cent residual copper. (*c*) See test.
(*b*) About 0.05 per cent residual copper. (*d*) Aimed at.

Basic open-hearth heat No. 8805 corresponds to heat No. 6807 (grades 2 to 11 inclusive) and the same additions were made in exactly the same way and in the same order. The composition is quite similar to No. 6807 *except that the copper* (*residual*) is about 0.04 per cent in all grades except those to which copper was added. Comparison of the results on sheets from these two heats affords information relative to the influence of comparatively small copper contents. The grade numbers for heat No. 8805 are the same as for No. 6807 except that an "X" has been added to each.

Basic open-hearth heat No. 7699 corresponds to

---

[1] Metallurgical Engineer, American Sheet and Tin Plate Company, Pittsburgh, Pa.

[2] Director of Laboratories of the Pittsburgh Testing Laboratory, Pittsburgh, Pa.

[3] This Journal, 6 (1913), 447; *Iron Age*, June 3, 1915; *Iron Trade Review*, June 10, 1915.

[4] Institute of Industrial Research, *Bull.* 5.

[5] Sheets are rolled in packs and the two outside sheets of the pack always carry on their surfaces much more mill scale (magnetic oxide of iron) than do the inside sheets.

heat No. 8815 and the additions were the same. *This heat, however, contained 0.05 per cent residual copper.*

SHEET MANUFACTURE AND EXPOSURE OF TEST PIECES

All of the operations of blooming, rolling, sheet rolling, etc., were conducted according to regular mill practice and were under the personal supervision of the authors. Enough sheet bars were taken from the product of each ingot to give us a large excess of sheets for our tests. The bars were taken from the piles at such points as to represent the whole ingot from top to bottom, thus securing the average product of the ingot. All grades were given exactly the same treatment in all of the manufacturing operations, and each sheet received the customary one (straightening) pass through the cold rolls.

TABLE II—LOSS IN OUNCES PER SQUARE FOOT PER MONTH FOR EACH PERIOD OF EXPOSURE IN TESTS AT SCOTTDALE AND MCKEESPORT, PENNSYLVANIA

	PERCENTAGES PRESENT						Annealing temp.	SCOTTDALE TESTS			MCKEESPORT TESTS				RANK	
GRADE	C	Mn	S	P	Si	Cu	° F.	6.5 mo.	9.53 mo.	Av.	8.2 mo.	10.9 mo.	Av.	GRAND Av.	See Text	ELEMENT ADDED
2	0.06	0.41	0.039	0.032	0.004	0.272	1400	0.1411	0.1361	0.1386	0.1134	0.1057	0.1095	0.1241	9	Copper
							1600	0.1405	0.1382	0.1393	0.1041	0.1045	0.1043	0.1218		Copper
3	0.06	0.43	0.045	0.041	0.004	0.549	1400	0.1423	0.1345	0.1384	0.1089	0.1047	0.1068	0.1226	8	Copper
							1600	0.1374	0.1338	0.1356	0.1043	0.0961	0.1002	0.1179		Copper
4	0.07	0.43	0.039	0.036	0.004	1.085	1400	0.1389	0.1319	0.1354	0.1039	0.1007	0.1023	0.1188	3	Copper
							1600	0.1375	0.1353	0.1364	0.0991	0.0962	0.0976	0.1170		Copper
5	0.06	0.42	0.042	0.040	0.004	2.180	1400	0.1314	0.1294	0.1304	0.1005	0.0941	0.0973	0.1138	1	Copper
							1600	0.1332	0.1303	0.1317	0.0966	0.0905	0.0935	0.1126		Copper
6	0.06	0.45	0.047	0.035	0.004	0.018	1400	0.3723	0.4202	0.3962	0.1843	0.2215	0.2029	0.2996	19	None
							1600	0.2632	0.3831	0.3231	0.1634	0.2007	0.1820	0.2526		None
7	0.06	0.44	0.047	0.089	0.009	0.016	1400	0.3040	0.3564	0.3302	0.1589	0.1682	0.1635	0.2469	16	Phosphorus
							1600	0.2692	0.3258	0.2975	0.1460	0.1620	0.1540	0.2257		Phosphorus
8	0.06	0.41	0.045	0.034	0.319	0.016	1400	0.3521	0.4747	0.4134	0.2016	0.2027	0.2021	0.3078	20	Silicon
							1600	0.3186	0.3909	0.3547	0.1527	0.1656	0.1593	0.2569		Silicon
9	0.06	0.43	0.047	0.036	0.007	0.017	1400	0.3764	0.4732	0.4248	0.2103	0.2335	0.2219	0.3233	22	Aluminum
							1600	0.3591	0.4758	0.4174	0.1932	0.1890	0.1911	0.3043		Aluminum
10	0.06	0.43	0.075	0.028	0.008	0.019	1400	0.4327	0.5144	0.4735	0.2341	0.2926	0.2633	0.3684	24	Sulfur
							1600	0.4211	0.5206	0.4708	0.1960	0.2464	0.2212	0.3460		Sulfur
11	0.05	0.44	0.037	0.030	0.003	0.014	1400	0.3746	0.4538	0.4142	0.1923	0.2204	0.2063	0.3103	21	Steel
							1600	0.3023	0.3693	0.3358	0.1717	0.1823	0.1770	0.2564		Steel
12	0.06	0.46	0.028	0.035	0.003	0.242	1400	0.1386	0.1381	0.1383	0.1073	0.1030	0.1051	0.1217	5	Copper
							1600	0.1406	0.1394	0.1400	0.1107	0.1056	0.1081	0.1241		Copper
13	0.06	0.56	0.034	0.033	0.010	0.266	1400	0.1388	0.1401	0.1394	0.1043	0.1064	0.1053	0.1224	7	Copper
							1600	0.1431	0.1377	0.1404	0.1079	0.1073	0.1076	0.1240		Copper
14	0.08	0.60	0.035	0.032	0.006	0.014	1400	0.3344	0.3477	0.3410	0.1785	0.1745	0.1765	0.2588	17	None
							1600	0.2729	0.3104	0.2916	0.1788	0.1914	0.1851	0.2384		None
15	0.06	0.50	0.140	0.093	0.006	0.256	1400	0.1332	0.1458	0.1395	0.1022	0.1020	0.1021	0.1208	4	Copper
16	0.06	0.47	0.142	0.096	0.004	0.008	1400	0.4221	0.5018	0.4619	0.2547	0.2353	0.2450	0.3535	23	None
17	0.07	0.48	0.048	0.112	0.012	0.260	1400	0.1280	0.1358	0.1319	0.1028	0.0963	0.0995	0.1157	2	Copper
18	0.07	0.49	0.052	0.112	0.010	0.004	1400	0.3301	0.3911	0.3606	0.1895	0.1922	0.1908	0.2757	18	None
19	0.07	0.29	0.029	0.016	0.009	0.265	1400	0.1403	0.1366	0.1384	0.1074	0.1037	0.1055	0.1220	6	Copper
20	0.06	0.31	0.039	0.018	0.005	0.102	1400	0.1469	0.1478	0.1473	0.1155	0.1125	0.1140	0.1307	10	Copper and scale
21	0.06	0.26	0.030	0.017	0.005	0.014	1400	0.2849	0.2984	0.2916	0.1649	0.1711	0.1680	0.2298	14	Scale
22	0.06	0.29	0.033	0.018	0.123	0.016	1400	0.3026	0.3342	0.3184	0.1604	0.1606	0.1605	0.2394	15	Silicon
23	0.06	0.29	0.035	0.068	0.006	0.015	1400	0.2366	0.2571	0.2468	0.1406	0.1476	0.1441	0.1955	12	Phosphorus
24	0.06	0.30	0.027	0.016	0.004	0.014	1400	0.2752	0.2939	0.2845	0.1677	0.1684	0.1680	0.2263	13	None
50	0.02	0.03	0.031	0.005	0.002	0.041	1400	0.1588	0.1577	0.1582	0.1156	0.1178	0.1167	0.1375	11	———

All sheets (except those annealed at higher temperature) were annealed at one time in the same furnace, thus securing uniform heat treatment. To determine the possible influence of higher annealing temperature, one-half of the sheets of grades 2 to 14, inclusive, were annealed at a temperature about 200° F. higher than the normal temperature for sheets. The remainder of the sheets of these grades and all other grades were annealed at the usual temperature (1400° F.). After the annealing process the sheets were laid out in piles and the twenty-four (24) sheets required for our tests were taken at regular intervals from the piles, an average product being thus obtained.

TABLE III—LOSS IN OUNCES PER SQUARE FOOT PER MONTH FOR EACH PERIOD OF EXPOSURE

	PERCENTAGES PRESENT						MCKEESPORT TESTS			
GRADE	C	Mn	S	P	Si	Cu	8.2 mo.	10.9 mo.	Av.	ELEMENT ADDED
2X	0.06	0.49	0.033	0.029	0.004	0.290	0.1033	0.1057	0.1045	Copper
3X	0.04	0.45	0.033	0.033	0.004	0.555	0.1021	0.1035	0.1028	Copper
4X	0.05	0.46	0.033	0.031	0.004	0.990	0.1038	0.1022	0.1030	Copper
5X	0.05	0.46	0.031	0.025	0.011	1.940	0.1001	0.0979	0.0990	Copper
6X	0.06	0.48	0.034	0.032	0.002	0.041	0.1293	0.1296	0.1294	None
7X	0.06	0.46	0.039	0.085	0.003	0.040	0.1187	0.1210	0.1198	Phosphorus
8X	0.06	0.43	0.028	0.030	0.332	0.036	0.1352	0.1267	0.1309	Silicon
9X	0.06	0.47	0.032	0.029	0.006	0.037	0.1241	0.1301	0.1271	Aluminum
10X	0.06	0.46	0.082	0.028	0.004	0.044	0.1493	0.1810	0.1651	Sulfur
11X	0.06	0.46	0.033	0.032	0.010	0.037	0.1257	0.1314	0.1285	Steel
12X	0.06	0.53	0.033	0.033	0.004	0.270	0.1046	0.1012	0.1029	Copper
13X	0.06	0.41	0.031	0.022	0.006	0.314	0.1072	0.1047	0.1059	Copper
14X	0.06	0.41	0.031	0.024	0.006	0.050	0.1173	0.1167	0.1170	None
25	0.06	0.15	0.032	0.012	0.005	0.017	0.1922	0.2195	0.2058	None
26	0.06	0.16	0.030	0.012	0.004	0.404	0.1096	0.1055	0.1075	Copper

Each sheet was stamped with a distinguishing mark, and they were numbered consecutively from 1 to 24. In the case of the grades 2X to 14X inclusive, and also grades 25 and 26, six sheets of each were selected in the same manner as above, and were numbered from 1 to 6. All sheets were 26 gauge, 26 in. × 96 in.

A strip 2 in. wide was cut lengthwise from each sheet, and these strips were given the same distinguishing numbers as the sheets from which they were cut, and were sent to the laboratories, where *each one* was carefully analyzed. As soon as this work had been completed, and we were thus assured that no mistakes had been made in marking the sheets, they were corrugated and forwarded to Scottdale and McKeesport, Pennsylvania. Twelve (12) sheets of each grade, 2 to 24 inclusive, were exposed at each station, while the other grades 2X to 14X, 25 and 26 were exposed at McKeesport only.

Meanwhile, there had been obtained in the open market, from three different sources, three lots of one of the so-called "pure irons," which on analysis proved to have a copper content of 0.041 per cent. Several sheets of each lot were exposed exactly as received, without pickling or cleaning of any kind (this has been the invariable practice on all corrugated sheets of all grades in this test and in all previous tests made by one of us).

All of the grades above mentioned, including the so-called "pure iron" (grade 50), were exposed as roof panels at McKeesport on July 7, 1914, and at Scottdale on July 9, 1914. At approximately the same time that the full size sheets were exposed, a series of 2 in. × 4 in. test pieces cut from the 2 in. strips before mentioned, and consisting of one piece from each sheet (636 in all), was exposed. These test pieces were cleaned by a very light wash of sulfuric acid, dipped in ammonia water to neutralize all acid, then thoroughly washed, dried, weighed and arranged in wooden racks in such a manner as to afford all free and equal exposure to the weather.

The method of removing, cleaning and weighing these test pieces will be discussed later. The results obtained are given in Tables II and III.

INSPECTION OF EXPOSED SHEETS

At the time of exposure of the full size corrugated sheets careful notes were taken concerning the physical appearance of the sheets as affected by the amount of mill scale which was present, and as to whether they were outside or inside sheets of the packs. During the progress of the test, this feature was carefully watched, and the time of ultimate failure of sheets whose surfaces were comparatively free from mill scale was compared with others of the same grade, whose surfaces were well covered with mill scale. From these observations, we concluded that the influence of this original surface oxide is slight, and is lost in the early stages of rusting, for no difference in final failure could be noticed. The photographs shown on pages 212 and 213 were taken from time to time during the tests, and show in a graphic manner the progress of the corrosion at various stages.

Careful inspections of the sheets were made approximately once every two months. At the first inspection, distinct differences were noticed in the physical conditions of the various panels: the corrosive action of the atmosphere had produced a decided difference in color, the steels with a copper content of 0.25 per cent or more being distinctly darker than the others which contained only a trace of copper; at the same time, these dark brown panels were smoother to the touch than the others, and the rust was denser and more adherent. Inasmuch as this same phenomenon had been noticed in former tests, it was thus indicated, even at this early stage, which steels would be the most resistant. It was also noted that several of the panels to which ingredients other than copper had been added, *e. g.*, sulfur and aluminum, gave indications that the rate of corrosion was proceeding even faster than with those steels to which no additions had been made. The fact that such early inspections are valuable, and that the relative merits of the various steels and irons can be predicted with fair accuracy, is borne out by the results of later inspections, and by the order of failure of the various panels.

The peculiar piebald appearance of the sheets (photographs were taken immediately after exposure of the sheets) in Cuts A-1, 2, and 3, is caused by the irregular distribution of mill scale. The outside sheets show a uniform dark color while the inside sheets are light in the areas where mill scale was absent and *vice versa.*

It will be noted that the twelve (12) sheet panels have been divided into two panels of six (6) sheets each. In the cases of Grades 2 to 14 inclusive the left half of these consists of sheets annealed at 1400°, while those in the right half were annealed at 1600°. In all other cases the two halves received identical treatment.

Referring to Cuts E-1, 2 and 3, an unusually severe wind storm occurred at Scottdale on Nov. 18, 1915, which blew away all fragments of sheets which were hanging by one end, only those sheets remaining which were in good condition and which still contained a considerable amount of uncorroded metal.

The rate of corrosion of the various grades may be observed by studying Photographs A, B, C, D and E, of the Scottdale test, and F, G, H and I, of the McKeesport test. While the corrosion at McKeesport was somewhat slower than at Scottdale, yet by a study of the photographs and tables, it will be seen that the relations between the various grades are approximately the same.

We call particular attention to the photograph of the Scottdale test taken December 1, 1915, 17 months after the test was erected. At this time all of the non-copper steels and the "pure iron" had completely failed, while every panel to which copper had been added was intact.

RELIABILITY OF TESTS ON SMALL PIECES

It has been claimed[1] that tests made by determining the losses in weight on exposure of comparatively small test pieces are inaccurate and misleading. A study of the tables which we present herewith, showing the weight losses due to corrosion of the various grades of steel and iron, in the shape of 2 in. × 4 in. test pieces, together with the photographs showing the conditions of the large size sheets, will prove that the results accord remarkably, and that the weight losses correspond to the relative endurances of the large sheets.

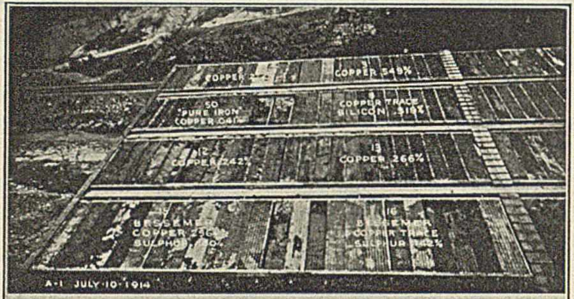
In these experiments, we adopted the practice of removing and cleaning one-half of the small test pieces after the lapse of several months, allowing the others to remain exposed for some time longer. This was done in an effort to determine if there was any tendency of the rust film to behave differently on different sheets. It was thought that the sponge-like rust which is normally formed on non-copper steels might accelerate corrosion more than the dense adherent film on copper steels. That this idea was correct, is shown by the results (discussed below).

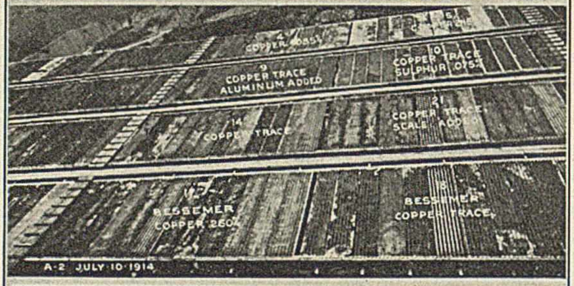
CLEANING OF SMALL TEST PIECES

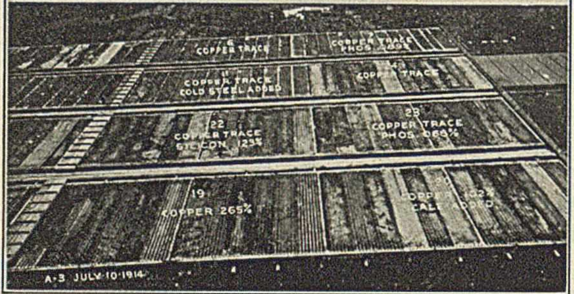
To clean the rust from the test pieces before final weighing, we used an ammoniacal solution of ammonium citrate. This solution completely removes the rust in about 12 hours, with the minimum attack upon the underlying metal. Careful experiments show that the attack on bare iron and steel by this solution is practically nil. On rusted pieces, due no doubt to electrolysis, it is a little greater, but still negligible compared with the total losses obtained. Furthermore it is approximately the same on all grades used in this test. This is further substantiated by the fact that the order of final failure of the large sheets coincided almost exactly with the weight losses obtained on the small pieces by this method.

---

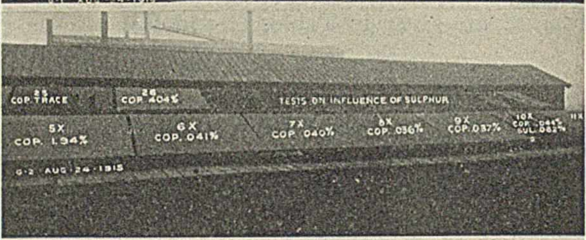
[1] Cushman, *Proc. Am. Iron and Steel Institute*, **1915**.

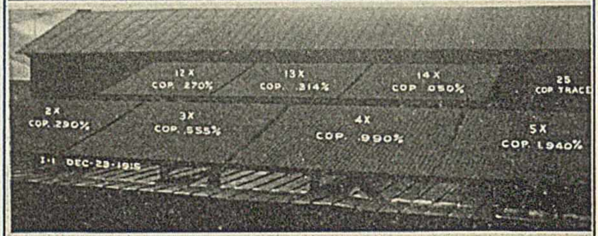

COPPER
COPPER .549%
50
"PURE IRON"
COPPER .041%
COPPER TRACE
SILICON .319%
12
COPPER .242%
13
COPPER .266%
BESSEMER
COPPER .256%
16
COPPER TRACE
SULPHUR .142%
A-1 JULY·10·1914

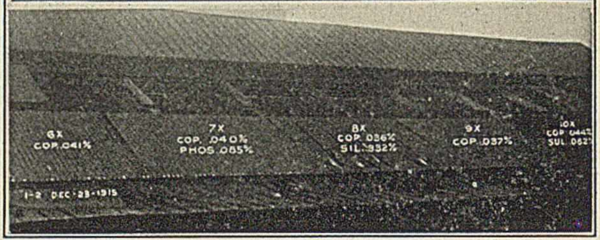

4
COPPER 1.085%
9
COPPER TRACE
ALUMINUM ADDED
10
COPPER TRACE
SULPHUR .075%
14
COPPER TRACE
21
COPPER TRACE
SCALE ADDED
17
BESSEMER
COPPER .260%
18
BESSEMER
COPPER TRACE
A-2 JULY·10·1914

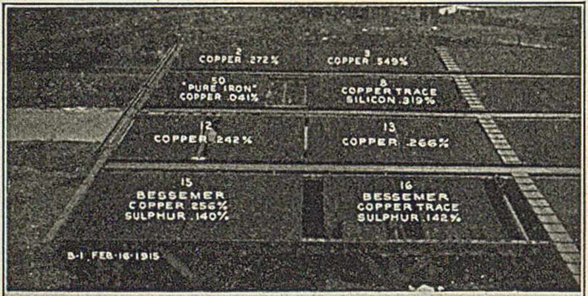

COPPER TRACE
COPPER TRACE
PHOS .089%
11
COPPER TRACE
COLD STEEL ADDED
COPPER TRACE
22
COPPER TRACE
SILICON .123%
23
COPPER TRACE
PHOS .068%
19
COPPER .265%
COPPER .102%
SCALE ADDED
A-3 JULY·10·1914

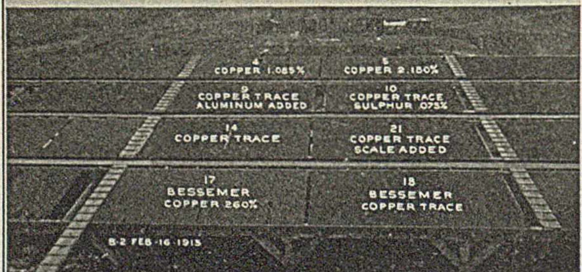

12X
COP. .270%
13X
COP. .314%
14X
COP. .050%
25
COP. TRACE
26
COP. .404%
2X
COP. .290%
3X
COP. .555%
4X
COP. .990%
5X
COP. 1.94%
6X
COPPER .041%


25
COP. TRACE
26
COP. .404%
TESTS ON INFLUENCE OF SULPHUR
5X
COP. 1.94%
6X
COP. .041%
7X
COP. .040%
8X
COP. .036%
9X
COP. .037%
10X
COP. .044%
SUL. .062%
11X
G-2 AUG·24·1915

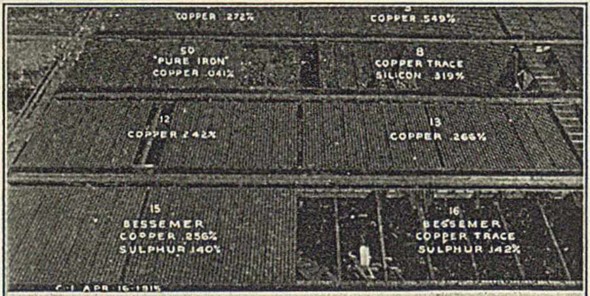

12X
COP. .270%
13X
COP. .314%
14X
COP. .050%
25
COP. TRACE
2X
COP. .290%
3X
COP. .555%
4X
COP. .990%
5X
COP. 1.940%
I-1 DEC·23·1915

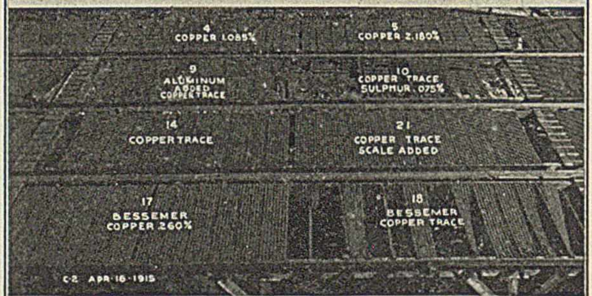

6X
COP. .041%
7X
COP. .040%
PHOS. .085%
8X
COP. .036%
SIL. .332%
9X
COP. .037%
10X
COP. .044%
SUL. .062%
I-2 DEC·23·1915


2
COPPER .272%
3
COPPER .549%
50
"PURE IRON"
COPPER .041%
8
COPPER TRACE
SILICON .319%
12
COPPER .242%
13
COPPER .266%
15
BESSEMER
COPPER .256%
SULPHUR .140%
16
BESSEMER
COPPER TRACE
SULPHUR .142%
B-1 FEB·16·1915

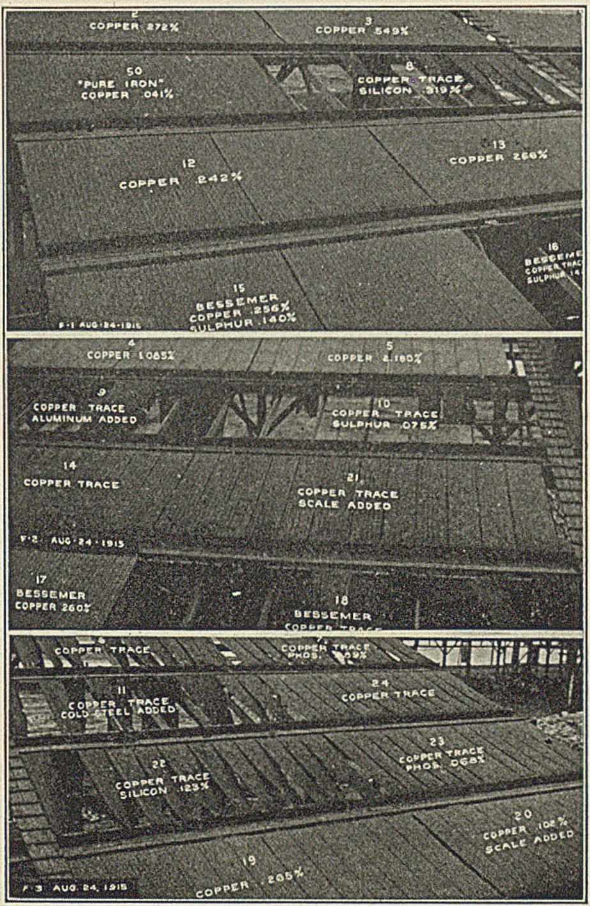

4
COPPER 1.085%
5
COPPER 2.180%
9
COPPER TRACE
ALUMINUM ADDED
10
COPPER TRACE
SULPHUR .075%
14
COPPER TRACE
21
COPPER TRACE
SCALE ADDED
17
BESSEMER
COPPER .260%
18
BESSEMER
COPPER TRACE
B-2 FEB·16·1915

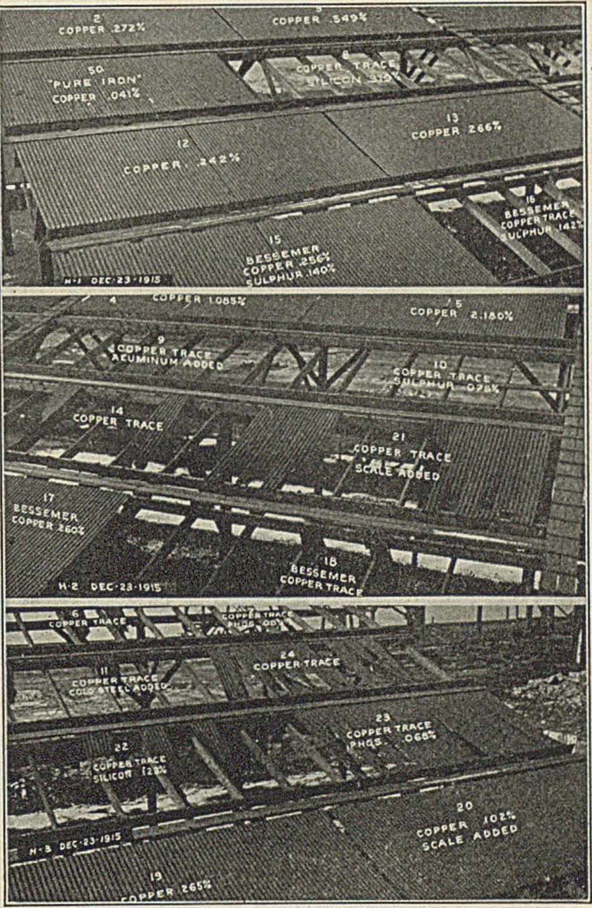

6
COPPER TRACE
7
COPPER TRACE
PHOS. .089%
11
COPPER TRACE
COLD STEEL ADDED
24
COPPER TRACE
22
COPPER TRACE
SILICON .123%
23
COPPER TRACE
PHOS. .068%
19
COPPER .265%
20
COPPER .102%
SCALE ADDED
B-3 FEB·16·1915

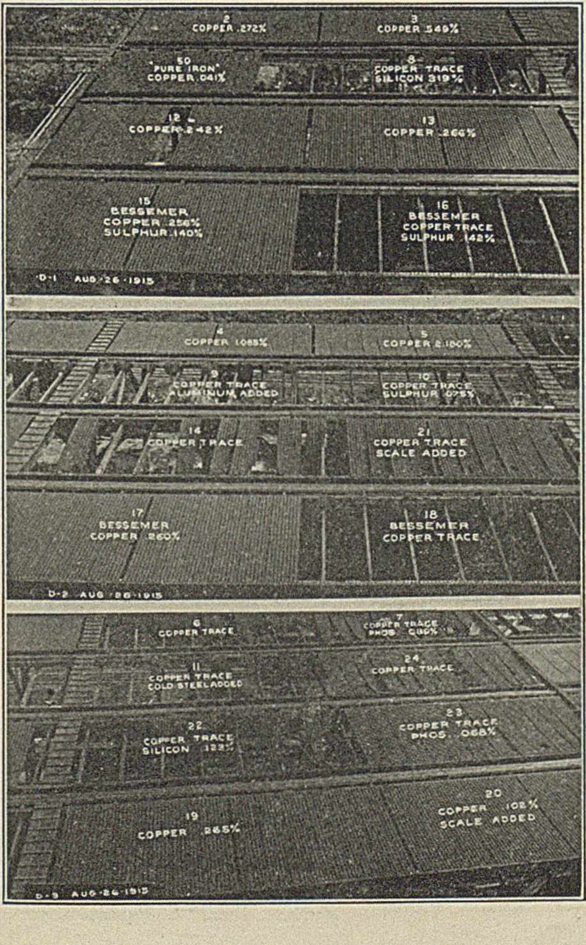

COPPER .272%
3
COPPER .549%
50
"PURE IRON"
COPPER .041%
8
COPPER TRACE
SILICON .319%
12
COPPER .242%
13
COPPER .266%
15
BESSEMER
COPPER .256%
SULPHUR .140%
16
BESSEMER
COPPER TRACE
SULPHUR .142%
C-1 APR·16·1915

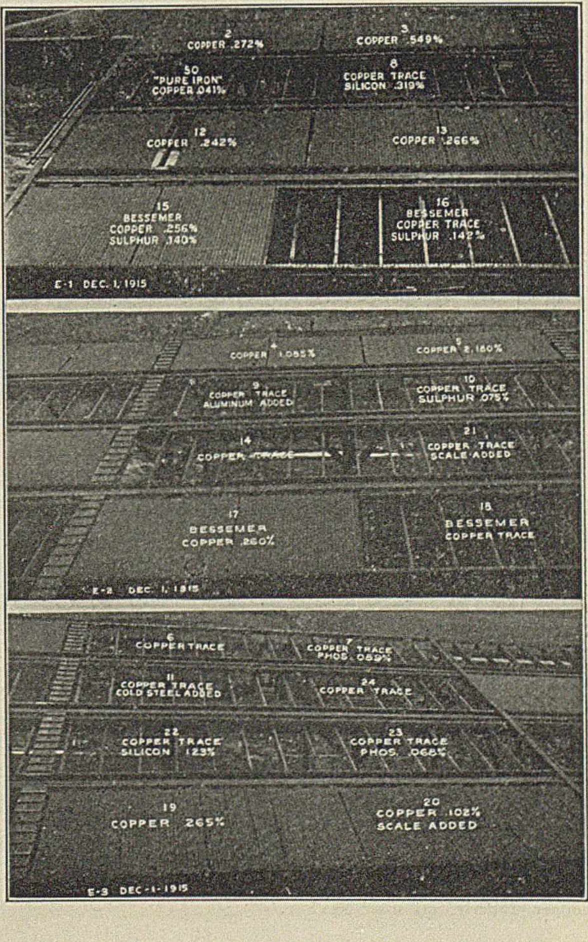

4
COPPER 1.085%
5
COPPER 2.180%
9
ALUMINUM
ADDED
COPPER TRACE
10
COPPER TRACE
SULPHUR .075%
14
COPPER TRACE
21
COPPER TRACE
SCALE ADDED
17
BESSEMER
COPPER .260%
18
BESSEMER
COPPER TRACE
C-2 APR·16·1915


6
COPPER TRACE
7
COPPER TRACE
PHOS. .089%
11
COPPER TRACE
COLD STEEL ADDED
24
COPPER TRACE
22
COPPER TRACE
SILICON .123%
23
COPPER TRACE
PHOS. .068%
19
COPPER .265%
20
COPPER .102%
SCALE ADDED
C-3 APR·16·1915


2 COPPER .272%
3 COPPER .549%
50 "PURE IRON" COPPER .041%
8 COPPER TRACE SILICON .319%
12 COPPER .242%
13 COPPER .266%
16 BESSEMER COPPER TRACE SULPHUR
15 BESSEMER COPPER .256% SULPHUR .140%
F-1 AUG-24-1915
4 COPPER 1.085%
5 COPPER 2.180%
9 COPPER TRACE ALUMINUM ADDED
10 COPPER TRACE SULPHUR .075%
14 COPPER TRACE
21 COPPER TRACE SCALE ADDED
F-2 AUG-24-1915
17 BESSEMER COPPER .260%
18 BESSEMER COPPER TRACE
6 COPPER TRACE
7 COPPER TRACE PHOS. .069%
11 COPPER TRACE COLD STEEL ADDED
24 COPPER TRACE
22 COPPER TRACE SILICON .123%
23 COPPER TRACE PHOS. .068%
20 COPPER .102% SCALE ADDED
19 COPPER .265%
F-3 AUG. 24. 1915


2 COPPER .272%
3 COPPER .549%
50 "PURE IRON" COPPER .041%
8 COPPER TRACE SILICON .319%
13 COPPER .266%
12 COPPER .242%
16 BESSEMER COPPER TRACE SULPHUR .142%
15 BESSEMER COPPER .256% SULPHUR .140%
H-1 DEC-23-1915
4 COPPER 1.085%
5 COPPER 2.180%
9 COPPER TRACE ALUMINUM ADDED
10 COPPER TRACE SULPHUR .075%
14 COPPER TRACE
21 COPPER TRACE SCALE ADDED
17 BESSEMER COPPER .260%
18 BESSEMER COPPER TRACE
H-2 DEC-23-1915
6 COPPER TRACE
7 COPPER TRACE PHOS. .069%
11 COPPER TRACE COLD STEEL ADDED
24 COPPER TRACE
22 COPPER TRACE SILICON .123%
23 COPPER TRACE PHOS. .068%
20 COPPER .102% SCALE ADDED
H-3 DEC-23-1915
19 COPPER .265%


2 COPPER .272%
3 COPPER .549%
50 "PURE IRON" COPPER .041%
8 COPPER TRACE SILICON .319%
12 COPPER .242%
13 COPPER .266%
15 BESSEMER COPPER .256% SULPHUR .140%
16 BESSEMER COPPER TRACE SULPHUR .142%
D-1 AUG-26-1915
4 COPPER 1.085%
5 COPPER 2.180%
9 COPPER TRACE ALUMINUM ADDED
10 COPPER TRACE SULPHUR .075%
14 COPPER TRACE
21 COPPER TRACE SCALE ADDED
17 BESSEMER COPPER .260%
18 BESSEMER COPPER TRACE
D-2 AUG-26-1915
6 COPPER TRACE
7 COPPER TRACE PHOS. .069%
11 COPPER TRACE COLD STEEL ADDED
24 COPPER TRACE
22 COPPER TRACE SILICON .123%
23 COPPER TRACE PHOS. .068%
20 COPPER .102% SCALE ADDED
19 COPPER .265%
D-3 AUG-26-1915


2 COPPER .272%
3 COPPER .549%
50 "PURE IRON" COPPER .041%
8 COPPER TRACE SILICON .319%
12 COPPER .242%
13 COPPER .266%
15 BESSEMER COPPER .256% SULPHUR .140%
16 BESSEMER COPPER TRACE SULPHUR .142%
E-1 DEC. 1. 1915
4 COPPER 1.085%
5 COPPER 2.180%
9 COPPER TRACE ALUMINUM ADDED
10 COPPER TRACE SULPHUR .075%
14 COPPER TRACE
21 COPPER TRACE SCALE ADDED
17 BESSEMER COPPER .260%
18 BESSEMER COPPER TRACE
E-2 DEC. 1. 1915
6 COPPER TRACE
7 COPPER TRACE PHOS. .069%
11 COPPER TRACE COLD STEEL ADDED
24 COPPER TRACE
22 COPPER TRACE SILICON .123%
23 COPPER TRACE PHOS. .068%
19 COPPER .265%
20 COPPER .102% SCALE ADDED
E-3 DEC-1-1915

This report does not include details of the various inspections nor detailed tables showing losses of individual test pieces, but presents tables of summaries giving average results. The losses are in each case expressed in ounces per square foot of exposed surface per month, and the results are averages of from six to twelve determinations in each case. Complete detailed notes may be found at the authors' offices, and are available to anyone who wishes to study them.

RESISTANCE TO CORROSION OF VARIOUS GRADES

Table II summarizes the results on all grades which were exposed in both locations, and compares losses during each entire period of exposure, and also grand averages. The column headed "RANK" gives the order of resistance to corrosion of the various grades—1 being best, and 24 poorest. In this ranking we have compared only those grades annealed at 1400° F. In this list there are ten grades to which copper was added in amounts from 0.25 to 2.00 per cent.[1] These have taken the ten highest positions, and there is a remarkable uniformity in corrosion rate among them, the greatest loss being 0.1307 and the lowest 0.1138. Higher amounts than 0.25 per cent copper give slightly better results, but the differences are so small as to be negligible, especially when considering the added cost.

The so-called "pure iron" with a copper content of 0.041 per cent takes 11th place, while the other grades which have only the usual traces of copper take positions from 12 to 24, the poorest being those to which sulfur was added (No. 10) and which contained high sulfur residually (No. 16), the latter showing losses approximately three times as great as the copper steels.

TABLE IV—AVERAGE CORROSION PER MONTH (FROM TABLE I): RESULTS IN OUNCES PER SQUARE FOOT

	(A) Both Temperatures		(B) From Grand Average		(C) Grades 2 to 24			
					Scottdale		McKeesport	
Steels Averaged	Scottdale	McKeesport	1400°	1600°	1st period	2nd period	1st period	2nd period
Grades 2 to 50	0.2596	0.1502	....	....	....	....	....	....
Copper steels	0.1376	0.1037	0.1206	0.1196	0.1379	0.1369	0.1066	0.0917
All others	0.3528	0.1857	0.3021	0.2686	0.3383	0.5122	0.1875	0.2343

The addition of aluminum, silicon and cold steel in each case has slightly increased the corrosion rate (compare Nos. 9, 8 and 11 with No. 6). A phosphorus addition has somewhat lessened the corrosion (compare No. 7 with No. 6 and No. 23 with No. 24): this is in line with some of our previous work.

Grades 19 to 24, although from a heat which was supposed to be highly oxidized, have shown somewhat lower losses than the other heats. From other work we have done, we ascribe this to the somewhat lower sulfur content (compare Nos. 6 and 14 with No. 24).

In studying the results on Grades 15, 16, 17 and 18 (Bessemer), we note the accelerating effect of very high sulfur. At the same time, the addition of 0.25 per cent copper to the same steel has entirely neutralized this influence and the results are quite comparable to those obtained with normal copper steels.

Considering Table III, Grades 2X to 14X, to which the same additions were made as to Nos. 2 to 14 (Table II), we find that as low a copper content as 0.04 seems to have materially lessened corrosion —compare 6X with 6, 14X with 14, and 10X with 10, etc.: from the latter we learn that 0.04 per cent copper partially neutralizes the influence of as much as 0.082 per cent sulfur.

Panel 25, from a heat to which no deoxidizer was added, and which was comparatively low in manganese, shows a corrosion rate greater than that of normal basic open-hearth steels, indicating no benefit because of lower manganese but a possible detriment, from the steel not having been deoxidized. Panel 26 from the same heat, with copper addition, is quite the equal of other steels to which copper was added.

Table IV(A) indicates the relative rates of corrosion in the two different atmospheres, of all varieties of steel tested. On plain steels we find that the corrosion in the coke regions, that is, at Scottdale, is nearly twice as great as that at McKeesport in a normal mill district. The difference is very much less when considering copper-bearing steels, the ratio being approximately as follows:

All steels: 100 at McKeesport to 173 at Scottdale
Copper steels: 100 at McKeesport to 133 at Scottdale
Plain steels: 100 at McKeesport to 190 at Scottdale

From Table IV(B) we learn that the benefit of higher annealing temperatures in the case of plain steels is approximately 12 per cent greater endurance, while for copper steels it is practically negligible.

In determining the losses of the weighed test pieces, the authors adopted the practice of removing them from the racks at different periods. At the end of these periods, which were 6.5 and 8.2 months, respectively, we removed one-half of the test pieces and cleaned and weighed them. The remaining half we left exposed for approximately 3 months longer, at the end of which time they also were taken down, cleaned and weighed. Various conclusions may be drawn from a study of corrosion rates during these two periods of exposure.

In Table IV(C) in the Scottdale test we notice that in the first period the rate of corrosion of copper steels was 0.1379 and of the same steels in the second period, 0.1369, showing that the corrosion rate does not increase for successive periods of exposure, while with the plain steels, we find a decided increase in the second period over the first, *viz.*, 0.3383 in the first to 0.5122 in the second, a 51 per cent increase in corrosion rate. Similar results were obtained in the McKeesport test.

TABLE V—COMPARISON OF COPPER STEELS OF NORMAL ANALYSIS WITH OTHER STEELS TO WHICH NO ADDITIONS WERE MADE: (FROM TABLES I AND II)

Test	Period	Copper steels 0.25% Cu (2–12–13–17)	Plain steels (6–14–18)	"Pure Iron" (50)	Low copper steels (6X)	Low copper steels (14X)
Scottdale	1st	0.1366	0.3456	0.1588	....	....
	2nd	0.1394	0.4737	0.1554	....	....
McKeesport	1st	0.1069	0.1841	0.1156	0.1293	0.1173
	2nd	0.0905	0.2325	0.1244	0.1307	0.1147

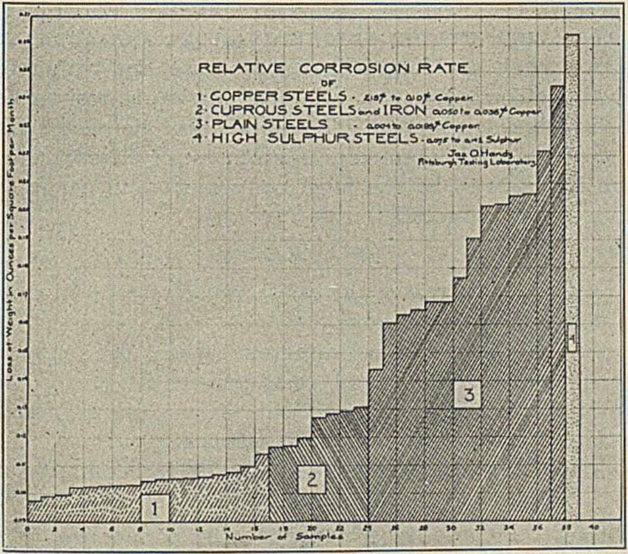
---

[1] In grade No. 20, the steel was so wild that it was very difficult to add the copper properly, and some was lost.

In Table V, we have set apart the copper steels which agree in copper content with the amount used in the average material which is placed on the market, that is, 0.25 per cent, and we have compared these with plain steels to which no additions have been made, and also with so-called "pure iron." Such comparisons have been made both in the Scottdale test and in the McKeesport test. We find again that with copper steels, as in Table IV(C), the corrosion rate does not accelerate in the second period of exposure, whereas with plain steels, the reverse is true, the corrosion ratio being 100 : 177. The pure open-hearth iron containing 0.04 per cent copper has shown greater total corrosion loss than the copper steels, yet, probably due to its copper content, it ranges itself with the copper steels, in that the corrosion rate is not increased in the second period. The same statement applies to the normal open-hearth steels containing 0.04 per cent copper, as will be noted by the results on Panels 6X and 14X. It will also be noted that Grade 6X, a normal open-hearth steel with 0.041 per cent copper is nearly as good as No. 50 (pure iron with 0.041 per cent copper), while Grade 14X with 0.05 per cent copper is better than No. 50. (The test roofs have been shown at the different stages of rusting to many parties of metallurgists and other investigators of corrosion problems.)

ADDITIONAL "PURE IRON" TESTS

In addition to the tests reported above, one of the authors[1] has conducted some tests, the results of which give further corroborative evidence on the behavior of low copper "pure irons" under atmospheric influences, and also on the progress of rusting during successive periods of exposure. A description of these tests follows:



At the request of one of the authors, two manufacturers of "pure iron" furnished sheets of their material, which were analyzed, corrugated and included in the weather exposure tests at McKeesport. Test pieces were also cut from the sheets and the losses of weight determined by exposure, in the Pittsburgh atmosphere, under the same conditions, with copper-bearing steels and plain steels. The sheets were of 26 gauge, except in the case of Type A, 1st lot, which had a thickness of 0.022 in. instead of 0.0185 in. They were first exposed on July 16, 1914, November 7, 1914 and August 5, 1914, respectively. The analyses of the "pure iron" sheets were as follows:

PERCENTAGES	Type A: Low-copper 1st lot	 2nd lot	Type B 0.04 to 0.05% Cu
Carbon	0.013	0.020	0.014
Manganese	0.04	0.094	0.049
Phosphorus	0.004	0.005	0.003
Sulfur	0.030	0.018	0.033
Silicon	0.002	0.002	...
Copper	0.027	0.020	0.045
Oxygen	0.031	...	...
Aluminum	0.005	...	...

TYPE A, 1ST LOT—Observations showed that in less than 1 month this lot was rusting badly and the rust had the light brown color which had been found to be characteristic of the more rapidly corroding steels; in less than 2 months the same sheet had become very rough, resembling in this respect the most rapidly rusting steels containing added sulfur and silicon; in 9 months it had become as thin as paper at the edges; in 12 months it had frayed and broken at the bottom, but did not break transversely when pressed; in 15 months it had broken through near the bottom, though fairly strong at the upper end; after 18 months, one square foot of it had rusted away at the bottom, and it was cracked half way up; it cracked transversely when lightly pressed near the top.

TYPE A, 2ND LOT showed a thick, light brown rust after about 2 months' exposure; after 4 months, there was a thick, light brown scale; after 6 months, the sheets were thin at the bottom, but could not then be broken by light pressure; after 9 months, the sheets were rusted away at the bottom—one sheet was full of holes in the lower half and the rusting had proceeded further than in the case of the 1st lot at this period; after 12 months the sheets had become detached and were rusted so badly that they could be broken easily by hand in any part.

The more rapid corrosion of the second lot of this "pure iron" is believed to be due to the lower copper content.

TYPE B—It will be noticed that this type of "pure iron" contained more than twice as much copper as the "pure iron" of Type A. The percentages of copper in the different sheets were 0.043, 0.044 and 0.048, which places it in the class with the "pure iron" in the main test and with the sheets 6X and 14X, already described as being far more durable than plain steel or "pure iron" of Type A, especially in the 2nd lot. After 6 months, they were graded as showing no more corrosion than the copper-bearing steels which had been exposed for 7 months; after 8 months they were graded as being no longer as resistant to corrosion as the copper-bearing steels containing approximately 0.25 per cent copper—the rust was quite rough, resembling 7X, 14X and the "pure iron" in the main test; after 11 months, while the rust was rough and deep, there was no perceptible thinning at the edges and no sagging; after 14 months, one sheet broke when lightly pressed; after 17 months, one sheet was perforated and cracked—the second sheet was cracked and had a small perforation while the third sheet was not then broken through.

QUANTITATIVE WEIGHT LOSSES of the test pieces exposed for approximately equal periods, though at slightly different seasons, in the Pittsburgh atmosphere were as follows:

	Time	Loss in ounces per sq. ft.
Type A, 1st lot	6 mo. (Oct. to Apr.)	2.70
Type A, 2nd lot	$5^1/_2$ mo. (Nov. to Apr.)	2.34
Type B.	$5^2/_3$ mo. (Oct. to Apr.)	1.64

---

[1] Mr. Handy.

The test pieces, of which there were three in each case, were, after cleaning with ammonium citrate solution and weighing, exposed for three months longer.

Time, 3 mo. (May to Aug.)	Loss in oz. per sq. ft.	Copper percentage
Type A, 1st lot	1.26	0.027
Type A, 2nd lot	1.66	0.019
Type B	0.99	0.045

It will be seen that, when exposed under exactly the same conditions, the losses of weight were inversely proportional to the small and slightly varying copper percentages.

The following experiment shows the comparison between weight losses during one, two and three months' exposures of *separate* test pieces of "pure iron," Type A, 2nd lot.

	Loss in oz. per sq. ft.
June 1st to July 1st	0.74
" " " August 1st	1.42
" " " September 1st	2.27

It had been noticed in other experiments that the copper-bearing steels showed less loss of weight for equal periods of exposure, after the first dense rust coating had formed. These experiments show that the nearly equal corrosion loss during the second month and the greater corrosion loss during the third month place this low copper "pure iron" in the same class of inferior weather-resisting material with plain steel free from copper.

CORROSION LOSSES (OZ. PER SQ. FT.) OF COPPER-BEARING STEEL, PLAIN STEEL AND "PURE IRON"

Test pieces were exposed in racks for *one-month periods* in the Pittsburgh atmosphere. The results in the following table do not represent progressive rusting, a new test piece having been exposed on the first of each month.

CORROSION LOSS	Copper-bearing steel 0.25% Cu	Plain steel	"Pure iron" 0.045% Cu
May	0.52	0.90	0.64
June	0.38	0.65	0.49
July	0.56	0.95	0.76
August	0.54	0.75	0.68

Test pieces were exposed for from 1- to 5-month periods in the Pittsburgh atmosphere with the following results. These results represent progressive losses, six (6) pieces having been exposed at the start and one taken down at a time at the end of each month.

Period exposed Months	Copper-bearing steel 0.25% Cu	Plain steel	"Pure iron" 0.045% Cu
1	0.52	0.90	0.64
2	0.64	1.82	0.92
3	0.95	3.00	1.41
4	1.13	3.64	1.46
5	1.13	4.41	1.61
6	1.17	5.53(*a*)	1.76

(*a*) This piece of plain steel was at this time reduced from an original weight of 18.3 grams to 0.9 gram, and was wholly disintegrated.

From the above tables, it will be noticed that the progress in rusting under the original rust coat is much more rapid in the case of the plain steel than in the case of the copper-bearing steel, and materially less rapid in the case of the copper-bearing steel than in the case of the "pure iron." However, this "pure iron" contains enough copper to account for its approximating in corrosion resistance the copper-bearing steel. It is of great interest to note that corrosion practically stopped in the case of the copper-bearing steels after the fourth month: the rust had formed an efficient protective coating.

SUMMARY

Sheet steel or iron containing COPPER shows greatly increased corrosion resistance when exposed to atmospheric conditions. The most effective amount of copper to be used for this purpose is approximately 0.25 per cent. Smaller amounts of copper down to as little as 0.04 per cent have a considerable influence in lessening corrosion, but the results are not as good as with the higher amount mentioned above. Work previously done by one of us has indicated that 0.15 per cent copper is in nearly all cases as efficient as 0.25 per cent. Higher amounts of copper, up to 2 per cent, give little or no added benefit. Copper is as necessary in the so-called "pure irons" to insure corrosion resistance as it is in normal open-hearth and Bessemer steels.

PHOSPHORUS added to open-hearth steel slightly lowers the corrosion rate. SILICON, while probably without effect in the amounts normally present in open-hearth and Bessemer steels, accelerates corrosion when added in amounts from 0.10 to 0.30 per cent. The addition of small amounts of ALUMINUM probably has little influence on corrosion: the above tests indicate it to be harmful rather than beneficial. The addition of SULFUR to steel greatly increases the corrosion rate and when residually present in abnormal amounts, it is probably also detrimental from a corrosion standpoint. The addition of COLD STEEL to molten steel does not lower the corrosion rate, but, if it has any influence at all, it is to increase the corrosion.

LOSS IN WEIGHT DETERMINATIONS ON SMALL TEST PIECES are found to be accurate and valuable when determining the relative corrosion resistance of various sheet metals. The method of cleaning such test pieces with ammoniacal ammonium citrate solution is found to be the most convenient and accurate thus far investigated.

CONCLUSIONS

I—Copper increases the resistance of steel and iron to atmospheric corrosion:

  1—Its influence is apparent when the copper content reaches only 0.03 per cent.
  2—Its effect is almost at a maximum when the copper reaches 0.05 per cent.
  3—The best amount of copper for commercial steel has been found to be 0.25 per cent.

II—Steel containing 0.25 per cent copper outlasts "pure iron" containing 0.04 per cent copper.

III—Steel containing 0.05 per cent copper lasts as long as "pure iron" containing 0.04 per cent copper.

IV—Sulfur in steel accelerates corrosion very markedly.

V—Sulfur oxides in the air accelerate the corrosion of steel.

VI—Copper in steel counteracts or retards both the corroding influences noted in IV and V.

PITTSBURGH

PREPARATION OF PURE IRON AND IRON-CARBON ALLOYS[1]

By J. R. Cain, E. Schramm and H. E. Cleaves

Received January 24, 1916

INTRODUCTION

The fundamental importance of the iron-carbon thermal equilibrium diagram in the scientific metallurgy of iron and steel and its utility to practical workers have long been realized, and accordingly this subject has received attention from many points of view and from many investigators during the past two decades.

In view of this fact, it might seem superfluous to add to the existing literature except for the following considerations. Earlier workers have for the most part confined their attention to special portions of the diagram or to disputed questions of theory. Their thermal studies have not been carried out with the degree of accuracy now attainable. They have practically, without exception, employed commercial materials of varying degrees of purity. In two papers[2] published in 1913 Prof. H. M. Howe, as a result of a thorough examination of the literature, has fixed the most probable position of the equilibrium lines. His net conclusions are that "this calculated line is not entitled to great weight because of the weakness of the evidence," and that "much better data are needed, reached with pure materials and with the many causes of error reduced to a minimum." In Table I, compiled from Prof. Howe's papers, are given analyses of the materials used in some of the more important recent investigations. A glance at the table will show the justice of the conclusions quoted above. The analyses are incomplete even for the impurities ordinarily determined, and entirely ignore the possible presence of other impurities, such as Cu and Ni; but so far as they go, they indicate a very appreciable degree of contamination by S, Si, Mn, elements which we know exert a marked effect on the critical ranges. It may be said that the iron-carbon diagram has never been worked out with pure iron-carbon alloys. The present paper describes the preparation of a series of high degree of purity to be used as the basis of a more accurate study of the equilibrium diagram than has heretofore been attempted.

Table I—Percentage Composition of Iron-Carbon Alloys Used by Various Investigators in Determinations of Critical Points

No.	Authority	Date	C	Si	Mn	P	S
1	Carpenter and Keeling(*a*)	1904	0.38	0.06	Trace	0.03	0.01
2	Carpenter and Keeling..	1904	1.85	0.09	..	...	...
3	Carpenter and Keeling..	1904	3.98	...	..	...	...
4	Carpenter and Keeling..	1904	4.50	0.12	..	...	...
5	Carpenter and Keeling..	1904	2.63	...	..	...	...
5A	Carpenter and Keeling..	1904	2.85	...	..	...	...
6	Carpenter and Keeling..	1904	2.85	...	Trace?	...	...
7	Heyn(*b*)................	1904	0.39	0.04	0.03	...	...
8	Heyn..................	1904	0.95	0.04	0.06	...	...
9 10	Rosenhain(*c*).......... on Brayshaw's steel A_2	1910	1.14	0.09	0.40	0.014	0.018
11	Benedicks(*d*)...........	1908	1.00	...	0.25	...	...
12	Charpy and Grenet(*e*)...	1903	0.64	...	..	...	...
13	Charpy and Grenet.....	1903	0.64	...	..	...	...
14	Charpy and Grenet.....	1903	0.93	...	..	...	...
15	Charpy and Grenet.....	1903	0.93	...	..	...	...
16	Charpy and Grenet.....	1903	1.50	...	..	...	...
17	Brayshaw(*f*) No. W_4....	1910	1.15	0.21	0.31	0.011 ±	0.012 ±
18	Brayshaw No. W_2......	1910	1.16	0.10	0.37	0.014	0.023
19	Brayshaw No. A_2.......	1910	1.14	0.09	0.40	0.014	0.018
20	Levy(*g*)...............	1913	0.23	0.039	0.05	0.013	0.010
21	Levy..................	1912	0.92	0.14	0.123	0.009	0.011
22	Howe and Levy(*h*)......	1913	0.027	...	0.26	0.005	0.024
23	Howe and Levy........	1913	0.105	0.013	0.24	0.015	0.028
24	Howe and Levy........	1913	0.214	0.039	0.05	0.013	0.010
25	Howe and Levy........	1913	0.227	0.039	0.05	0.013	0.010
26	Howe and Levy........	1913	0.235	0.039	0.05	0.013	0.010
27	Howe and Levy........	1913	0.244	0.050	Nil	Nil	0.007
28	Howe and Levy........	1913	0.382	0.027	0.22	...	0.004
29	Howe and Levy........	1913	0.40	0.103	0.16	0.014	0.012
30	Howe and Levy........	1913	0.563	0.18	0.15	0.013	0.013
31	Howe and Levy........	1913	0.59	0.144	0.17	0.018	0.013
32	Howe and Levy........	1913	0.73	0.141	0.07	0.012	0.019
33	Howe and Levy........	1913	0.92	0.14	0.123	0.009	0.011

(*a*) Carpenter and Keeling, *Jour. Iron and Steel Inst.*, **65** (1904), 244; Collected Researches of the Nat'l Phys. Lab., **1**, p. 227.

(*b*) Heyn, "Verh. des Vereins zur Beförderung des Gewerbfleisses," **1904**, p. 371.

(*c*) Rosenhain, *Proc. Inst. Mech. Eng.*, **1910**, p. 688.

(*d*) Benedicks, *Jour. Iron and Steel Inst.*, **77** (1908), 218.

(*e*) Charpy and Grenet, *Bull. Soc. d'Encouragement pour l'Industrie Nationale*, **1903**, p. 480.

(*f*) Brayshaw, *Proc. Inst. Mech. Eng.*, **1910**, pp. 525, 537, 656, 670.

(*g*) Howe, *Bull. Am. Inst. Mining Eng.*, **1913**, p. 1068.

(*h*) Howe and Levy, *Ibid.*, **1913**, p. 1076.

For the production of pure iron on a fairly large scale, the electrolytic refining method was obviously most suitable and was therefore adopted in this work. Pure carbon was made by calcining in a Dixon graphite crucible the pure sugar used as stock for Bureau of Standards analyzed sample No. 17. The latter contains, as the only impurity of importance for present purposes, 0.003 per cent ash, and the carbon obtained from it has an ash content of 0.17 per cent.

MAKING THE ELECTROLYTIC IRON

The electrolytic method, using soluble anodes, has been frequently employed in similar investigations[1] and its essentials are well known, so that we give details only for the sake of completeness and because, in one respect, our method deviates from that usually followed, namely, in the use of porous anode compartments. The first iron was made on a small scale. The essential details of the bath are as follows: Two cylindrical anodes of ingot iron[2] about 2 in. in diameter by 5 in. long, contained in porous clay cups; three cathodes of sheet iron, each 4 in. square; electrolyte, 25 to 30 per cent $FeCl_2$ solution (made by dissolving the ingot iron in chemically pure hydrochloric acid), prepared as nearly neutral as possible; current density about 0.5 to 0.7 ampere per square decimeter; temperature during electrolysis approximately that of the room. No attempt was made to determine the yield or to secure high current efficiency. Good adherent deposits were obtained, the greatest thickness being about 0.5 cm. Owing to the unfavorable current distribution when working with anodes and cathodes of such unequal sizes, the thickness of deposit was not uniform all over the plates. Qualitative tests of the sludge from the anode cells showed that there

---

[1] Published with the permission of the Director of the Bureau of Standards.

[2] "Ae_1, the Equilibrium Temperature for A_1 in Carbon Steel," *Bull. Am. Inst. Mining Eng.*, **1913**, p. 1066; "A Discussion of the Existing Data as to the Position of Ae_3," *Ibid.*, **1913**, p. 1099.

[1] Lenz, *J. prakt. Chem.*, **108** (1869), 438; Cailletet, *Compt. rend.*, **80** (1875), 319; Roberts-Austen, *Jour. Iron and Steel Inst.*, **1** (1887), 71; Arnold and Hadfield, *Stahl u. Eisen*, **1894**, p. 526; Hicks and O'Shea, *Electrician*, **1895**, p. 843; Winteler, *Z. Elektrochem.*, **4** (1898), 338; Haber, *Ibid.*, **4** (1898), 410; Abegg, *Stahl u. Eisen*, **1901**, II, p. 736; Skrabal, *Z. Elektrochem.*, **10** (1904), 749; C. F. Burgess and Hambuechen, *Trans. Am. Electrochem. Soc.*, **5** (1904), 201; Maximowitsch, *Z. Elektrochem.*, **11** (1905), 52; Ryss and Bogomolny, *Ibid.*, **12** (1906), 697; Cowper-Cowles, *C. A.*, **3**, 1371; **5**, 3013; **8**, 3648; C. F. Burgess and Watts, *Trans. Am. Electrochem. Soc.*, **9** (1906), 229; Amberg, *Z. Elektrochem.*, **14** (1908), 326; Kern, *Trans. Am. Electrochem. Soc.*, **3** (1908), 103; Müller, *Metallurgie*, **6** (1909), 145 (contains bibliography); Pfaff, *Z. Elektrochem.*, **16** (1910), 217; Tucker and Schramm, This Journal, **2** (1910), 237; Watts and Li, *Trans. Am. Electrochem. Soc.*, **25** (1914), 529; Yensen, University of Illinois, *Bull.* **72**, 1914.

[2] Analysis as follows: C, 0.016; S, 0.022; Mn, 0.029; P, 0.001; Si, 0.002; and Cu, 0.15.

was an accumulation of manganese and copper derived from anodic impurities. The porous cups therefore seemed to be of service in preventing anode impurities from migrating to the cathodes, and they were accordingly used in one of the larger baths to be described later. In another similar tank the cups were omitted. Table II shows that the cathode deposits from the bath without the cups were a little higher in copper than the others but were otherwise of similar quality. It was found that there was much oxidation of the surface layers of the electrolyte as the electrolysis went on, resulting in the production of basic salts of iron, which floated in the bath and which migrated to some extent to the cathodes. With the intention of avoiding or minimizing this oxidation, the small bath was provided with a hydraulically sealed cover having windows for observation and conduits for the current leads. The air in the space over the electrolyte was displaced with purified carbon dioxide and the electrolysis conducted as before. This method led to no marked improvement and it was abandoned, especially as there seemed to be a tendency toward higher percentages of carbon in the cathodic deposits. Although the greater part of the sediment settled to the bottom, the bath was never quite free from turbidity caused by these basic salts, and there is no doubt that the deposits were contaminated by them in slight degree. This was of no consequence, inasmuch as these impurities were either volatilized or were reduced to iron in subsequent melting operations. The analysis of the iron stripped from cathodes of the small electrolytic bath is given in Table II. About 2 or 3 kg. were made in this bath.

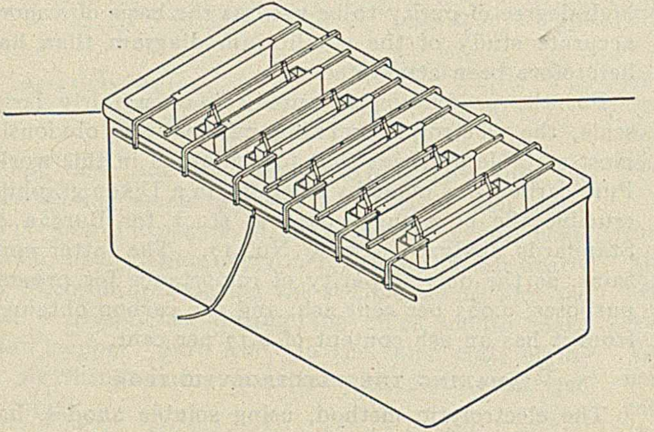


FIG. I—TANK FOR PREPARING ELECTROLYTIC IRON

TABLE II—PERCENTAGE COMPOSITION OF ELECTROLYTIC IRON FROM VARIOUS SOURCES

Source	C	S	P	Mn	Si	Cu	Ni and Co	Total impurity	Analysis by
1(*a*, *b*).....	0.004	0.002	Trace	Trace	0.003	0.005	0.011	0.026	B. S.
2(*c*, *b*).....	0.004	0.003	Trace	Trace	0.006	Trace	0.011	0.024	B. S.
3(*d*, *b*).....	0.004	0.006	Trace	Trace	0.008	0.006	0.011	0.035	B. S.
4(*e*)........	0.004	0.004	Trace	Trace	0.005	0.008	0.011	0.033	B. S.
5(*f*)........	0.063	0.002	0.005	0.009	0.005	...	...	0.084	Müller
6(*g*)........	0.008	Trace	0.002	0.009	0.014	...	...	0.033	Stead
7(*h*)........	0.008	0.004	Trace	Trace	0.006	0.011	...	0.029	B. S.
8(*i*)........	0.009	0.003	Trace	Trace	0.006	0.006	...	0.024	B. S.

(*a*) B. S. (with porous cups).

(*b*) Bureau of Standards analysis of anodes from which this iron was made: C, 0.013 per cent; S, 0.020 per cent; P, 0.003 per cent; Mn, 0.025 per cent; Si, 0.003 per cent; Cu, 0.024 per cent; and Ni + Co, 0.021 per cent. (Cf. Burgess and Crowe, *Bull. Bur. Stand.*, **10** (1914), 342.)

(*c*) B. S. (with porous cups).

(*e*) B. S. (from small tank).

(*d*) B. S. (without porous cups).

(*f*) A. Müller, *Metallurgie*, **6** (1909), 152.

(*g*) H. C. H. Carpenter.

(*h*) Langbein-Pfanhauser.

(*i*) C. F. Burgess.

The large electrolytic bath is shown in Fig. I. The anode cups were molded from a mixture of equal parts by volume of alundum cement and of clean white Ottawa sand; after careful drying in an oven the cups were burned at a temperature of 1000° to 1100° and were then found to have a satisfactory degree of porosity. The current density during electrolysis varied from 0.3 to 0.4 ampere per sq. dm. The electrolyte contained 23.3 per cent $FeCl_2$ (made from the ingot iron previously described) and 10.3 per cent NaCl, and was nearly neutral. Analyses of electrolyte from the anode and cathode compartments made after a week's run were as follows:

	PER CENT IRON	
	Anode compartment	Cathode compartment
Original................	9.52	7.88
After one week's run.....	8.82	7.53

The character of the deposits is shown by Figs. II and III. Deposits of 5 to 7 mm. thickness were obtained; the characteristics of these were about the same as of those made in the smaller bath. They were very hard and brittle in consequence of contamination by hydrogen. On removal from the bath and after washing with distilled water they corroded rapidly in the air. No account was taken of this surface oxidation, inasmuch as the iron was to be used for making iron-carbon alloys in such a way that the oxidized compounds of iron would be reduced to metal and the hydrogen expelled. About 12 to 15 kg. of iron were made for use in preparing the alloys. In Table II are given analyses of this iron made with and without the use of porous anode compartments, and for comparison analyses of electrolytic iron from other sources.

MELTING THE ELECTROLYTIC IRON

The next step for the further utilization of the electro-deposited iron is to melt it into ingots. The material as taken from the bath is brittle and is contaminated with occluded chlorides from the electrolyte, with hydrogen, and with oxidized compounds of iron. Annealing at 600° to 800° suffices to remove most of the hydrogen and some of the chlorides; this renders the iron more malleable and resistant to corrosion, but to attain a still higher degree of purity and to simplify subsequent operations the iron must be fused, preferably in a reducing atmosphere, and held in a state of fusion for some

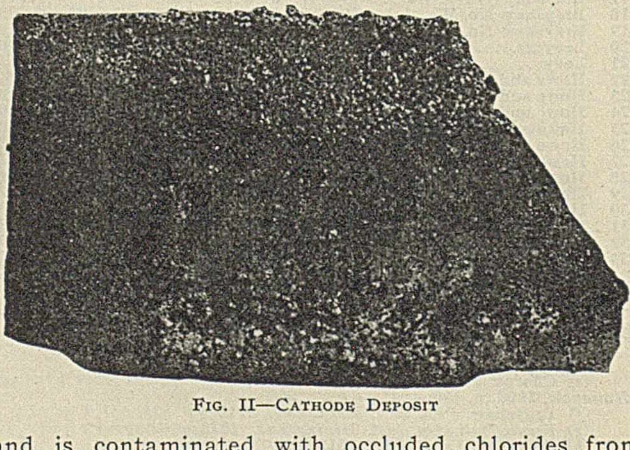


FIG. II—CATHODE DEPOSIT

minutes. Owing to the high melting point of iron (1530°), to its strong tendency to combine with or to be contaminated by substances likely to be present as vapors in electrically heated furnaces (Si, S, C, Pt, and the like), or as gases in the products of combustion of a fuel-fired furnace (CO, SO_2, SO_3, CO_2, H_2O), and especially because of the corrosive action on crucibles of molten oxides of iron, with resulting possible contamination of the melt by slags, etc., it is evident that great care must be taken in the choice of furnaces and crucibles for work of this kind. While it is true that iron in the molten condition containing as little as 0.1 to 0.2 per cent of the impurities ordinarily determined has been produced commercially for some time, the conditions of laboratory preparation on a small scale are entirely different and lead to new difficulties.

1—Contamination by the hearth, or crucible material, or by gases, is less in large-scale operations, owing to the relatively smaller surface exposed compared with the weight of metal being handled.

2—Additions, such as ferro alloys, aluminum, or titanium for purification of the melt, as used commercially, are not permissible in an investigation of this kind.

3—The use of slags for protection from the products of combustion or for eliminating impurities and controlling composition in desired ways is excluded.

The importance of the conditions for melting pure iron and its alloys to secure products of very high purity does not seem to have been recognized sufficiently in the past, and we shall therefore give full details of our methods.

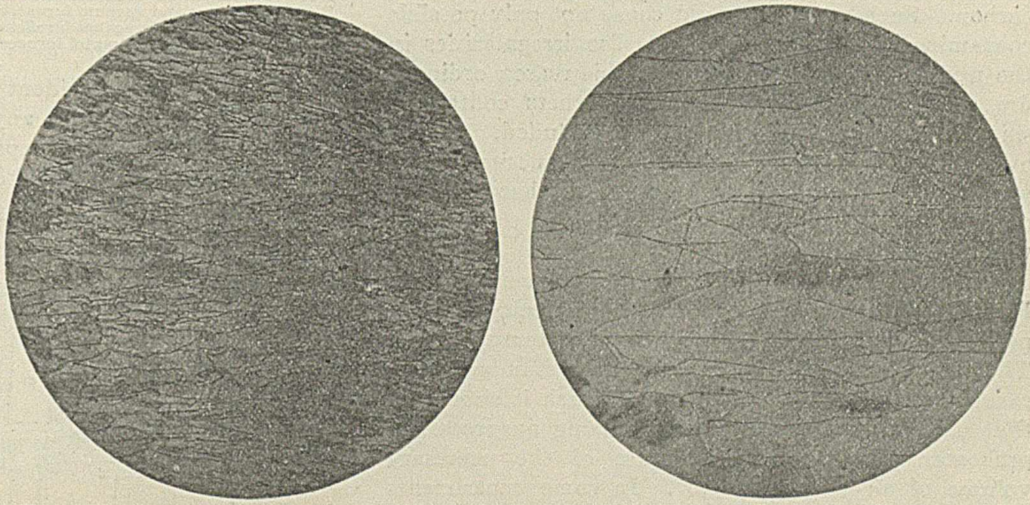

× 100 × 250

Fig. III—Electrolytic Iron as Deposited: Section Perpendicular to the Electrode

FURNACES

ELECTRIC FURNACES—For ease and convenience of manipulation a furnace used for melting pure iron should maintain continuously a temperature of not less than 1600°. The temperature required eliminates furnaces wound with nickel or nichrome; molybdenum or platinum-wound furnaces are not desirable for work in high vacua, owing to volatilization of these metals with resulting contamination of the melt and destruction of the heater. Tungsten windings could no doubt be used, but no suitable furnace of this type was available at the Bureau. Our work with electric furnaces has been confined, therefore, to those employing carbon in some form as resistor. A furnace of the kryptol type, shown in Fig. IV, was constructed and has been found satisfactory. The Arsem vacuum furnace,[1] shown in Fig. V, was extensively used and is very suitable for work of this character. The Helberger crucible furnace was used for melting some of our alloys. This furnace is intended to be used with conducting crucibles, but our work was done with amorphous carbon tubes as resistors. Because of the lack of protection of these from the oxidizing action of the air their life is inconveniently short. The resistance of Acheson graphite tubes was found to be too low to permit the desired temperatures to be reached. There were difficulties in securing good electrical contact between the terminals and the resistor so that this style of furnace as used by us is not to be recommended for work at 1600° or above. The difficulty common to all the types of electric furnaces used (unless the precautions mentioned later were observed) was that the melts were contaminated by volatile sulfur, silicon, or carbon derived from the resistors used. This contamination was least in the Arsem furnace when protecting the crucible, as shown in Fig. V, and was greatest in the Helberger furnace and in the kryptol furnace when using amorphous carbon as resistors.

Table III shows the amounts of contamination introduced by melting pure iron in various types of furnaces. An analysis of the amorphous carbon used as filling material in the kryptol furnace and for the resistor tubes of the Helberger furnace showed 0.75 per cent sulfur and 0.07 per cent silica. The high sulfur in the amorphous carbon resistors is due to the use of petroleum coke in their manufacture. Analyses of the best grades of petroleum coke obtained by the Geological Survey showed percentages of sulfur ranging from 0.63 to 1.37 per cent. After having discovered these defects in amorphous carbon we discontinued its use, employing granular Acheson graphite of the best grade for the kryptol furnace, and a graphite

Table III—Percentage Composition of Bureau of Standards Electrolytic Iron after Melting in Various Furnaces

Manner of melting	C	Si	S	Mn	P	Cu
Original iron not melted...	0.004	0.001	0.004	Trace	Trace	...
In kryptol furnace filled with Acheson graphite...	0.012	0.01	0.004	Trace	Trace	...
In Helberger furnace.......	...	0.014	0.024	Trace	Trace	...
In Arsem furnace..........	0.010	0.007	0.007	Trace	Traee	0.012
In Helberger furnace and remelted in Arsem furnace.	0.009	0.004	0.005	Trace	Trace	...
In gas furnace...........	0.012	0.003	0.02	Trace	Trace	...

---

[1] W. C. Arsem, *Trans. Am. Electrochem. Soc.*, 9 (1906), 152.

spiral for the Arsem furnace. A resistor from the Arsem furnace contained 0.02 per cent sulfur and 0.03 per cent silica. The results were satisfactory. It may be concluded that if carbon resistance furnaces are intended for making melts with minimum contamination by volatile substances from the heating element, the best material available at present is first-quality graphite; and that the resistors should be carefully analyzed to insure against impurity before installing them in the furnace. It is further evident that if the refractory walls of the furnace are in immediate contact with the heater, the former should be made of material not likely to react with the heated carbon. Such reaction would cause not only possible contamination of the melt, but also irregularities in the working of the furnace. For this reason ordinary fire clay or silica bricks, or any others containing silica in considerable amount, are excluded. In our own kryptol furnace commercial magnesite bricks were used, and while they were not all that could be desired they proved serviceable, provided the resistor was renewed occasionally.

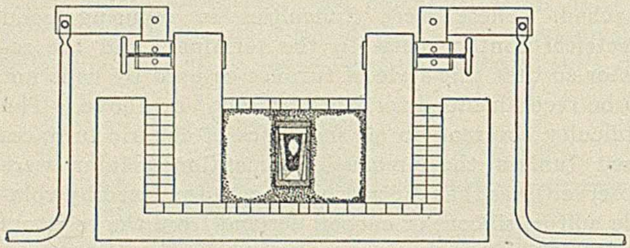


FIG. IV—KRYPTOL FURNACE WITH CRUCIBLE IN POSITION

GAS FURNACES—Two types of gas furnace, shown in Figs. VI and VII, were used and no difficulty was experienced in maintaining the necessary temperatures. The furnace shown in Fig. VI was a standard type except in respect to the blowpipe, which is similar to that used in tool forges, or for brazing purposes. A preheater raised the temperature of the necessary volume of air to about 350°. In some experiments made with this furnace pure platinum wire was melted, indicating that a temperature in excess of 1750° had been attained. The refractory lining supplied by the manufacturers was found to have a very short life under these conditions, so that we later covered it with alundum cement, or with a mixture of alundum cement and clay, which prolonged the life. The surface combustion furnace (Fig. VII) proved to be very suitable. This furnace has already been illustrated and briefly described.[1] The same trouble was experienced with the original refractory lining, and repairs were again made with alundum and clay. The highest temperature reached in this furnace, 1670°, was obtained when burning about 180 cubic feet of city gas per hour. In using this type of furnace for pure melts, the crucible must be protected from the large amount of very fine dust blown out of the contact material during operation.

CRUCIBLES

A few preliminary experiments with clay crucibles showed that it would be out of the question to use these for melting pure iron-carbon alloys. The clays used for making the crucibles which we tried were not sufficiently refractory and were badly corroded by the iron oxide which coats the surface of all melts made in gas-fired furnaces. This did not occur in the electric furnaces, but here the reducing atmosphere, which prevented oxidation, also caused the introduction of relatively large amounts of silicon from the clay. Alundum crucibles were tried, but gave the same trouble as those of clay. Crucibles made of electrically fused or sintered magnesia from two different sources were given a trial in the various types of furnaces, but with these also there was more contamination of the melts by silicon than seemed desirable (Table IV).

TABLE IV—PERCENTAGE COMPOSITION OF ALLOYS MADE IN CRUCIBLES OF COMMERCIALLY PURE MAGNESIA

No.	METHOD OF MELTING	C	Si	S
P 27	Gas and vacuum furnaces	0.584	0.056	0.004
P 28	Gas and vacuum furnaces	0.022	0.029	0.030
P 29	Gas and vacuum furnaces	0.367	0.015	0.029
P 41	Single melt in Helberger furnace	0.886	0.024	0.013
P 39	Melted twice in Helberger furnace	0.688	0.054	0.026
P 31	Helberger and vacuum furnaces	0.210	0.032	0.020
P 32	Helberger and vacuum furnaces	0.252	0.022	0.010
P 33	Helberger and vacuum furnaces	0.094	0.041	0.024
P 35	Helberger and vacuum furnaces	0.146	0.050	0.029
P 37	Helberger and vacuum furnaces	0.088	0.050	0.039
P 40	Helberger and vacuum furnaces	0.765	0.033	0.015
P 42	Helberger and vacuum furnaces	0.058	0.070	0.016
P 36	Melted twice in kryptol furnace	0.927	0.045	0.019

As it had become evident that the desired results could not be secured with any kind of crucible on the market, we began the experiment of making our crucibles of various grades of chemically pure magnesia calcined in the electric furnace at 1600° to 1800°. Although our product contained usually not over 0.05 to 0.10 per cent silica the alloys melted in crucibles made from such magnesia still carried too much silicon (see Table IV). Because of the difficulty of securing from chemical dealers magnesia suffi-

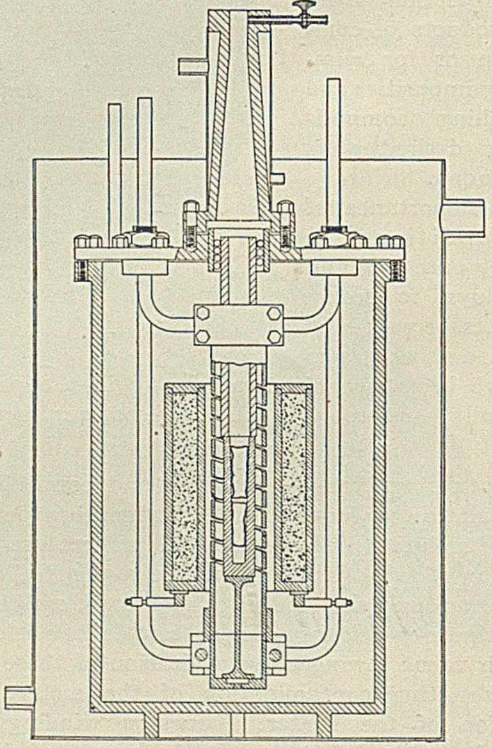


FIG. V—ARSEM FURNACE WITH CRUCIBLE AND PROTECTING TUBE IN PLACE

---

[1] Lucke, THIS JOURNAL, 5 (1913), 801.

ciently low in silica, the high cost of a good grade of this material, and the need of large quantities for several contemplated investigations, we decided to prepare our own material. An endeavor was made to develop a method free from too many complicated manipulations. As raw material we used two or three grades of pharmaceutical magnesium carbonate carrying 0.1 or 0.2 per cent silica, and later a calcined Grecian magnesite with about 3.5 per cent silica. Attempts to prepare silica-free magnesia from these sources by dissolving them in hydrochloric acid, evaporating the solutions to dryness and baking, followed by solution of the $MgCl_2$, filtration and precipitation of magnesium carbonate by ammonium carbonate were not very successful on the scale tried, for the technique was difficult and the product unsatisfactory, as well as expensive. After trials of several other methods we developed the following procedure, which has produced a magnesium oxide carrying usually not over 0.01 per cent silica, and at low cost:

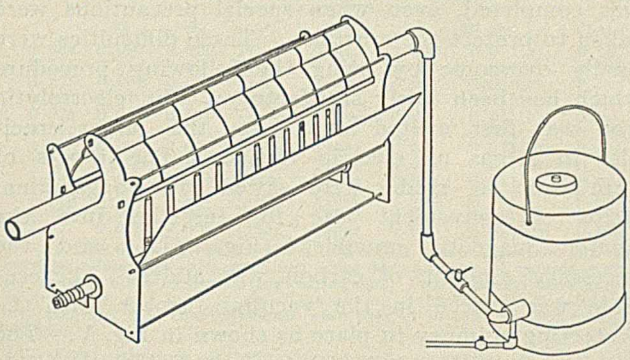


FIG. VI—SMALL GAS FURNACE WITH PREHEATER

The Grecian magnesite was dissolved in commercial acetic acid (70 per cent), using a slight excess of the latter; more of the magnesite was then added until the solution was alkaline to litmus paper, after which the solution was diluted with about twice its volume of water, the whole thoroughly stirred and allowed to stand in barrels for a day or two; at the end of this time the clear solution was siphoned off into a large wrought-iron basin and rapidly evaporated over a large Fletcher burner, adding fresh liquid at intervals until a sufficient amount of the magnesium acetate had separated. The evaporation was then carried to the point where the solution solidified on cooling, after which the decomposition of the acetate into oxide was effected by directing the flame from a large Teclu burner over the surface of the separated salts. The magnesium oxide so obtained is contaminated by carbon, undecomposed acetate, and a little iron, but after calcining is quite suitable for use in making crucibles. The calcining was done in large gas furnaces which gave a temperature of from 1550° to 1650°. The magnesia, as taken from the iron basin, was moistened slightly with water and made up into large balls, which were placed inside an ordinary No. 20 plumbago crucible coated on the inside with alundum cement, or lined with an Acheson graphite crucible. The crucible was carefully covered during the calcining operation, which lasted about two hours. As a result of this treatment the magnesia had shrunk to about one-third its original volume, all the carbon had burned out, and the silica content was very slightly increased. We found it important to blow air through the furnace for several minutes after shutting off the gas, in order to remove the last traces of products of combustion carrying sulfur. If these are allowed to remain in the furnace during the cooling period, the magnesia takes up some sulfur; our best material contained less than 0.01 per cent of this element. Calcining in the gas furnace at the temperature named gives a product which still shrinks a little when used in crucibles heated to higher temperatures, but we had no serious trouble with crucible failures on this account.

Two sizes of crucibles were used which, together with the molds employed for making them, are shown in Fig. VIII. The calcined material was mixed with about 10 per cent by weight of uncalcined magnesia and the whole wet with water until it formed a pasty mass. The thin brass cups used for lining the molds were put in place and there was introduced into the mold a sufficient amount of the material (ascertained by preliminary trials); a pressure of 5,000 to 10,000 pounds per square inch was applied to the head of the plunger and kept there a minute or two after the plunger had been driven down as far as it would go. The mold was then opened by removing the rings, the brass cup carrying the crucible removed, and the plunger taken out. The crucibles were dried at 100° to 120° for a day and the brass cups stripped off by melting the solder from the joints. They were then either used directly for melts, or after heating to 1200° to 1600° in a gas or electric furnace. The

TABLE V—PERCENTAGE OF SILICA IN MAGNESIA FROM DIFFERENT SOURCES

SOURCE	SiO_2
Calcined Grecian magnesite	3.15 and 4.61
University of Illinois electrically calcined MgO	1.99
Magnesium aluminate tube	5.39
MgO reagent (uncalcined) A	0.03
MgO reagent (uncalcined) B	0.07
Bureau of Standards MgO prepared from acetate	0.008
Bureau of Standards MgO calcined in gas furnace	0.013 and 0.017
Crucible made from Bureau of Standards calcined MgO	0.025

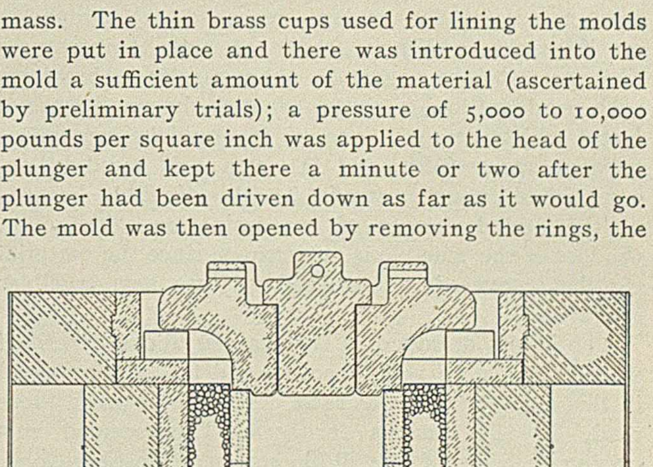


FIG. VII—SURFACE COMBUSTION CRUCIBLE FURNACE latter procedure is necessary for all crucibles that are to be used in vacuum furnaces.

PROCEDURE IN MAKING ALLOYS

We first attempted to make ingots in the following manner:

The iron as stripped from the cathodes was dried, broken into small pieces, and placed in one of the larger magnesia crucibles (Fig. VIII), together with a suitable quantity of carbon. These were brought gradually to temperatures above the melting point of iron and left in the furnace for 10 or 15 minutes. After cooling, the crucibles were removed and broken away from the ingots. This procedure, while apparently wasteful, was necessary for several reasons: (1) Magnesia crucibles are extremely fragile at high temperatures and any attempt to handle them results in breakage with resultant loss of melts; (2) with the small mass of metal which we used (100 g.) it would be impossible to pour successfully; and (3) even if it could be accomplished, pouring would be objectionable because of the added danger of contamination. Moreover, the loss of the crucible is not serious, since the material can be recovered and worked up into new crucibles repeatedly.

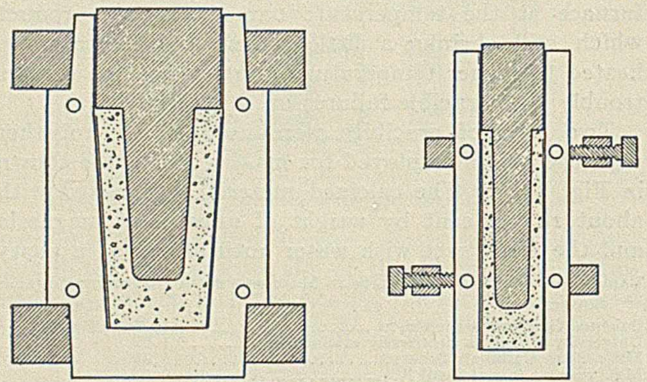


FIG. VIII—CRUCIBLE MOLDS

The ingots obtained in the manner above described were found to be very unsound and full of blowholes; in this respect there was little difference between those made in the various furnaces. This seemed surprising in view of the difference in atmosphere over the melt in a gas furnace, where the conditions are oxidizing to iron, and in an electric furnace, where carbon dioxide, water vapor, or oxygen—the gases which would oxidize iron at high temperatures—are present only in very small amounts. It would thus appear that the blowholes in iron may be caused by carbon monoxide as well as by any or all of the other gases named, and that the maintenance of a reducing atmosphere is no guarantee of freedom from blowholes. That the melts made in the kryptol furnace were made under reducing conditions is evident from Fig. IV, which shows that the crucibles are completely covered with carbon at all times; this is further evident from an oxygen determination made on drillings from an ingot melted in the kryptol furnace. The percentage of oxygen in this ingot, notwithstanding the fact that no deoxidizer had been used, was 0.03.[1] The weight of these ingots was about 100 g. Fig. IX(*a*) is a photograph of a split ingot, showing the unsound structure.

The introduction of a regulated amount of carbon into the alloys gave a good deal of trouble. In the gas furnace the amount of oxidizing gases was so great, relative to the weight of carbon introduced, that the latter was all burned out before the melting operation was completed, even when special precautions were taken to protect the crucibles. These difficulties were finally overcome by using the following procedure which has been fairly satisfactory: The electrolytic iron was first melted down in the larger crucibles in a gas or electric furnace. The ingots of pure iron so made were sawed into longitudinal strips of convenient size for insertion into the smaller magnesia crucibles (Fig. VIII) and the necessary amount of carbon was added. The crucible was placed in the vacuum furnace with the protecting chimney in place as shown in Fig. V. The furnace was evacuated to 0.2 mm., and the current through the heater was increased gradually until the iron had melted and dissolved the carbon; this point was determined by observation through the window. As soon as this stage was reached a violent ebullition took place; sometimes the contents of the crucible were ejected. We attribute this principally to the expulsion of gases from the cavities in the ingots. In 10 or 15 minutes the surface of the melt became quiescent and the operation was ended. After cooling, the ingots were removed by breaking the crucibles.

Fig. IX(*b*) shows the sound structure of these ingots, which were usually entirely or nearly free from blowholes. After discarding the surface down to clean metal, the ingots were turned down to the size required for the thermal test specimens, Fig. IX(*c*), retaining the chips for analysis. Complete analyses of typical samples are given in Table VI. For comparison, Table VII is given, showing the results of attempts by two earlier workers to make pure iron-carbon alloys.

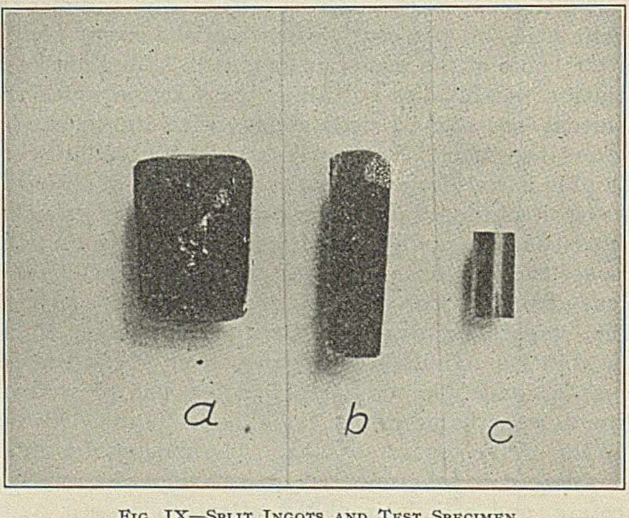


FIG. IX—SPLIT INGOTS AND TEST SPECIMEN

We are now building a larger vacuum furnace for producing large ingots of pure iron and iron-carbon alloys, which will be examined either as made or after forging, rolling, and application of heat-treatment

---

[1] We are indebted to J. A. Aupperle, metallurgist of the American Rolling Mill Co., for this analysis.

as to physical properties, magnetic and electrical characteristics, resistance to corrosion, and related properties. Reports of progress in this work will be issued as they are justified. Later we shall deal with the effect of alloying elements other than carbon on the properties of iron.

TABLE VI—PERCENTAGE COMPOSITION OF TYPICAL BUREAU OF STANDARDS IRON-CARBON ALLOYS

C	Si	S	P	Mn	Cu	Ni and Co	Total
0.084	0.007	0.009	Trace	Trace	0.020	0.011(*a*)	0.047
0.376	0.013	0.009	Trace	Trace	0.005	0.011(*a*)	0.038
0.395	0.008	0.013	Trace	Trace	0.012	0.011(*a*)	0.044
0.597	0.010	0.008	Trace	Trace	0.004	0.011(*a*)	0.033
0.624	0.004	0.010	Trace	Trace	0.008	0.011(*a*)	0.033
0.692	0.006	0.011	Trace	Trace	0.008	0.011(*a*)	0.036
0.860	0.006	0.006	Trace	Trace	0.007	0.011(*a*)	0.030
1.087	0.006	0.006	Trace	Trace	0.013	0.011(*a*)	0.036
1.797	0.010	0.005	Trace	Trace	0.018	0.011(*a*)	0.044
2.240	0.005	0.005	Trace	Trace	0.020	0.011(*a*)	0.041
2.560	0.005	0.005	Trace	Trace	0.014	0.011(*a*)	0.035
3.27	0.006	0.006	Trace	Trace	0.016	0.011(*a*)	0.039

(*a*) The figures given for nickel and cobalt do not represent individual determinations for each specimen since the amount of sample was insufficient to allow of these being carried out. Four representative analyses on pure iron and iron-carbon alloys having given the result indicated, it was assumed that these elements were present in that amount in all the samples.

TABLE VII—DEGREE OF CONTAMINATION (PERCENTAGES) OF IRON MELTS MADE BY OTHERS

	C	Si	P	S	Mn
Müller's electrolytic iron	0.0630	0.0053	0.0045	0.0024	0.0090
Müller's electrolytic iron after remelting *in vacuo* in "pure MgO crucible"(*a*)	0.017	0.089	0.028	0.037	0.025
C. F. Burgess' electrolytic iron	0.009	0.006	0.001	0.010	Trace
C. F. Burgess' electrolytic iron melted with sugar carbon in magnesia crucible by Howe(*b*)	2.954	0.040	0.050	0.035	None

(*a*) A. Müller, *Metallurgie*, **6** (1909), 159.
(*b*) Howe, *Bull. Am. Inst. Mining Eng.*, **1913**, p. 1118.

DISCUSSION OF THE SOURCES OF CONTAMINATION

SILICON—In our earlier experiments, where we were obliged to make crucibles of magnesia higher in silica than that produced by the acetate method already described, we noted that occasionally an alloy of very low silicon content would result from a melt made in a crucible relatively high in silica. The use of our purified magnesia had eliminated all trouble from silicon contamination of melts, but we later decided to make some experiments to determine the relationship between the introduction of silicon and temperature of melting. For this purpose a series of runs was made in the vacuum furnace varying independently the temperature of melting and the silica content of crucibles. One per cent of carbon was added to all these melts since in the presence of carbon there is additional likelihood of contamination of silica at high temperatures. The results in Table VIII show that if the temperature is not allowed to rise much above 1600°, crucibles containing as much as 0.9 per cent silica may be used safely. This is of importance when a great deal of work is being done, for it enables one to use repeatedly old crucible material until the silica becomes dangerously high.

TABLE VIII—FACTORS GOVERNING CONTAMINATION OF MELTS BY SILICON

Temperature of melting (degrees)	SiO_2 in crucible Per cent	Si in melt Per cent
1610	0.57	0.007
1610	0.67	0.007
1610	0.75	0.007
1610	0.91	0.006
1610	1.14	0.015
1610	1.66	0.023
1650	1.35	0.032
1720	1.27	0.040
1780	1.20	0.042
1770	0.19	0.007
1720	0.24	0.006
1760	0.31	0.021
1740	0.60	0.031

SULFUR—As has been shown, contamination by sulfur may result from the use of gas furnaces or of petroleum coke carbon in electric furnaces. On abandoning the use of gas furnaces and employing Acheson graphite as resistor material this difficulty disappeared, as is apparent from a comparison of Tables V and VII.

MANGANESE AND PHOSPHORUS—Both these elements have been reduced to mere traces (less than 0.001 per cent) in all our alloys.

COPPER—This impurity, one of the most difficult to guard against, is present in objectionable quantities in some of our melts and to some extent in all. The ingot iron used for anodes contains copper which is not completely removed in the electrolytic refining process, so that our deposits contain about 0.005 per cent of this element. This copper persists through the melting operation, and unless great care is taken, more is introduced, owing to the use of copper connections in furnaces. In particular, the copper blocks used in the vacuum furnace must be smooth and make good contact with the graphite heater, since any arcing causes the vaporization of considerable quantities of copper with resulting contamination of the melt.

NICKEL AND COBALT—Our anode iron contains 0.02 per cent (Ni + Co); in the electrolytic refining this is reduced to 0.01 per cent which persists through the melting operations.

MAGNESIUM—As all our melting was done in magnesia crucibles it was thought desirable to look for this element as a possible impurity. Several analyses of ingots made in the regular way showed that Mg was not present in any determinable quantity. A rather interesting result, however, was obtained on analyzing some ingots which had been melted at high temperatures (over 1700°). It was found that these contained appreciable amounts of Mg (from 0.005 to 0.01 per cent). Furthermore, the samples were so brittle that the pieces broke while turning in the lathe. It appears at least possible that there may be a direct connection between the two circumstances, though our present data are not sufficient to justify a definite conclusion to that effect.

OXYGEN—Unfortunately, the Bureau is not at present prepared to make accurate oxygen determinations on this class of material, but it is hoped later to publish analyses of some of the alloys for this element, if it is found to be present. In our method of preparation, starting with an ingot already low in oxygen and carburizing in a vacuum furnace where the carbon monoxide resulting from interaction of oxides or oxygen with carbon would be removed as formed, the deoxidation would tend toward completion, and accordingly the alloys should contain but small residual amounts of oxides and oxygen.

SPECTROSCOPIC EXAMINATION

In order to confirm the results of the chemical analyses for small quantities of impurities, the arc spectra of a number of samples of iron and iron-carbon alloys were studied by Dr. K. Burns[1] of this Bureau, to whom we are indebted for the data given below:

MAGNESIUM—The spectra fully confirmed the chemical tests. Line 2851.1A showed strong in two samples containing 0.007 and 0.010 per cent Mg while it was very faint or absent in

---

[1] For an account of the methods used, cf. K. Burns, *Bull. Bur. Stand.*, **12** (1916), 179–196.

unfused irons and in alloys which failed to give magnesium by the chemical method.

SILICON—Line 2881.5A showed presence of silicon in the alloys, but unfused iron showed no traces.

MANGANESE—Several manganese lines show in various samples of electrolytic iron that have been melted. These lines are absent from the spectrum of unmelted electrolytic iron. The faintness of the manganese lines as compared with those given by a specimen containing 0.01 per cent of this metal indicate a very low manganese content.

CHROMIUM—The statements made in regard to manganese also apply to chromium.

COPPER—Lines 3247.7 and 3274.1A are always present though so faint as to be questionable in unmelted specimens.

NICKEL AND COBALT—Several nickel and cobalt lines show faintly in the various samples.

In the course of the examination of the arc spectrum of pure iron several faulty identifications have been corrected.

2795.542 ascribed to magnesium is iron;
3369.555 ascribed to nickel is iron and nickel;
3412.347 ascribed to iron is probably cobalt; and
3443.645 ascribed to iron is no doubt cobalt.

No attempt has as yet been made to clear up all the doubtful identifications in the iron spectrum; the above list is given to show the possibilities in this direction which may be realized by means of the use of pure iron.

METHODS OF CHEMICAL ANALYSIS

The analyses recorded in this paper were carried out according to well-known principles with suitable precautions, and the methods are given below merely for reference.

The chips obtained when making the thermal test specimens were thoroughly mixed before weighing portions for analysis. Chips from high-carbon alloys which contained admixed graphite were finely ground and mixed before weighing.

CARBON was determined by the barium-carbonate titration method devised by one of the authors.[1] The chips (1 to 5 g.) were burned in purified oxygen, passing the products of combustion into a solution of barium hydroxide; the barium carbonate was filtered and washed in an atmosphere free from carbon dioxide (see the original for details of apparatus used), and the barium carbonate was titrated against standard hydrochloric acid, using methyl orange as indicator.

SULFUR was determined by dissolving 5 g. of the metal, contained in an appropriate evolution apparatus having all ground-glass connections, in concentrated hydrochloric acid, the gases given off being passed into an ammoniacal solution of hydrogen peroxide. After complete solution of the metal the contents of the evolution flask were boiled for 10 minutes while a slow current of purified hydrogen was passed through the solution. The ammoniacal peroxide solution was transferred to a beaker and boiled a few minutes, then the solution was slightly over-neutralized with hydrochloric acid and the sulfur precipitated at boiling temperature as barium sulfate. After digestion for a sufficient length of time the precipitate was filtered, washed, ignited and weighed, and the percentage of sulfur calculated.

SILICON—Five to 10 g. of metal were dissolved in an Erlenmeyer flask in hydrochloric acid (equal volumes of water and hydrochloric acid of specific gravity 1.20), the solution evaporated to dryness and the flask heated on the hot plate at about 200° for an hour. The residue was digested with hydrochloric acid of the same strength as that used for dissolving; the insoluble matter containing the silica was filtered off, washed with dilute hydrochloric acid and water, ignited in a platinum crucible and weighed, after which the silica was volatilized with hydrofluoric acid and its amount determined from the change in weight of the crucible after again igniting. The results were then calculated to silicon.

PHOSPHORUS—The usual method of precipitation as ammonium phosphomolybdate was employed, and the phosphorus estimated by comparing the volume of the precipitate with that produced by treating a standard steel in the same way.

MANGANESE—The sodium bismuthate method was used.

COPPER—Ten to 20 g. of metal were dissolved in a slight excess of hydrochloric or sulfuric acid, and hydrogen sulfide passed into the hot solution until all the copper was precipitated. The precipitate was filtered off, and, after washing the paper carrying it, was transferred to a porcelain crucible, and the whole ignited until all the carbon was burned off. A little potassium bisulfate was added and the copper oxide brought into solution by fusion, following by leaching with water and filtration. The solution was compared with a standard solution colorimetrically, either by an ammonia or ferrocyanide method, or by both.

MAGNESIUM—Ten to 20 g. of metal were dissolved in aqua regia, the solution evaporated to dryness, and dehydrated. The residue was dissolved in 1 : 1 HCl and silica removed by filtration. The iron was extracted by the ether method. After the removal of the iron, hydrogen sulfide was passed through the solution (acidified with acetic acid) to precipitate copper, etc. Manganese and residual iron were removed from the filtrate by bromine and ammonia and the magnesium precipitated as magnesium-ammonium phosphate. The accuracy of the above procedure was checked by running duplicates to which small amounts of a magnesium salt had been added.

NICKEL AND COBALT—The solution of 10 g. of the iron in $HNO_3 + HCl$ was evaporated to dryness, dehydrated, taken up with HCl of 1.1 specific gravity, filtered, the filtrate evaporated to a small volume, and the iron removed by the ether method. Copper was precipitated with hydrogen sulfide, and the iron and manganese in the filtrate were precipitated by ammonia and bromine. The filtrate was acidified with acetic acid, and nickel and cobalt were precipitated as sulfite from the boiling solution. The two metals were either weighed as oxides or deposited electrolytically from ammoniacal solution, the two methods giving concordant results. The oxides (or metals) were dissolved in hydrochloric acid, the solution was neutralized, and finally made acid with acetic acid and the cobalt precipitated as $K_3Co(NO_2)_6$. After filtering and igniting this precipitate at a low temperature, the cobalt was dissolved, reprecipitated with hydrogen sulfide, and finally weighed as $CoSO_4$. The nickel was determined by the dimethylglyoxime method in the filtrate from the cobalt. The sum of these determinations checked very closely with the total (Ni + Co) found directly.

SUMMARY

Methods have been developed for producing laboratory samples of iron-carbon alloys, of a very high degree of purity; sources of contamination of melts and means of eliminating them have been described; a method for producing magnesia of a satisfactory degree of purity for making crucibles to be used in work of this kind has been developed; a procedure for making small ingots, which are sound and free from blowholes, without the use of deoxidizers has been worked out. A series of iron-carbon alloys containing 99.96 per cent of the two elements has been prepared, to serve as a basis for the redetermination of the iron-carbon equilibrium diagram.

BUREAU OF STANDARDS
WASHINGTON, D. C.

---

[1] J. R. Cain, "Determination of Carbon in Steel and Iron by the Barium Carbonate Titration Method," *Technologic Paper* No. **33** of the Bureau of Standards.

RECOVERY OF GALLIUM FROM SPELTER IN THE UNITED STATES

By W. F. Hillebrand and J. A. Scherrer

Received February 5, 1916

Some months ago a few grams of gallium of American production were received by one of us (S.) from Mr. F. G. McCutcheon, Chemist of the Bartlesville Zinc Company, Bartlesville, Oklahoma. Recently the other (H.) received 50 g. more from Mr. McCutcheon.

The first material contained a little indium and zinc and a trace of calcium, as determined spectroscopically by Dr. K. Burns at the Bureau of Standards. The second lot is of similar composition, presumably. An as yet incompleted test by one of us (H.) indicates an indium content probably of less than one per cent.

The metal or alloy is a liquid resembling mercury in appearance, but it wets glass and porcelain and adheres so tenaciously that if agitated in a glass vial the contents can be seen only as a coating on the walls. This latter property is not in evidence if the metal is covered with hydrochloric or sulfuric acid.

Although gallium melts at about 30°, it is said to remain liquid far below this temperature, indefinitely unless inoculated with solid gallium.

Inquiry of Mr. Kurt Stock, Superintendent of the Bartlesville Zinc Company, brought out some exceedingly interesting information, as shown by the following extracts from his letter of reply, dated October 21, 1915:

> "His attention [Mr. McCutcheon's] was drawn to peculiar beads and drops, in appearance like mercury, which seemed to sweat out of zinc-lead dross plates after these had been exposed to the weather for a time. Mr. McCutcheon, with the help of his two assistants, made a great number of tests, proving the material to be an alloy of gallium and indium with small amounts of zinc * * * * *."
>
> "Your hope that a new source of supply for both metals has been opened up, with the prospect of continued manufacture, is not shared by me, as the conditions leading to the concentration of gallium and indium are very unusual and are based on the abnormal state of the spelter market. You are aware that the present demand for high-grade spelter has led zinc smelters to the practice of redistillation, and it is the final leady residue from such continued redistillation that carries gallium in noticeable quantities * * * *. We are not at all sure which of the large variety of ores is responsible. Gallium is not found in all dross and where it is found it does not occur continuously * * * * * * *"
>
> "That the amount in the original ores must be extremely small can well be realized when you consider that the residue from the continued distillation of about 12,000 lbs. of spelter weighs about 60 lbs., and represents our raw material from which we can obtain a few grams of the alloys. However, we have at present about 45 tons of dross on hand, which we suspect carries gallium."
>
> "A very interesting feature is that both gallium and indium are volatile at the temperature prevailing in our ore furnaces, where a maximum of 1350° C. is reached for only a few hours, but they resist distillation if kept for three weeks and longer at the temperature at which we operate our redistilling furnaces, namely about 1000° C."
>
> "Please be assured that we shall leave nothing untried to save these rare metals, but do not get impatient if results are not forthcoming for a while * * * *."
>
> "You may use this very general information any way you desire."

It will be of interest to determine if this metal, hitherto such a rarity, possesses qualities of value in itself or when combined in small amounts with other metals, and if it has such, whether their importance will justify continued production after the price of spelter falls.

So far as known to us, the only uses for gallium that have been so far suggested are in alloy with aluminum as cathode material in metal vapor lamps[1] and for the production of optical mirrors. The fact that it wets quartz would seem to negative the suggestion that it might be suitable in quartz thermometer tubes for measuring temperatures too high for glass instruments. The authors would gladly receive further suggestions.

Also of interest is the particular source of this gallium. Mr. Stock assures us that it comes from domestic ores, probably from certain as yet undetermined ones of Joplin. Its presence has been reported in the past in a number of domestic blendes, including one from Joplin. A very recent statement from Mr. Stock is to the effect that the dross produced of late shows no gallium and that the amount of gallium at first thought to be available will not come up to expectations: "I am more convinced than ever that gallium will remain a rarity and that a commercial production is out of the question."

Since the foregoing was written, spectroscopic tests have been made at the Bureau of Standards by Dr. K. Burns upon seven samples of zinc ore kindly supplied by Mr. S. M. Rodgers of the American Steel and Wire Company. Germanium was also included in the metals looked for. The data concerning the precise sources of some of the ores tested are unfortunately meager, particularly with respect to Nos. 2, 4 and 7, but the presumption is strong that No. 4 came from the Joplin district. Of special interest is the fact that this ore showed more of both gallium and germanium than any of the others. The tests obtained by Dr. Burns follow, accompanied by his comments:

SPECTROSCOPIC TESTS OF ZINC ORES

No.	KIND AND SOURCE OF ORE	Germanium	Gallium
1	Sulfide—Sunset, Idaho	Moderate	Moderate
2	Sulfide—Australia	Not found	Moderate
3	Sulfide—Frisco, Idaho	Weak	Moderate
4	Sulfide—Missouri	Strong	Strong
5	Carbonate—Monarch, Leadville	Absent	Moderate
6	Carbonate—Doctor Mine, Almont, Colo.	Moderate	Not found
7	Carbonate—Utah, Nevada	Very weak	Rather weak

> "By means of the carbon arc the spectrum was examined in the region 2800 A to 3600 A. Large amounts of iron were present in all these samples. This makes the determination of indium by our method not very accurate, as the most sensitive lines of indium coincide either with carbon lines or with iron lines. It is certain, however, that indium is not present in these ores in quantities approaching one-tenth of the gallium found in ores marked 'moderate.'"

BUREAU OF STANDARDS, WASHINGTON, D. C.

---

[1] T. W. Vogel, *Zentralblatt*, **1910**, I, 703. German patent.

A PROPOSED METHOD FOR THE PROFITABLE UTILIZATION OF WASTE SULFITE LIQUOR

By Herman V. Tartar

Received December 23, 1915

The utilization of the waste liquors resulting from the manufacture of paper pulp by the sulfite process is a problem that has received as much careful attention and systematic study perhaps as that of any other waste product of the present day. The technical literature contains reports of many exhaustive investigations on different phases of this problem. Over 150 patents have been secured for utilizing the waste sulfite liquor. In spite of all this experimental work, however, this material is still classed as a waste. Considering the amount, it is one of the most valuable waste materials known to industrial chemistry.

Most of the paper mills get rid of the waste liquor by emptying the same into streams. An estimate of the quantity of this material discharged annually into the streams of this country is given in the following table taken from Water-Supply Paper 226 of the United States Geological Survey:

Amount of Sulfite Waste Liquor Discharged into Streams of the United States during 1906

	Million gallons
Maine	560,000,000
Massachusetts	45,000,000
Michigan	175,000,000
New Hampshire	380,000,000
New York	1,000,000,000
Ohio	41,000,000
Oregon	52,000,000
Pennsylvania	217,000,000
Virginia	84,000,000
West Virginia	89,000,000
Wisconsin	540,000,000
All other states	44,000,000
	3,227,000,000

When one takes into account that of this enormous quantity of liquor discharged annually into streams there is 10 per cent by weight, or more than 2.5 billion lbs. of solid matter, largely organic, it must be conceded that its disposal is a problem of no small magnitude. In fact, the pollution of streams in this manner is one of the most serious water pollution problems confronting this and several foreign countries. "The seriousness of the problem is the direct result of two factors—the tremendous volume of such waste liquors and their high content of organic matter of extremely undesirable character."

Besides the usual objections to the addition of organic matter to streams, some of the paper mills of Oregon and other western states have met with the further objection that the sulfite liquor may be toxic and poisonous to fish. This latter objection is an important one when the waste liquors are discharged into streams where the salmon canning industry has reached considerable proportions.

At the suggestion of the Crown Willamette Paper Company of Portland, Oregon, Professor Charles Marchand, of the Pernot Laboratories of the same city, decided to devote some of his time and attention to the utilization of waste sulfite liquor. He began work during the summer of 1914 and carried out his investigations intermittently for some months. He finally succeeded in devising a process which, from small laboratory tests, indicated that it is possible to make alcohol profitably from the waste liquor and also to detoxicate the liquor so that it is not harmful to fish after it is diluted somewhat with water. The paper manufacturing company mentioned above desired to try the process on a scale sufficiently large that the results obtained would give some idea of its actual commercial value. The requirements specified by internal revenue laws regulating alcohol distilleries, however, are such that an experimental distillery could not be arranged for by the parties concerned without much inconvenience and considerable expense. The federal laws do accord to the agricultural experiment stations special privileges which make the establishment of an experimental distillery a comparatively simple matter. For this reason, the agricultural experiment station of this state was requested to take part in the work and establish what is known under the federal laws to be an "agricultural experiment distillery" for making alcohol for denaturation only.

Because of the great importance of the problem to this state and this country in general, the experiment station authorities decided to take up the work. An "agricultural experiment distillery" with proper stills, fermenting vats, etc., for handling 500 gallons of liquor, was established at the plant of the Crown Willamette Paper Company at Oregon City, Oregon, and Professor Charles Marchand, Mr. Vance P. Edwardes and the author undertook the necessary experimental work. Practically all of the details of the experiments were carried out by Professor Marchand and Mr. Edwardes, the writer having charge of the experimental plant and acting largely in an advisory capacity. The following is a brief description of the process used in the experiments:

The amount of sulfurous acid, free and combined, in the waste liquor is first quantitatively estimated by acidifying a known quantity of the liquor with sulfuric acid and then distilling the sulfur dioxide into a definite quantity of sodium hydroxide and finally titrating the excess of alkali. A determination of reducing sugar is also made, after the removal of tannin, by the usual reduction method with Fehling's solution. Sufficient diluted commercial sulfuric acid (the concentrated acid diluted 1 to 3) is then added to the liquor taken for treatment to be the reacting equivalent of the free and combined sulfurous acid present. This will give an excess of sulfuric acid because a portion of the sulfurous acid in the liquor is present as free acid.

The liquid is then evaporated, preferably *in vacuo*, to half its volume at a temperature not exceeding 85° C. A temperature higher than this may destroy some of the fermentable sugar. By this evaporation all but a trace of the sulfurous acid is removed. The sulfur dioxide driven off by the evaporation may be passed into milk of lime and magnesia to prepare new cooking acid.

The last trace of sulfurous acid remaining in the evaporated liquor is transformed into sulfuric acid by means of an oxidizing agent. This is a very vital step in the process because it finally effects the complete removal of sulfur compounds which are antiferments. Potassium permanganate seems to be one of the cheapest materials which can be used for this process.

After the oxidation of the remaining sulfurous acid is accomplished, the liquor is then neutralized with calcium hydroxide, using litmus paper to indicate the point of neutrality. Great care should be taken not to add an excess of the milk of lime; the liquid is next allowed to cool and is drawn off from the calcium sulfate, which settles out, into the fermenting tank.

The concentrated liquor contains, as a rule, about 6 per cent of fermentable sugar. Finally ordinary brewers' yeast is added and the fermentation is carried on for 40 to 60 hours at a temperature around 27° C. During the fermentation the liquid is agitated (or a little air is forced through it) to favor the process; the former method is preferable, because in the latter there is some loss of alcohol.

Finally, the alcohol is distilled off in the usual manner by means of a continuous still.

Several experiments were carried out by the above described process making some variation with the length of the time of fermentation, the acidity of the liquor fermented and the concentration of the liquor. The results of these experiments are summarized in Table I.

The figures for dextrose are somewhat high. Under the conditions which prevailed the experimental work had to be accomplished in a limited time and consequently in making the determination of fermentable sugar the tannin was not removed previous to the reduction with the Fehling solution. Since the tannin also reduces Fehling's solution, the results are a fraction of a per cent too high. The results are comparative, however, and that is all that is claimed. In Experiments 1, 2, 3 and 4, the fermentation was carried out under very slightly alkaline conditions, while in 5 and 6 the treated liquor was slightly acidified. The results obtained indicate that the fermentation proceeds much better under slightly acid conditions. The proper conditions may be obtained by adding 1 part of sulfuric acid to 1000 parts of the liquor obtained from the neutralization with lime.

TABLE I—RESULTS OF FERMENTATION EXPERIMENTS WITH THE TREATED WASTE SULFITE LIQUOR

Expt. No.	Gallons of liquor treated	Gallons of liquor after treatment	Per cent concentration	Gallons of concentrated liquor after fermentation	Fermentation period Hours	Fermentation temp. ° C.	Per cent Fermentable Sugar			Per cent of sugar fermented	Percentage by volume from original liquor Yield of Alcohol		
							In original liquor	In concentrated liquor before fermentation	In concentrated liquor after fermentation		Abs. alc.	190° proof alc.	Theoretical yield abs. alc.
1	490	200	40.8	?	?	?	2.80	5.75	2.71	3.04	(a)	(a)	0.64
2	1270	432	34.0	394	60–72	23.3–25.5	1.70	5.40	2.60	2.80	(b)	(b)	0.49
3	488	245	50.2	181	36–56	18.3–24.0	3.33	6.66	3.43	3.23	0.80	0.84	0.84
4	505	253	50.1	181	40–50	22.2–24.4	2.98	7.47	3.19	4.28	0.76	0.80	1.11
5	552	237	43.0	186	36–46	20.0–22.2	2.91	6.88	2.30	4.58	0.79	0.83	1.03
6	515	259	50.3	200	45–55	23.3–25.0	3.02	7.66	2.44	5.22	0.86	0.90	1.36

(a) The distillation was lost because of imperfect apparatus. (b) Acetic acid fermentation set in before distillation.

The liquor is easily fermented after treatment; the process appears to effect the complete removal of the sulfur compounds which act as antiferments. No special yeast is required as is the case in some of the proposed processes of securing alcohol from sulfite liquor. Ordinary brewers' yeast was used with good success in all the experiments which have been tried. The fermentation takes place rapidly and, under the conditions here reported, it is complete in about 48 hours. In some of the experiments a small portion of the liquor was allowed to ferment over 100 hours without any further production of alcohol.

The treatment of every 500 gallons of liquor required about 23 lbs. of sulfuric acid and 0.5 ounce of potassium permanganate. The apparent percentages of fermentable sugar in the liquor before and after concentration indicate that the digestion with sulfuric acid increases the quantity of fermentable sugar; there seems to be no other way of accounting for the increase in sugar during the concentration of the acidified liquor. The yield of alcohol was somewhat low considering the theoretical yield. The low yield was undoubtedly due to volatilization permitted by the imperfectness of the apparatus used. The writer believes that a yield of 1 per cent of absolute alcohol could be obtained with a properly constructed and controlled plant.

A few tests, made to ascertain the quantity of sulfur dioxide removed by the sulfuric acid treatment, indicated that the quantity of sulfur dioxide liberated was approximately 0.8 per cent of the original liquor.

The solids of the liquor are reduced nearly 30 per cent by the above described process and the liquor remaining after the distillation of the alcohol is, when somewhat diluted, apparently not noticeably toxic to fish. Experiments were tried placing gold fish in the diluted liquor; the fish seemed not to be injured by the liquor. Similar experiments made using the untreated liquor caused the death of the fish in a few seconds. Although the treated liquor is detoxicated, it must still be considered a source of stream pollution because of the large amount of organic matter present. Further experiments have not been made to ascertain if the liquor remaining after the fermentation can be utilized profitably.

It was practically impossible with an experimental plant of the size used in the work here reported to get at the cost of producing alcohol on a large plant basis. Careful and conservative estimates indicate, however, that the production of alcohol by the above described process is an economic possibility. The experiments made showed that approximately 5 cents worth of sulfur was recovered for each gallon of alcohol produced.

Several other methods have been proposed for the manufacture of ethyl alcohol from waste sulfite liquor. Of these, the one which compares most favorably is the Ekström[1] process. It is now being used in Sweden and at one large plant in this country. In

---

[1] For references to patents see *Chem. Abs.*, **8** (1914), 1669.

this process the sulfites are partially removed by precipitation as the calcium salt. The liquor is then concentrated and fermented by a special sulfur-resisting yeast. The method here given, however, appears to have several advantages over the Ekström process.

On the whole, the above described process appears to be sound. The reactions brought about are definite, simple and easily controlled.

CONCLUSIONS

1—A simple and easily controlled process has been proposed for the economic production of alcohol from waste sulfite liquor.

2—The process also detoxicates the sulfite liquor so as to make it, when diluted in the usual amount, practically harmless to fish.

Agricultural Experiment Station
Corvallis, Oregon

THE USE OF COPPER OXIDE FOR FRACTIONATION COMBUSTION OF HYDROGEN AND CARBON MONOXIDE IN GAS MIXTURES

By G. A. Burrell and G. G. Oberfell[1]

Received October 6, 1915

The purpose of this paper is to record the authors' experience in using copper oxide for the determination of hydrogen and carbon monoxide in gas mixtures. The method had given us much better satisfaction than methods that demand the use of acid or ammoniacal solutions of cuprous chloride for determining carbon monoxide, or of palladium asbestos, palladium sponge, or colloidal palladium solution for determining hydrogen. It is believed that this method should be more widely used than it is.

In the use of copper oxide the oxygen for the combustion comes from the reagent itself. After it has been used for a time some red cuprous oxide begins to show or even some completely reduced copper. It is then necessary to heat it and pass air over it, when it is again ready for use.

A great advantage of the method over the use of absorbents for carbon monoxide and hydrogen is the elimination of the preparation of solutions and the fact that copper oxide does not become poisoned as at times do some palladium preparations that are used for the hydrogen determination.

Cuprous-chloride solutions for the carbon monoxide determination are somewhat tedious to prepare and have a small absorption capacity. In addition, two solutions have to be used for precise work. Copper oxide, on the other hand, lasts for practically an indefinite number of determinations, and is easily restored to activity when partly reduced by drawing air over it when hot.

Jäger[2] was the first to use copper oxide for the fractional combustion of hydrogen in the presence of methane. He found that hydrogen was completely burned when passed over copper oxide kept at a temperature of 250° C. The tube containing the copper oxide was surrounded by an oven heated with a gas flame. Jäger recommended that next the methane be burned by heating the tube containing the copper oxide to bright redness. Knorre,[1] in using the method, replaced the soft glass used by Jäger, by one made of transparent quartz. L. Uebbelohde and de Castro[2] also used a quartz tube for holding the copper oxide: the tube was surrounded by an asbestos oven: they used a temperature of 270° C. for burning the hydrogen and copper oxide and a red heat for burning paraffin hydrocarbons.

E. Terres and E. Manguin[3] state that hydrogen is burned completely at 250° to 300° C. They found that dry carbon monoxide by itself in the dry state is only 90 to 94 per cent burned at 300° C.; also that even when hydrogen was mixed with acetylene and ethylene the latter did not burn completely because of the deposition of carbon on the copper oxide. They add further that benzene resembles ethylene as regards completeness of combustion, and that methane begins to burn at 310° C., the temperature being lowered a few degrees, however, by the presence of hydrogen, and is completely burned at a red heat. The oxidation of dry carbon monoxide began at 145° C., and of wet carbon monoxide below 100° C., but was not complete at 310° C. Hydrogen began to oxidize at 160° to 170° C. and at 250° C. the oxidation was complete. Carbon monoxide burned completely, however, in the presence of sufficient hydrogen at 300° C.

J. G. Taplay[4] uses a temperature of 270° C. for hydrogen and 850° C. for the paraffin hydrocarbons. S. H. Worrell[5] confines the copper oxide in a silica tube of $^1/_4$-in. bore and 7 in. long, and heats it with a gas flame. He states that copper oxide passing an 80-mesh sieve should not be used. A temperature of 250 to 260° C. is used by him for burning hydrogen and carbon monoxide, and red heat for methane.

Dennis[6] confines the copper oxide in a soft glass tube and burns the hydrogen and carbon monoxide together at 270° C., but prefers to burn paraffin hydrocarbons, if present in the gas mixture, by means of a platinum spiral in a Dennis combustion pipette. His chief objection to the method of determining methane with copper oxide lies in the fact that prolonged heating of the combustion tube to a high temperature and repeated passage of the gas through it are necessary for the complete oxidation of the methane."

Wibaut[7] mixes cerium oxide with the copper oxide in sufficient quantity to produce a grayish white mixture with the latter. He states that the combustion is made more rapid by this means.

Taylor[8] heats the copper oxide in a glass tube by means of a small electric furnace. The hydrogen and carbon monoxide are burned at a temperature of 275° C. for gases in which the average value of n in C_nH_{2n+2} is as high as 1.65, and paraffin hydrocarbons are burned with oxygen by means of a heated platinum

---

[1] Published by permission of the Director of the Bureau of Mines.

[2] *J. Gasbel.*, **41** (1898), 764.

[1] *Chem. Ztg.*, **33** (1909), 717.

[2] *J. Gasbel.*, **54** (1911), 810–814.

[3] *Ibid.*, **58** (1915), 8–11.

[4] *J. Gas Lighting*, **118** (1912), 217, 285.

[5] *Met. Chem. Eng.*, **11** (1913), 245–247.

[6] L. M. Dennis, "Gas Analyses," **1913**, pp. 198–206.

[7] *Chem. Weekblad*, **11** (1914), 498.

[8] *Jour. Soc. Chem. Ind.*, **6** (1914), 845.

spiral. He says the exact temperature that can be used will depend upon the nature of the hydrocarbons present, and that with methane only, 300° C. is probably not too high, but at this temperature there is danger of oxidation of the higher homologs of methane. Tests by Taylor also showed that not only may hydrogen and carbon monoxide be burned in the presence of methane without danger of oxidation of the latter but also in the presence of high concentrations of higher paraffins. He states that the time required for the complete burning of the hydrogen and carbon monoxide does not seem to be a function of the quantities present as much as the nature of the gas mixture. For ordinary illuminating gas he found that the hydrogen is usually completely removed in 6 to 10 slow passes over the copper oxide. With some low-temperature coal distillates, not scrubbed, there were required as high as 40 minutes to remove 3 to 5 cc. Taylor concludes that, in general, when the contraction due to the burning of the hydrogen has ceased, the carbon monoxide may be assumed to have been completely oxidized, unless it be present in much greater concentration than the hydrogen, in which case passage through the copper oxide should be continued some minutes longer.

Nemsjelow[1] uses a temperature of 250° C. He found that silver oxide could also be used, although it is not as practical.

EXPERIMENTAL

The apparatus with which the authors performed their work is shown in Fig. I. The burette *a* has a capacity of 100 cc. and is graduated in 0.1 cc.; an attachment, *j*, *n*, compensates for outside changes of temperature and pressure during the course of the analysis; *h* and *i* are three-way stop-cocks; *b* contains caustic potash solution for the removal of carbon dioxide; *c*, fuming sulfuric acid for removing unsaturated hydrocarbons; *d*, alkaline pyrogallate solution for removing oxygen; *e* is a slow-combustion pipette containing an electrically heated platinum spiral. This coiled spiral is 4$^1/_2$ in. long and No. 30 B. & S. gauge. The glass tubes supporting the spiral are filled with mercury. The latter acts as electrical contacts between the ends of the platinum spiral and the platinum wires sealed into the bottom of each tube. The ends of the platinum spiral are fused to the inside of the open glass tubes at the top. Thus fastened and with the ends of the spiral dipping into the mercury, they always stay in place. A current of about 4 to 4.5 amperes at 6.2 volts is used to raise the wire to a white heat for burning the paraffin hydrocarbons. Mercury is used in this pipette, also in the burette; *f* is a glass tube (inside diameter, 4 mm.) containing the copper oxide, surrounded by an electrically heated oven, *g*,[2] which is supported by a standpipe, by means of which it can be raised from the copper oxide tube when not in use. Copper oxide that passes a 100-mesh sieve is not used in the tube. One U-tube used by the authors for holding copper oxide contained 3.3 grams and a free space volume of 1.89 cc. In Fig. I, *o* and *p* are three-way T stop-cocks, so that the gas can be passed either through the branch *o,p* into the pipette *d* or through the copper oxide tube and thence into the pipette *e*. The bulbs *m* and *t* slide up and down on two standpipes (not shown). A simpler burette is shown at *l*, in case it is desired to use water in the burette instead of mercury.

USE OF THE APPARATUS SHOWN IN FIG. I

There follows the method of making an analysis of a gas mixture containing carbon dioxide, unsaturated hydrocarbons (principally ethylene), oxygen, carbon monoxide, methane, ethane, hydrogen and nitrogen.

Before proceeding with the analysis the capillary train and U tube are swept free of oxygen or residual gases from a previous determination by drawing a sample of air into the burette and passing it into the alkaline pyrogallate pipette *d* to remove oxygen. The residual nitrogen is then passed into all the pipettes and through the CuO tube to sweep out other gases (usually oxygen) that may have been contained therein. Instead of extracting nitrogen from the air for this purpose each time, a supply of nitrogen may be kept on hand. The electric current is then turned through the oven. Preliminary trials will have shown the current strength demanded. The ovens in use by the authors require about 2.4 amperes at 30 volts. Connection is made through regulating resistances to the 220 volt lighting circuit of the building through a lamp bank rheostat. The current is switched on at the beginning of an analysis so that the oven will be heated to the desired temperature (275° to 300° C.) by the time the analyst is ready to make the fractional combustion analysis.

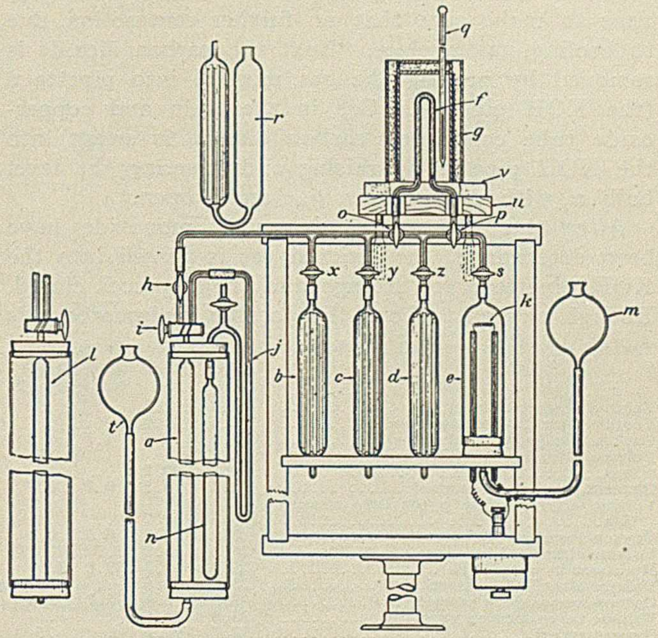


Fig. I—Complete Gas Analysis Apparatus Including Copper Oxide Tube

Some of the gas mixture is then drawn into the burette, measured and passed into the pipettes *b*, *c* and *d*, for the removal of carbon dioxide, illuminants and oxygen. After the percentage of these constituents

---

[1] *Z. anal. Chem.*, **48** (1909), 232–272.

[2] Similar to the one used by Taylor (*loc. cit.*).

has been recorded, the stop-cocks *o*, *p* and *s* are turned so that communication is made between the burette and the pipette *e*, through the copper oxide tube. By this time the latter will have reached the desired temperature. The furnace is next lowered over the copper oxide tube and the gas mixture slowly passed back and forward through it between the burette and slow-combustion pipette *e* until no further diminution in volume is noted by reading the gas volume in the burette. The authors have found that a maximum of about 15 minutes is required to burn completely the carbon monoxide and hydrogen in various gas mixtures. Carbon monoxide burns readily in the presence of hydrogen, but much more slowly when burned alone. After combustion is complete the electric oven is raised from the copper-oxide tube and the latter allowed to cool. The authors hasten the cooling by playing a blast of cold air from a compressed air pipe on the tube: this operation requires about 5 minutes. A safe way is to make a second reading of the gas volume after a few minutes' time to make sure that no further contraction, due to cooling, takes place. Next the carbon dioxide is removed by passing the gas mixture into pipette *b* (the KOH pipette). Gas in the train and copper-oxide tube containing carbon dioxide is swept into the KOH pipette by raising and lowering the level bulb *m*, with stop-cocks *s*, *p*, *o* and *x* open.

After the hydrogen and carbon monoxide have been determined, the residual gas is passed into the KOH pipette *b* for storage and the stop-cock closed. Enough oxygen to burn the paraffin hydrocarbons is then drawn into the burette, measured and passed into the slow-combustion pipette *e* (not through the U-tube *f*), and the platinum spiral therein heated to almost a white heat. Next the residual gas is withdrawn from the pipette *b* into the burette and from there slowly passed, at the rate of about 10 cc. per minute, into the pipette *e*. Slow combustion between the oxygen and combustible residual gas therein takes place as fast as the oxygen enters and an accumulation of the mixture necessary for an explosion cannot take place.[1] Only enough of the residual gas should be taken for the final combustion analysis so that there will be an excess of oxygen for the combustion. In case of doubt a final determination of oxygen by means of the alkaline pyrogallate solution in pipette *d* can be made. After combustion is complete the resulting contraction and carbon dioxide are measured and the gas mixture again passed into the slow-combustion pipette and burned again. There always results further slight contraction and a small amount of carbon dioxide.

TABLE I—ANALYSIS (BY CuO METHOD) OF GAS FROM COAL DISTILLATION

	No. 1 cc.	No. 2 cc.	Percentage No. 1	Percentage No. 2
Volume of sample taken	40.2	41.5	..	..
Volume after KOH absorption	39.6	40.9	..	..
Carbon dioxide (CO_2) absorbed	0.6	0.6	1.5	1.5
Volume after fuming sulfuric acid absorption	39.3	40.7	..	..
ILLUMINANTS, etc., absorbed	0.3	0.2	0.7	0.5
Volume after alkaline pyrogallate absorption	39.3	40.7	..	..
Oxygen absorbed (O_2)	0.0	0.0	0.0	0.0
Volume after CuO burning	26.1	27.0	..	..
Hydrogen in sample (H_2)	13.2	13.7	32.8	33.0
Volume after KOH absorption	23.8	24.6	..	..
Carbon monoxide in sample (CO)	2.3	2.4	5.7	5.8
Volume taken for slow combustion	23.8	24.6	..	..
Oxygen added	92.7	92.2	..	..
Total volume	116.5	116.8	..	..
Volume after burning	69.1	68.0	..	..
Contraction due to burning	47.4	48.8	..	..
Volume after KOH absorption	45.2	23.3	..	..
Carbon dioxide absorbed	23.9	24.7	..	..
Methane in sample (CH_4)	23.3	23.9	58.0	57.6
Ethane in sample (C_2H_6)	0.3	0.4	0.7	1.0
Nitrogen in sample (by difference)	...	...	0.6	0.6

Table I gives the observed data of the analysis of a sample of gas collected from coal distillation at high pressures and temperatures.[1]

Table II shows analyses of two samples of gas. In one case the carbon monoxide and hydrogen were determined by burning them with copper oxide, and in the other case the carbon monoxide was absorbed by means of ammoniacal cuprous chloride solution and the hydrogen by colloidal palladium solution.[2]

TABLE II—PERCENTAGE ANALYSES OF A SAMPLE OF GAS BY TWO METHODS

	SAMPLE 1		SAMPLE 2	
	Colloidal palladium and cuprous chloride	CuO Method	Colloidal palladium and cuprous chloride	CuO Method
CO_2	0.2	0.4	0.0	0.0
C_2H_4, etc.	44.6	44.6	12.7	12.5
O_2	1.7	1.6	0.2	0.2
CO	0.8	0.9	1.0	0.8
H_2	7.7	6.7	42.3	42.2
CH_4	26.4	26.4	41.2	41.1
C_2H_6	11.4	11.2	0.0	0.0
N_2	7.2	8.2	2.6	3.2

Table III shows two analyses of the same sample. One was made by burning the hydrogen and carbon monoxide over copper oxide with the apparatus shown in Fig. I. The other was made by burning the carbon monoxide, hydrogen and methane together (triple combustion) and a slow-combustion pipette of a Haldane gas-analysis apparatus. With the latter, gas volumes as small as 0.002 cc. could be measured.

TABLE III—PERCENTAGE ANALYSES BY COPPER OXIDE AND BY TRIPLE COMBUSTION

ANALYSIS BY	CO_2	C_2H_4, etc.	O_2	H_2	CO	CH_4	N_2
Copper oxide	3.9	0.0	15.5	0.0	0.3	0.9	79.4
Triple combustion	3.90	0.00	15.46	0.02	0.17	0.84	79.61

Next a gas mixture was prepared containing 4 per cent each of hydrogen, carbon monoxide and methane, and 88 per cent air. Analysis No. 1 shows the results obtained by burning the hydrogen and carbon monoxide at a temperature of 290° C. and methane at a temperature of 800° C. The copper-oxide tube was made of quartz. Analysis No. 2 shows the results obtained by absorbing the carbon monoxide with cuprous chloride, the hydrogen by colloidal palladium, and the methane in a slow-combustion pipette with a hot platinum spiral.

TABLE IV—PERCENTAGE ANALYSES OF A SAMPLE OF GAS BY TWO DIFFERENT METHODS

No.	ANALYSES BY	CO	H_2	CH_4
1	Copper oxide	3.8	3.6	4.2
2	Cuprous chloride, colloidal palladium and hot spiral	4.1	4.0	4.0

Next a mixture of hydrogen (50 per cent) and natural gas[3] (50 per cent) was prepared. No. 1 analysis was made by burning the hydrogen with copper oxide and the methane with a hot platinum spiral (slow combustion).

---

[1] To protect the operator from possible accident, the combustion pipette *e* should be surrounded with a wire gauze.

[1] The copper oxide was heated to 290° C. in this and other analyses that follow in determining hydrogen and carbon monoxide. Temperatures ranging from 275° to 300° were found to work satisfactorily.

[2] THIS JOURNAL, 6 (1914), 992.

[3] Containing 84.7 per cent CH_4, 9.4 per cent C_2H_6, 3.0 per cent C_3H_8, 1.3 per cent C_4H_{10}, 1.6 per cent N_2.

No. 2 was made by absorbing the hydrogen with colloidal palladium solution and burning the methane with a hot platinum spiral.

TABLE V—PERCENTAGE ANALYSES OF A MIXTURE OF NATURAL GAS AND HYDROGEN BY TWO DIFFERENT METHODS

No.	ANALYSES BY	H_2	Natural gas
1	Copper oxide and slow combustion.........	50.7	48.3
2	Colloidal palladium and slow combustion....	50.2	48.1

The above analyses showed that the paraffin hydrocarbons higher than methane were not oxidized, at least in any significant amount, by the copper oxide.

Lastly, there is shown work upon the analysis of the artificially mixed coal and water gas of Pittsburgh. The first analysis was made by burning the carbon monoxide and hydrogen with copper oxide at about 290° C. and paraffin hydrocarbons in the slow-combustion pipette with a hot platinum spiral. The second analysis was made by using copper oxide at about 290° C. to burn the carbon monoxide, a solution of colloidal palladium to absorb the hydrogen, and a hot platinum spiral to burn the paraffin hydrocarbons. The third analysis was made by burning carbon monoxide and hydrogen at about 290° C. with copper oxide and by burning the paraffin hydrocarbons at a red heat with copper oxide.

TABLE VI—PERCENTAGE ANALYSES OF THE ARTIFICIAL ILLUMINATING GAS OF PITTSBURGH

No.	CO_2	Illuminants	O_2	CO	H_2	CH_4	C_2H_6	N_2	TOTAL
1.....	2.5	7.4	0.4	11.5	43.6	30.6	2.1	1.9	100.0
2.....	2.6	7.0	0.4	11.7	43.9	30.7	2.2	1.5	100.0
3.....	2.4	7.5	0.4	11.5	43.4	30.4	2.2	2.2	100.0

SUMMARY

I—The authors' experience with the copper-oxide method, devised by Jäger for the fractional combustion of hydrogen and carbon monoxide, is described.

II—A gas-analysis apparatus, embodying a copper-oxide tube somewhat different in form from others on the market, but containing no new principle, is also described.

III—A temperature of the copper oxide of between 275° and 300° is adapted for burning hydrogen and carbon monoxide in a wide variety of mixtures. Most previous experimenters have adopted temperatures in this range.

LABORATORY GAS INVESTIGATIONS
BUREAU OF MINES, PITTSBURGH, PA.

A NEW ACCURATE METHOD OF GAS ANALYSIS

By O. A. KRONE

Received August 26, 1915

Figs. I and II show the apparatus used for estimating the quantities of carbon dioxide, illuminants, oxygen, carbon monoxide, methane, ethane, hydrogen and nitrogen in gaseous mixtures.

B,B_1 are 100 cc. burettes graduated the entire length in 0.1 cubic centimeter. C,C_1 are water jackets for the burettes. D is a three-way glass Geissler cock of 2 mm. bore. E,E_1 are bent capillary tubes of 1 mm. bore. F is a three-way Geissler cock, G is a two-way cock having a T capillary fused to F. H is a bent 1.5 mm. bore capillary, whose orifice, H_1, is melted to measure 0.3 mm. I is a piece of glass tubing having walls of sufficient strength, and an internal diameter of 1.75 cm. drawn down to a capillary of 1.5 mm. internal diameter. J is the brass body holding the combustion tube. K is a three-way glass cock of 2 mm. bore. N is a two-way glass cock of 5 mm. bore. P is a glass-covered pipette stand whose height is adjustable. Q is a set screw for adjustment of P. J, the brass body holding the combustion tube, has two small holes, a little smaller than 1.5 mm. diameter, drilled from the posterior side into $^1/_3$ of the body J. Into these are fitted the two legs of a platinum combustion tube of 1.5 mm. outside and 0.5 mm. inside diameter. The small holes are 1 cm. apart. The platinum tube is about 10 to 11 cm. long and is bent to form a U, the two legs of which run parallel about 1 cm. apart. Into the forepart of the body two large holes, about 8 mm. in diameter, are drilled, whose centers meet the centers of the 1.5 mm. holes drilled from the rear.

The brass body has grooves milled in large enough to have a water circulation to keep the rubber tubing cool, which holds the bent glass capillaries of 1.5 mm. bore fitting tightly into the larger holes A,A. These glass capillaries are bent so that the combustion tube protrudes in the rear of the apparatus. Around the brass body is soldered a piece of sheet copper to form a cup for water. The platinum tube is then soldered in, gas-tight.

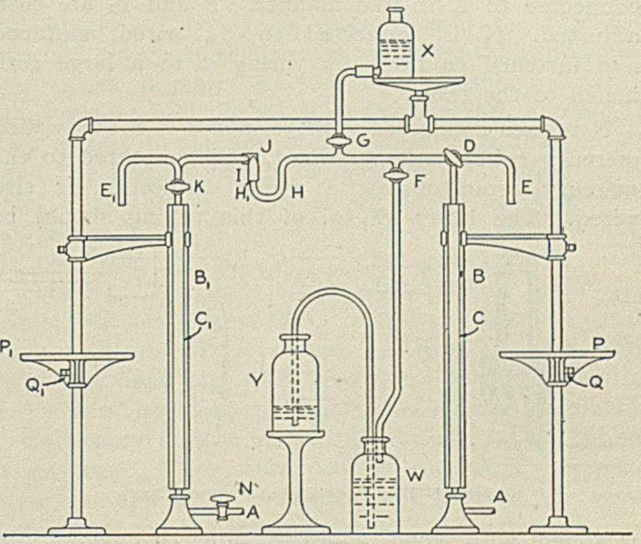


FIG. I—ARRANGEMENT OF APPARATUS

W, a 4 liter bottle for storing oxygen over water, is connected to bottle Y of the same size placed above it to keep the oxygen under pressure

If mercury is used as the confining fluid in burette B, the platinum tube is either brazed or silvered in, gas-tight. The ends of the platinum tube are tapered so that tight joints are secured by forcing the ends into the brass body.

A small piece of asbestos paper is fitted onto the platinum capillary to prevent the unused heat from softening the solder.

A Méker or Bausch and Lomb high temperature burner is used to heat the tube and is adjusted to position with an iron clamp fastened to the apparatus support. All rubber connections should be made with the best heavy-walled rubber tubing which should be of small enough size to give a tight joint.

All glass capillaries should fit shoulder to shoulder when connections are made, and all rubber connections should be wired by iron wire 1 mm. in diameter, at the edge of the tubing. All joints that are to be rigid should be stiffened by wrapping a piece of sheet copper of suitable size around the rubber within the space of the two iron wires which hold the tubing tight at the edge and then wiring this sheet on tightly with three iron wires, 1 mm. in diameter.

ASSEMBLY OF APPARATUS

D is fastened to the body of burette B with rubber tubing, wired and stiffened. K is fastened in like manner to B_1. B is then put into C, the rubber stoppers put into place at the ends of C. E and E_1 are fastened to D and K with rubber tubing and wired. The burette B is fastened to the right side of apparatus support with a universal clamp. The burette B_1 is fastened to the left side in the same way. F and G are connected to D, wired and stiffened. H is fitted tightly into I at H_1 with a piece of rubber tubing. I is connected to J with rubber tubing. J is connected to K in like manner. P and P_1 are then adjusted. N is connected to B_1, wired, stiffened and fastened to table by wiring it to a large cork nailed to the table.

N is then connected with 36 inches of heavy-walled mercury rubber tubing, wired, and connected to the mercury aspirator bottle which connection is also wired. The lower 18 in. of this tubing should be wrapped with good adhesive tape to prevent the mercury from bulging through the tubing when the aspirator bottle is raised. All stoppers are wired to the cocks. The mercury aspirator bottle is then filled with mercury.

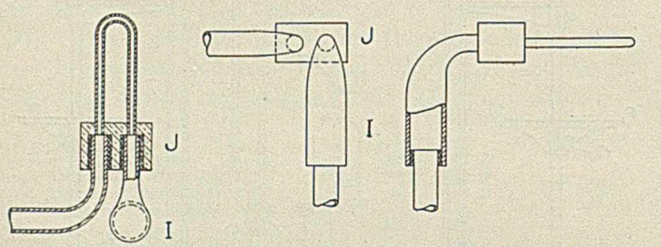


Fig. II—Detail of Capillary and Trap

A is connected and wired to 40 in. of smooth bore heavy-walled, best grade rubber tubing, which is then connected to a 500 cc. aspirator bottle which is filled with one part of HCl (sp. gr. 1.2) to 10 parts distilled water. The water jackets are filled with distilled water.

If preferred, manometers and compensating tubes may be added to the burette; otherwise compared Centigrade thermometers should be inserted in the water jackets through the top rubber stoppers.

Mercury should not be allowed to get into the platinum capillary nor should explosive mixtures be run through too fast when the joints are soldered, as this will destroy the solder joints.

For accuracy it is preferred to use mercury in burette B also.

A small amount of water on the surface of the mercury may be allowed, provided the burettes are calibrated for mercury and the water meniscus for the amount of water on the mercury surface.

REAGENTS USED

(1)—One part of purified stick potash to one part pure water by weight: 150 cc. of this solution are poured into a stoppered, single Hempel pipette filled with clean iron turnings to increase the absorbing surface of the potash.

(2)—Nordhausen sulfuric acid, or where preferable, saturated bromine water.

(3)—Yellow phosphorus cast into 5 mm. sticks set upright in a stoppered, single Hempel pipette covered by 150 cc. of pure distilled water.

The Hempel pipette body is painted black. A $^1/_2$-inch strip extending lengthwise on the front side of the phosphorus bulb and the capillary are left unpainted so that the action of the phosphorus may be observed.

(4)—A stoppered, double Hempel pipette filled completely with straight 1.5 mm. copper wires and covered by 125 cc. of the following solution: one part by weight of ammonium hydroxide (sp. gr. 0.90) to four parts by weight of pure distilled water. A large excess of ammonium chloride is then added to this diluted ammonium hydroxide and a saturated solution is made at about 80° F. After being sure the solution is saturated, the excess of ammonium chloride is allowed to settle and the clear solution decanted into a clean flask, stoppered, and kept for use. This copper pipette is the best absorbing agent for oxygen but can not be used when carbon monoxide or dioxide is present. Saturated ammonium chloride in ammonium hydroxide (sp. gr. 0.90) should not be used as the nitrogen of the theoretically ionized NH_4 is, to a certain extent, oxidized to free nitrogen when a 99% oxygen is analyzed. Weaker solutions of ammonium chloride should likewise be avoided.

Phosphorus, according to G. Lunge's 1914 publication, is the best reagent for absorbing oxygen from illuminating or heating gases. This assertion has been proven to be correct.

Low concentrations of oxygen, up to 5 per cent oxygen, mixed with gases such as hydrogen, water gas, coal gas, etc., were separated by treatment with phosphorus and in no case was a perceptible excess contraction noticed. On the other hand, high concentrations of oxygen, 98.6% pure, with hydrogen and other combustible gases, when treated with phosphorus, showed excess contraction due to chemical combination with some of the hydrogen or other gas with the oxygen.

With high concentrations of oxygen the phosphorus melted, trapping gas. Even air, when allowed to come into contact with the phosphorus, gradually melted the phosphorus, necessitating the recasting of the phosphorus. Hence for low concentrations of oxygen, when carbon monoxide is present, phosphorus was considered the best reagent to be used.

The oxygen is absorbed very rapidly. As soon as the white phosphorus pentoxide fumes have nearly settled or if the pentoxide fumes are washed into solution giving the small amount of oxygen diffused in the gas the opportunity of coming in contact with the moist phosphorus, as the pentoxide fumes retard the movement of the molecules of the gas, the absorption is complete. Further treatment of the gas with phosphorus causes no contraction.

Phosphorus gives valuable indication of the complete absorption of the unsaturated hydrocarbons by the fuming sulfuric acid or bromine water. A phosphorus pipette lasts much longer than a pyrogallate pipette and one pipette can be used for all of the gases while when using alkaline pyrogallol it is necessary to have a separate pipette for each kind of gas analyzed.

Phosphorus is much speedier in action than pyrogallate; besides, continuously accurate results are obtained by its use, which can not be said of pyrogallol. Pyrogallol prepared as directed by R. P. Anderson[1] is also very unpleasant to handle.

Fuming sulfuric acid should always be fresh enough so that the reaction between the oxygen and phosphorus is not interfered with, due to presence of remaining hydrocarbons.

For concentrations of oxygen higher than 5 per cent and where carbon monoxide or dioxide is not present, the best method for absorbing oxygen is by copper with the ammonium chloride solution as directed previously. Such a pipette lasts a very long time. We have used one daily for about two months without renewing any part of it and it does not at present show any signs of becoming exhausted. It must be remembered to use the ammonium chloride solution as specified.

The results obtained by this method agree exactly with those secured by combustion.

Samples of air analyzed gave a value of about 20.87 per cent oxygen, and samples of commercial oxygen analyzed checked among themselves to the hundredths of one per cent when measurements were performed accurately and these results checked with the oxygen determined by combustion over a large number of determinations.

The pipette should have as much copper surface as possible; therefore the copper wires should be thin and straight and should fill the entire length of the pipette body as otherwise the absorption of oxygen is not as rapid as is possible.

The copper wires should be very clean and bright before putting them into the pipette and the last bulb of the pipette should have a little of the ammonium chloride solution in it also. The copper going into solution by chemical change seems to be precipitated back onto the metallic copper as the metal, to some extent. When making an absorption of oxygen by copper it should be remembered that the absorption takes place on the moist surface of the copper; consequently the aim should be to wash gently over the copper with the ammonium chloride solution so that the blue compound is dissolved, giving a fresh copper surface, and not to shake the pipette to have the liquid absorb the oxygen.

When using a mercury burette care should be taken thst no mercury comes in contact with the copper surface as it readily amalgamates at the surface of the copper. The salts of mercury also precipitate on the surface of the copper as metallic mercury and this spoils the pipette.

APPLICATION OF THE METHOD TO ANALYSIS

Exactly 100 cc. of the sample of gas to be analyzed are drawn into the water burette. The capillary is then washed by turning cock G, and to seal the gas in the burette, acidulated water is then allowed to completely fill all of the capillaries and trap I up to the edge of the cock K. The potash pipette is then connected to the capillary E, and the gas in the burette aspirated back and forth three times. This procedure removes all of the carbon dioxide. The residue is measured and the reading recorded. The difference between 100 cc. and this reading gives the per cent of carbon dioxide present in the sample.

The potash pipette is disconnected, the capillary washed, the gas in the burette put under slight pressure, the thumb is placed on the end of capillary E, cock D is opened and the water in the capillary allowed to run almost to the end of E. Cock D is then closed and the fuming sulfuric acid pipette attached to E. Not more than 0.02 cc. of air should be introduced at this point, if the pinching up of the sulfuric acid in the pipette capillary and the connection is made carefully. The gas is aspirated back and forth two times, the acid drawn back to the same mark in capillary and cock D is closed. A quick, smooth pull with one hand and with the thumb and finger of the other hand pinching the rubber tube connecting pipette with E prevents the acid from getting into the rubber connection. The other thumb is quickly slipped over the end of E, preventing diffusion of the small amount of gas in the capillary with the air.

Water from a wash bottle is now blown into the rubber connection of the potash pipette and this pipette quickly connected to E, at the same time withdrawing the thumb. To take out the sulfuric fumes, the gas is passed back and forth four times. The reading is taken and recorded. The difference between this and the previous reading gives the per cent of illuminants (unsaturated hydrocarbons, benzene vapor, etc.). If all of the illuminants are not withdrawn by two passages through the sulfuric pipette they should be removed by passing through one more time.

Next remove the oxygen with phosphorus. Allow the gas to remain in contact with the moist phosphorus until most of the fumes disappear. The gas is then drawn into the burette, measured and the amount recorded. The difference between this and the previous reading gives the per cent of oxygen in the mixture.

A gas holder is made by connecting two 500 cc. aspirator bottles with rubber tubing, which is wired on. A 1-hole rounded rubber stopper is fitted to

---

[1] This Journal, 7 (1915), 587.

the neck of one of the aspirator bottles and a piece of capillary glass tubing inserted. The end of this capillary is then closed with a piece of rubber tubing and a pinch-cock just as the pipettes for the reagents. Enough acidulated water (distilled) is added to this holder to completely displace the air in the bottle having the capillary. The other bottle is fitted with a tube and rubber stopper to blow the water out of the capillary.

The rubber stopper for the capillary bottle should be rounded into an inverted basin-like depression so that the air may be quickly and completely displaced. This is done by heating a heavy copper wire to redness and moulding the stopper to the proper shape. The stopper is then rather soft and unfit for use, but it should be hardened by immersing it in a little fuming sulfuric acid.

The residue of gas left after determining the oxygen is transferred to this holder, a measured excess of oxygen is then added by opening cock F and allowing the oxygen to flow into the water burette. After measuring, the oxygen is transferred to the holder and the entire gaseous mixture shaken, at the same time pinching the rubber connection between the two aspirator bottles to prevent air from entering or gas from leaving the holder. Mercury might be used in this holder having a very slight amount of acidulated water on its surface.

After thoroughly mixing the gas and oxygen, 100 cc. of the mixture or a close approximation to 100 cc. are drawn into the water burette and the amount accurately measured. The mercury burette is then adjusted so as to contain 15 or 20 cc. of air. Water fills all of the capillaries, including the trap I up to cock K.

A 250 cc. aspirator bottle can be made a part of burette B, using a small rubber stopper, then the entire mixture may be burned instead of 100 cc. in one operation.

After recording all of the measurements the water in the trap I is forced into the water burette by putting the measured amount of air in the mercury burette under pressure and opening cocks D and K so that the flow is into the water burette. As soon as the water reaches the orifice H_1 cock D is closed, the mercury in the burette leveled, and cock N closed. Cock K is kept open. The burner heating the platinum capillary is then lighted. It should give a flame hot enough to melt to a globule the end of a piece of copper wire 1 mm. in diameter in 5 to 8 seconds. A Bausch and Lomb high temperature burner or a Méker burner should be used. After the platinum tube becomes heated to a bright red, D is opened, the aspirator bottle on the water burette is raised slowly so that the water remaining in the capillaries is not forced through the heated tube, and then put on the high shelf.

The small amount of water, not more than 0.1 cc., which is forced into the trap, prevents the explosion of the mixture of gases from traveling back into the burette, which, if it should occur, would wreck the apparatus.

Cock N is now slightly opened and the explosive mixture of gases allowed to bubble through the water in trap I at a moderate rate and as soon as all of the gas has passed through the water seal, the water is allowed to rise until the beginning of the heated portion of the tube is reached.

Cock N should be closed as soon as water flows through the orifice H_1. Cock D should next be closed when the heated portion of the combustion tube is reached. The heating is then stopped and water thrown on the hot tube from a wash bottle to cool the tube rapidly. Cock D is opened and the water allowed to come to the edge of cock K, which is then closed.

This residue of gas, after combustion, is measured and the amount recorded. The potash pipette is now connected to E_1 and the gas aspirated back and forth four times. The amount of gas left is measured and recorded and the pipette disconnected. The pressure on the gas is now slightly decreased and 1 cc. of acidulated water drawn into the mercury burette. This is done to prevent mercury from fouling the copper in the copper pipette. The copper pipette is connected to E and the residue of gas completely transferred thereto. In order to absorb oxygen completely in this step it is not necessary to disconnect the copper pipette to shake it. It is only necessary to see that the copper wires have a clean coppery color by washing over them a time or so gently with the solution in the pipette. As soon as the clean copper color is seen the oxygen is completely absorbed, the absorption being very rapid.

After drawing the residue of gas into the burette, it is measured, then passed into a dilute solution of sulfuric acid to see whether any ammonia fumes are taken out. This last residue is then measured and the amount recorded.

It is necessary to heat the platinum combustion tube to the degree mentioned, as otherwise the paraffins will not be completely decomposed.

Mercury should not be run into or through the combustion tube. The burettes should be calibrated and the proper meniscus used. One passage through the properly heated tube decomposes all of the gases quantitatively. Cock K and burette B should be thoroughly washed out with acidulated water by opening N and drawing through 1 part of sulfuric acid to 4 parts water. Cock K is completely revolved several times while drawing the acidulated water into the burette. The formula used for calculating the combustion results is easily remembered. Representing the oxygen used in the chemical combination by O_2, the contraction by C, we have:

$$H_2 = C - O_2$$

$$CH_4 = \frac{3O_2 - (C + CO_2 \text{ formed})}{3}$$

$$CO = CO_2 \text{ formed minus } CH_4$$

The nitrogen is found by difference. It can also be calculated by the residual nitrogen. Both methods give the same results.

When a part of the mixture of gas and oxygen is taken for combustion as directed above, a proportion must be made between the amount of the mixture used for combustion and the total amount on hand. The following example taken from practice illustrates the method of writing down the measurements and making the computations.

ANALYSES BY H. L. DAHM
Sample of water gas July 3, 1915

	Burette reading cc.		Per cent
	5.4	CO_2	5.4
	20.2	C_nH_{2n}	14.8
	20.8	O_2	0.6
		CH_4	17.86
Residue for combustion....	79.2	CO	25.94
		H_2	31.56
		N_2	3.84
			100.00

Residue of gas for combustion.............. 79.2 cc.
Amount of oxygen taken.................... 77.2 cc.

Total mixture........................ 156.4 cc.
Amount of mixture taken for combustion.... 100.00 cc.
53.6 cc. reading after combustion
—15.0 cc air in mercury burette

38.6 cc. measurement of the residue of the 100 cc. of gas taken for combustion
100.00 cc. taken for combustion
—38.6 cc. residue after combustion

61.4 cc. contraction for 100 cc. of the mixture
53.6 cc. reading of gas after combustion plus the 15.0 cc. of air
—25.6 cc. reading of residue after using potash pipette

28.0 cc. equals the CO_2 formed in 100 cc. of the mixture
25.6 cc. reading after using potash pipette
—15.0 cc. reading after using copper pipette

10.6 cc. of O_2 left which did not take part in the combustion. This amount also contains the oxygen in 15.0 cc. of air used
10.6
— 3.1 amount of O_2 in 15.0 cc. air

7.5 cc. equals the oxygen not taking part in the chemical combustion of 100 cc.

Compute the contraction, the carbon dioxide formed, and the excess oxygen for the 156.4 cc. of the mixture, to get the proper figures for the entire mixture, by using the proportions 156.4 : 100.0 cc.

$61.4 \times \frac{156.4}{100.0} = 96.03$, contraction for total gas
$28.0 \times \frac{156.4}{100.0} = 43.8$, CO_2 for total gas
$7.5 \times \frac{156.4}{100.0} = 11.73$, excess oxygen for total gas

77.2 cc. of commercial oxygen is added to the 79.2 cc. gas for combustion. This oxygen contains 1.3 per cent nitrogen.

$77.2 \times 0.013 = 1.0$ cc. of nitrogen in 77.2 cc. O_2
— 1.0 cc. nitrogen

76.2 cc. pure oxygen added
—11.73 cc. excess oxygen, left after combustion

64.47 cc. equals the oxygen used to combine chemically with the gas
96.03 — 64.47 (oxygen used) = 31.56 per cent hydrogen
3×64.47 (oxygen used) = 193.41 minus
96.03 + 43.8 (CO_2 formed) = —139.83

$\frac{53.58}{3} = 17.86$ per cent CH_4

43.8 (CO_2 formed) — 17.86 (CH_4) = 25.94 per cent CO.

Nitrogen is found by computing as follows: In the 15.0 cc. of air used we have 11.9 cc. N_2. The residue of nitrogen after burning the 100.0 cc. of the mixture plus the nitrogen of the air after taking out all the oxygen equals 15.0 cc.

15.0 cc.
—11.9 cc. N_2 in the air used

3.1 cc. N_2 in 100 cc. of mixture
In total mixture 156.4 we will have
$\frac{3.1 \times 156.4}{100} = 4.84$ cc. N_2 due to the nitrogen in the original gas plus the nitrogen in the commercial oxygen used. In this case the nitrogen as calculated previously equals 1.0 cc. in the commercial oxygen added
4.84
—1.0

3.84 cc., amount of nitrogen in the original gas

When it is desirable to measure the total contraction—that is, the contraction due to the formation of the $H_2O + CO_2$—the following formulae may be used:

Representing the total contraction by C and the oxygen used in the chemical combination of the gases by O_2 we have:

$CH_4 = \frac{3O_2 - C}{3}$
$CO = CO_2 - CH_4$
$H_2 = C - (O_2 + CO_2)$
Nitrogen is figured by difference

Should we use these formulae, the figures of the previous water gas analysis would appear as follows:

Burette reading			Per cent
	5.4	CO_2	5.4
	20.2	Illuminants	14.8
	20.8	O_2	0.6
Residue of gas.......	79.2 cc.	CH_4	17.86
Impure oxygen added.	77.2 cc.	CO	25.94
Total mixture	156.4 cc.	H_2	31.55
		N	3.85
			100.00

53.6 cc. residue after combustion
—25.6 cc. residue after using potash
28.0 cc. CO_2 formed in 100 cc. of mixture
100.0 cc. of mixture taken for combustion
+15.0 cc. air

115.0 cc.
—25.6 cc. residue after using potash

89.4 cc. total contraction for 100 cc.
25.6 cc. residue after using potash
—15.0 cc. residue after using Cu pipette

10.6 cc. unused oxygen plus oxygen in 15.0 cc. air
— 3.1 cc. oxygen in 15.0 cc. air.

7.5 cc. unused oxygen in 100 cc. of mixture
$28.0 \times 1.564 = 43.80$ = total $CO_2 = CO_2$
$89.4 \times 1.564 = 139.82$ = total contraction = C
$7.5 \times 1.564 = 11.73$ = total unused oxygen
77.2 cc. = impure oxygen added
— 1.0 cc. N_2 = 1.3 per cent nitrogen in impure oxygen

76.2 cc. = pure oxygen added
—11.73 cc. unused oxygen

64.47 cc. = used oxygen = O_2
$CH_4 = \frac{3O_2 - C}{3} = 64.47 \times 3 = 193.41$
—139.82

$\frac{53.59}{3} = 17.86$ per cent CH_4

$CO = CO_2 - CH_4 = 43.80$
—17.86

25.94 per cent CO
$H_2 = C - (O + CO_2) =$ 64.47 139.82
+43.80 —108.27

108.27 31.55 per cent H_2

Using this method, a complete analysis can be made in twenty minutes, as I have repeatedly made an analysis in this time.

A convenient way of cleaning phosphorus is by adding a 3 per cent solution of hydrogen peroxide, if possible free from acetanilide, to the pipette and allowing it to remain until phosphorus assumes the yellow waxy color.

When the ethane is to be estimated the hydrogen is absorbed in a colloidal palladium solution or in a palladium tube as directed in G. Lunge's (1914) "Technical Gas Analysis."

Another wash bottle containing pure water is attached to the apparatus along the side of the wash bottle containing the dilute hydrochloric acid.

After absorbing the hydrogen the residue consisting of carbon monoxide, methane, ethane and nitrogen is transferred to the gas holder and excess of oxygen added and the gases burned as before.

The theoretical formulae for calculating the constituents of the mixture, when O_2 equals the oxygen used in the chemical action, C equals the observed contraction, and CO_2 equals the observed carbon dioxide formed, are

$$C_2H_6 = O_2 - C$$

$$CH_4 = \frac{5C - 3O_2 - CO_2}{3}$$

$$CO = \frac{4CO_2 + C - 3O_2}{3}$$

It is usually necessary to remove the carbon monoxide before the absorption of hydrogen.

The mercury can be cleaned by putting it into a two or three liter bottle with some dilute nitric acid and shaking it until the mercury is finally divided. Repeat this operation with pure water.

When mercury is used in burette B, a glass cock exactly the same as is used at the bottom of burette B_1 is attached to B. The mercury surface should be leveled at the lowest part of the meniscus showing as a sort of bright line.

Burrell and Seibert in Bureau of Mines *Technical Paper* 54 (1913) again call attention to certain cases of gas analysis where corrections in calculating results are to be made due to certain of the gases not obeying the ideal gas laws.

Below is a new easier method of calculating corrected results and proven by simple stoichiometry to give at least as accurate results as the method given in Burrell and Seibert's paper.

When carbon monoxide, methane and ethane are estimated together, and the factors for the partial pressures of the carbon dioxide formed for each constituent are used, as is necessary in Burrell and Seibert's calculation, the sum of all of the separate parts of corrected carbon dioxide does not equal the total corrected carbon dioxide calculated by dividing the total measured carbon dioxide by its partial pressure factor.

Theoretically, according to Avogadro's hypothesis and Gay-Lussac's law, etc., the molecules in one volume of methane combine with the molecules in two volumes of oxygen to form the molecules in one volume of carbon dioxide and the molecules in two volumes of water vapor.

This water vapor should condense at the ordinary temperature and pressure if the original gases were saturated with moisture.

Therefore, 1000 cc. of methane should combine with 2000 cc. of oxygen to form 1000 cc. of carbon dioxide.

By observation it had been found that the number of molecules in 1000 cc. of methane combine with the molecules in $2002\frac{2}{999}$ cc. of oxygen to form the molecules in $995\frac{995}{999}$ cc. of carbon dioxide at the ordinary temperature and pressure.

If this amount of carbon dioxide is corrected by dividing by the quotient obtained by dividing the theoretical by the observed specific gravity of carbon dioxide at 20° and 760 mm., the corrected amount will equal the ideal amount of methane $1001\frac{1}{999}$ cc. and if this last amount is multiplied by the quotient of the theoretical, divided by the observed gravity of methane, as shown in Burrell and Seibert's paper, the product will be the actual amount of methane measured.

Now if the methane is to be calculated from the contraction the measured amount of methane must be divided by its pressure factor and the carbon dioxide formed also must be corrected in the same way. Divide the corrected contraction by 2 and the quotient will be the ideal volume of methane. Multiply this quotient by the pressure factor for methane and the product equals the measured volume of methane.

This method of reasoning can be extended to more complicated formulae.

Therefore, if the original amount of gas present as measured or calculated from the theoretical formulae be divided by the factors for the separate gases and the measured volume increased by the difference between the calculated amount and the measured amount, also if the carbon dioxide as measured is corrected by dividing by its pressure factor, the ideal quantities of all of the gases present can be calculated by the usual theoretical formulae by using the corrected values for the contractions and the carbon dioxide.

An oil gas gave these combustion measurements: C = 130.69 cc., O_2 = 117.78 cc., CO_2 = 55.51 cc.

By the usual theoretical formulae the methane equals 55.71 per cent, the carbon monoxide —0.20 per cent, the hydrogen equals 12.91 per cent, and the nitrogen equals 0.28 per cent. The total was 68.7 per cent of the original 100 cc. taken for analysis.

The carbon dioxide partial pressure equaled 50.3 per cent and the partial pressure of the methane was 84.7 per cent. From Burrell and Seibert's paper the molecular volume factor for the carbon dioxide is 0.99717 and for methane 0.99915. Divide 55.51 cc. by 0.99717; the quotient, 55.668, is the corrected volume of carbon dioxide. Divide 55.71 cc., the calculated amount of methane, by 0.99915; the quotient, 55.758 cc., is the corrected volume of CH_4 if 55.71 cc. was the measured volume of methane. This is not the case here; the idea is to get the increase of the corrected over the theoretically calculated methane; add this difference to the total volume of gas for combustion in order to arrive at the corrected figures for the contraction.

This difference is 0.048 and can be added to the uncorrected contraction provided the difference between the corrected and measured carbon dioxide is subtracted, as this last difference is 0.158 cc., the corrected contraction is 130.58 cc. The corrected carbon dioxide is 55.668 cc. The oxygen used is 117.78 cc.

By the ordinary theoretical formulae the calculations are completed and give the following values:

Methane	55.6 per cent
Hydrogen	12.8 per cent
Nitrogen	0.3 per cent

From the foregoing deductions, the molecular volume factors and the specific gravity of the pure gases can be determined by the ordinary combustion method as described in this paper provided pure gases can be obtained as directed in Bureau of Mines *Technical Paper*, **104** (1915) by Burrell, Seibert and Robertson.

For accurate work in these determinations larger measuring instruments should be used.

5120 Cologne Ave., St. Louis, Missouri

A RAPID METHOD FOR THE ANALYSIS OF RED LEAD AND ORANGE MINERAL

By John A. Schaeffer

Received August 4, 1915

In estimating the chemical value of red lead and orange mineral, it is essential that the true red lead, Pb_3O_4, content or the lead dioxide, PbO_2, content be determined. Where a large consumption of these products or their purchase on specifications necessitates a determination of these constituents at all times the methods in use at present are rather long and involved.

The following method has been perfected for this analysis and gives accurate results in a most rapid manner.

The method depends upon the initial decomposition of the true red lead, Pb_3O_4, with nitric acid, according to the following reaction:[1]

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + H_2O + H_2PbO_3.$$

The H_2PbO_3 or PbO_2 is then decomposed with hydrogen peroxide as follows:[2]

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2.$$

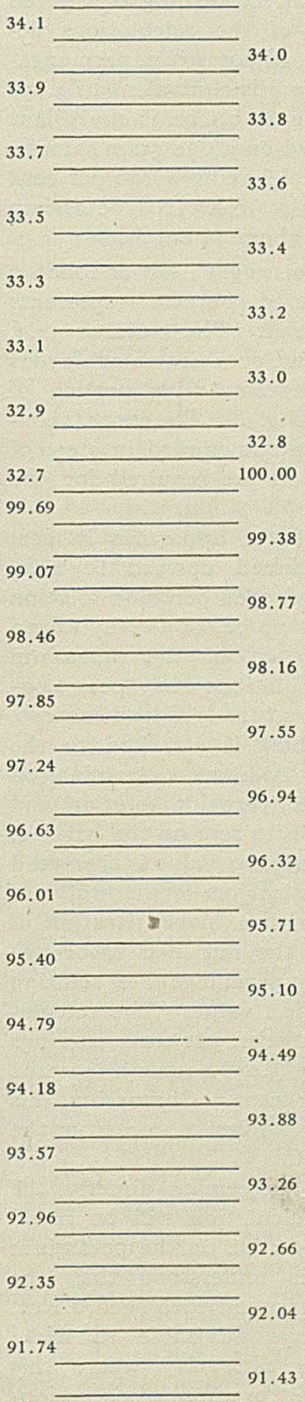
The excess of standard hydrogen peroxide used is then titrated with a standard potassium permanganate solution.

In carrying out the analysis, one gram of the red lead or orange mineral is treated with 15 cc. of nitric acid, having a specific gravity of 1.2. The mixture is then stirred until the first reaction given is complete, as is evidenced by an entire disappearance of all red color. There is then added from a calibrated burette or pipette exactly 10 cc. of dilute hydrogen peroxide, made up of a mixture of 1 part of 3 per cent hydrogen peroxide solution to 3.5 parts of water. It has been found that a 10 cc. automatic pipette, with a three-way stop-cock, is excellent for delivering a definite volume of hydrogen peroxide solution at all times.

After the addition of the hydrogen peroxide solution, the resultant mixture is stirred until almost complete decomposition of the lead peroxide has been effected, as shown by the second reaction. The decomposition is completed by the addition of a little hot water and stirring. The contents of the beaker, after complete decomposition and solution of the lead peroxide, are diluted with hot water to about 250 cc. volume and titrated directly with a standard potassium permanganate solution having an iron value of 0.005. The solution is titrated to a faint pink permanganate color.

A blank titration is then made on exactly the same volume of the hydrogen peroxide solution and nitric acid in the same manner.

The difference between the number of cc. of potassium permanganate solution required for the blank titration and the number of cc. required for the red lead titration is the amount required for the hydrogen peroxide necessary for the complete decomposition of the lead peroxide. This difference multiplied by 3.058 gives the percentage of red lead according to the following proportion:



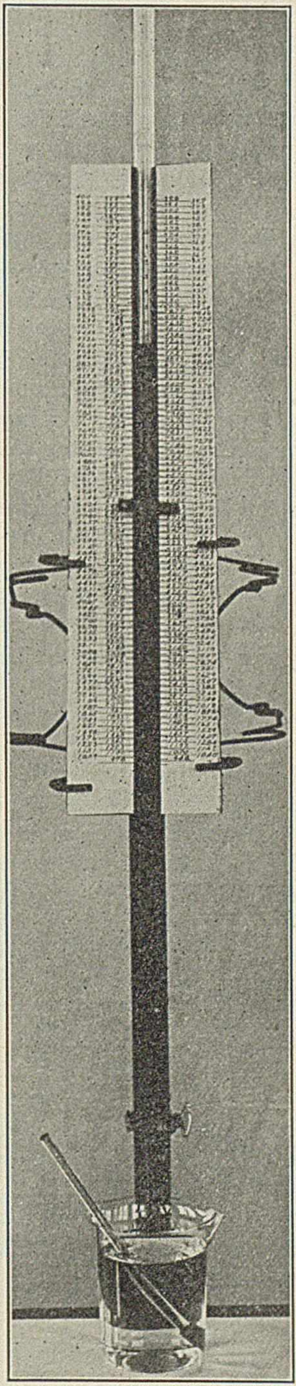


Fig. 1

$2Fe : Pb_3O_4 = 0.005 : X$, or, $112 : 685 = 0.005 : X$

whence, $X = 3.058$.

---

[1] Treadwell and Hall, "Analytical Chemistry," Vol. II, p. 623.

[2] *Ibid.*, Vol. I, p. 53.

To determine the lead peroxide present the difference is multiplied by 1.067, according to the following proportion:

$2Fe : PbO_2 = 0.005 : X$, or, $112 : 239.0 = 0.005 : X$
whence, $X = 1.067$.

These calculations have been arranged in a series so devised as to permit the direct reading of the red lead percentage. The basis of the calculations depends on the fact that each cc. of potassium permanganate solution (iron value, 0.005) is equivalent to 3.058 per cent of true red lead; or, each 0.1 cc. is equivalent to 0.3058 per cent true red lead on a one gram sample.

A red lead or orange mineral having a 100 per cent true red lead content requires 32.7 cc. potassium permanganate solution of the above strength.

The calculation, therefore, arranges itself as follows: Each 0.1 cc. on the selected burette represents 0.3058 per cent true red lead. The number 32.7, being equivalent to 100 per cent, occupies an analogous position on the chart. A representative portion of the series is shown alongside Fig. I. The series is continued upward in steps of 0.1 and downward in steps of 0.30 and 0.31 to such points as are required for the red lead usually examined.

Fig. I is an illustration of the apparatus in use; calculations have been continued upward to 40.0, or to that point where the hydrogen peroxide solution used is of such strength that 10 cc. of the hydrogen peroxide solution require 40 cc. of the potassium permanganate solution. Calculations have been continued downward to 9.48 per cent true red lead content.

In using the series the chart is attached to the burette by a screw clamp. A blank determination is first made on the hydrogen peroxide solution and the value found is placed opposite zero on the burette. In the analysis of the red lead the value is then read off directly. As a hypothetical case we will use hydrogen peroxide solution with a blank titration of 34.1 cc. In the analysis of the red lead or orange mineral 4.2 cc. of potassium permanganate solution are required for a final titration value. The calculation shows the difference between the two readings to be 29.9 cc. or multiplied by 3.058 equals a true red lead percentage of 91.43 per cent. Comparing this with the series of calculations we find 4.2 cc. from the value 34.1 to be 91.43 per cent.

Should it be preferred to determine directly the lead peroxide content, the calculation will be based on the value 0.1067 for each 0.1 cc. on the potassium permanganate burette. It is understood that the division must be made to correspond with each 0.1 cc. on the burette. It is always advisable to make several blank determinations each day where this analysis is constantly carried out, or when only occasionally used a blank titration should be made before the final analysis. The strength of the hydrogen peroxide solution will vary from time to time when a stock solution is kept on hand, but the permanence of the potassium permanganate solution renders the method accurate over a long period of time.

Chemical Laboratory, Picher Lead Company
Joplin, Missouri

CHROMIUM OXIDE ANALYSIS

By Allan J. Field

Received August 13, 1915

The chief difficulty in chromium oxide analysis is in the fusion. Sodium peroxide affords the quickest and most complete fusion but has the disadvantage of attacking nickel, copper and platinum crucibles. As nickel crucibles contain iron they cannot be used if iron is to be determined in the chromium oxide.

The method of heating the crucible as suggested by Treadwell-Hall[1] has given very good results. He recommends using a porcelain crucible which is placed inside a larger porcelain crucible and heated for fifteen or twenty minutes over a small flame. The fusion is dissolved out with water and evaporated down to dryness to remove the last traces of peroxide.

The author has found the following modifications to afford decided advantages. Instead of using a porcelain crucible, which interferes with the silica determination, a platinum crucible is used. The sodium peroxide has very little action on the platinum crucible when it is placed inside of a porcelain crucible and heated with a low flame. After making twenty determinations there was a loss of only 0.019 g. in the weight of the platinum crucible, which loss took place principally in the cleaning of the crucible after each determination.

Another modification is that it is not necessary to evaporate the solution to dryness to decompose all peroxide as 20 minutes' boiling decomposes it entirely; in fact after 10 minutes' boiling no peroxide could be found.

(To detect peroxide the following test was worked out: To 5 cc. of a 1 per cent solution of sulfanilic acid add one drop of the sodium chromate solution, which should be neutral, then 2 drops of a 5 per cent oxalic acid solution. If peroxide is present a pink color develops immediately. This is a very delicate test and will show minute quantities.)

For the determination of chromium the following volumetric method has given excellent results: One-half g. of the finely powdered chromium oxide is mixed intimately with 3 g. of sodium peroxide in a platinum crucible. The crucible is placed inside of a larger porcelain crucible and heated with a low flame so that the mixture just melts. After heating in this manner for 20 minutes all the chromium is converted into soluble sodium chromate. The fusion is dissolved out with water and the solution boiled for 15 or 20 minutes. If there is any iron it will be insoluble and should be filtered off before proceeding further. The solution is made neutral with hydrochloric acid and diluted to 250 cc. in a graduated flask. An aliquot portion of 100 cc. is taken out into a liter Erlenmeyer flask, 10 cc. conc. hydrochloric acid are added and the solution diluted to about 300 cc. with water. About 3 g. of potassium iodide are added and the liberated iodine is titrated with $N/10$ sodium thiosulfate.

The gravimetric determination of chromium as oxide does not give very accurate results probably due,

---

[1] "Analytical Chemistry," Vol. II (1913), 675.

according to G. Rothaug,[1] to the precipitate absorbing atmospheric oxygen during ignition with the formation of chromic chromate ($Cr_2O_3.3CrO_3$). If ignition takes place in a current of hydrogen, accuracy will be secured.

In the absence of sulfates the author used the following method to check up the volumetric method and obtained results agreeing very closely. The sample is fused as in the volumetric method, then dissolved out and made neutral with acetic acid, 0.5 cc. glacial acid is added in excess and the solution diluted to 400 cc. The chromate is precipitated at the boiling temperature with a dilute solution of barium acetate. The barium acetate should be added by drops so as to avoid carrying down some of the barium acetate with the barium chromate. After the precipitate settles it is filtered off on a Gooch crucible, washed with dilute alcohol and dried.

Chemical Laboratory, G. Siegle Company
Rosebank, Staten Island, New York

THE SOLUTION OF THE CERIUM GROUP OXIDES BY CERTAIN ACIDS

By W. S. Chase

Received September 13, 1915

As is well known, the oxides of the trivalent rare earth metals are moderately strong bases, resembling the alkaline earth oxides in that respect. With this fact in mind, one would expect that the addition of a dilute mineral acid to a mixture of cerium group oxides would effect the quick solution of the more basic earths with but slight action on the least basic. If this did occur, the result would be the complete separation of CeO_2, which is the least basic of all the rare earth oxides and very resistant to acids. Such a separation, which indeed would constitute a rapid and easy method for the extraction of cerium, might be expected when it is considered that the other oxides present are, for the most part, among the more basic of the rare earth oxides.[2]

Unfortunately, the addition of dilute or even concentrated acid does not produce the expected result, and this must be due to the influence of the CeO_2. This substance is practically insoluble even in hot concentrated acids, except sulfuric acid. It possesses the power of combining with the other rare earth oxides, and to this combination is undoubtedly due the failure of acids to react with the mixture of oxides in the manner that might be expected. Another result of this combination is that the CeO_2, when thus combined, dissolves readily in acids in which it is otherwise insoluble provided its value in the mixture does not exceed 55 per cent. Therefore, on treating the mixed oxides with acid the basic earths do not rapidly dissolve and the CeO_2 remain untouched, but, instead, the entire mixture goes into solution at a moderately rapid rate. This behavior is rather remarkable in view of the fact that CeO_2 itself is practically insoluble, and that the other oxides by themselves will dissolve instantly in a small excess of very dilute acid.

The rate of solution of the mixed oxides can be very greatly increased by the addition of some substance that will reduce cerium to the cerous condition. Hydrogen peroxide answers this purpose admirably, for not only is the reaction very rapid and complete but there is the added advantage that no other salt is introduced into the solution (as is the case for example when KI or $FeCl_2$, etc., are used).

EXPERIMENTAL

The rare earth residue obtained after the extraction of thorium from monazite sand was the material used in this work. This residue consists essentially of the oxides of the cerium metals though possibly small quantities of the yttrium elements may be present. No attempt was made to separate the latter as they were not in sufficient quantity to be detrimental in any way. The principal constituent of the mixed oxides was, of course, CeO_2, with a value of 52.70 per cent, the others in order of importance being Nd_2O_3, La_2O_3, Pr_4O_7 and Sa_2O_3.

The composition of the ordinary commercial residue is quite constant, the CeO_2 value for instance fluctuating between 50 and 60 per cent, and in most cases being around the mean of those values. The color of the mixed oxides varies from reddish brown to chocolate, depending on the composition of the sample, ignition temperature,[1] etc. Their solubilities in sulfuric, hydrochloric, nitric and acetic acid of different concentrations were studied, as was also the use of H_2O_2 as a reducing agent for CeO_2.

The theoretical quantity of acid required to react with 1 g. of sample was calculated on the basis of $RO_2 = 55$ per cent, $R_2O_3 = 45$ per cent (about the average composition of the residues handled in this laboratory) and the following figures were thus obtained:

Acid	Sulfuric	Nitric	Hydrochloric	Acetic
Approximate strength.....	96%	70%	38%	99.5%
Cc. per 1-g. sample.......	0.58	1.33	1.7	1.2

SULFURIC ACID—As is well known, with a large excess of acid and evaporation to strong fuming, complete solution is obtained. The CeO_2 dissolves with but slight reduction, so that the solution is of a yellow or yellowish red color due to the ceric sulfate. However, this process is rather tedious, and as it is desirable that the fuming operation be avoided, if possible, the action of H_2O_2 along with dilute H_2SO_4 was tried.

A few experiments sufficed to show that with a moderate excess of acid diluted as much as 1 : 10 or more, and a similar excess of H_2O_2, solution is rapid and thorough. For example, 1 cc. each of acid and 30 per cent H_2O_2 and 10 cc. of water were added to 1 g. of the oxides and the mixture heated for 3 minutes, by which time solution was complete. This experiment indicates that these oxides are dissolved by *dilute* $H_2SO_4 + H_2O_2$ much more rapidly than by *concentrated* H_2SO_4 *alone*, and further the fuming nuisance is also avoided.

NITRIC ACID—The mixed earths dissolve fairly readily in this acid, which is most efficient when concentrated. However, when diluted, even as much as

---

[1] *Z. anorg. Chem.*, **84** (1913), 165–189.

[2] Levy, "The Rare Earths," pp. 117, 118.

[1] Levy, "The Rare Earths," p. 119.

1 : 2, it still acts fairly satisfactorily though somewhat slowly. When the acid alone is employed it is always necessary that a considerable excess be taken, but the quantity of the latter naturally decreases as the size of the sample increases. With the smaller samples, in order to avoid the use of a very great excess of acid, the same should be diluted, which serves to increase the volume enough so that all the acid is not boiled off before complete solution can occur. These points are indicated by the following data:

Sample used Grams	NITRIC ACID USED			Total cc. of liquid at start	Minutes required for solution (approximate)
	Parts acid	Parts water	Times theoretical		
1	1	2	6	24	7
3	1	2	4	48	20
5	1	2	3	60	20
1	1	0	8	10.5	4
5	1	0	6	40	10

The use of H_2O_2, however, produces results greatly superior, in every way, to those obtained with the nitric acid alone, but especially so in regard to speed of reaction and excess of acid. Solution occurs so quickly and completely that even small samples can be readily dissolved in a slight excess of acid, it being unnecessary to have a considerable volume of liquid at the start, on account of the rapidity of the reaction. The following results indicate the advantages pertaining to the use of H_2O_2. Practically the same results could be obtained with considerably more dilute acid.

Sample used Grams	SOLUTION MIXTURE			Total cc. of liquid at start	Minutes required for solution (approximate)
	Parts HNO_3	Parts water	Cc. H_2O_2		
1	1	2	0.5	5	1
3	1	1	1.5	10	1

HYDROCHLORIC ACID—The action of this acid about parallels that of nitric, or if anything, it is somewhat more efficient, for although concentrated hydrochloric is only about one-half as strong as concentrated nitric acid, it acts with equal speed. Owing to its lesser concentration a larger volume is required for the same equivalent of acid than with nitric, and it was found that owing to this, a smaller excess of hydrochloric could be used for a given sample than is necessary when nitric is employed; *e. g.*, a 5 g. sample which was readily dissolved by 4 times the theoretical amount of hydrochloric acid, required 6 times the theoretical quantity of nitric acid to effect its solution.

This behavior with hydrochloric acid was quite unexpected, the writer having always been under the impression that these oxides were practically insoluble in it except in the presence of a reducing agent. The chloride ion apparently acts in the latter rôle, free chlorine being given off during the reaction. H_2O_2 acts with hydrochloric acid in exactly the same manner as with nitric.

ACETIC ACID—The acid used contained 99.50 per cent $HC_2H_3O_2$ and proved to be a very unsatisfactory solvent for these oxides. Its action is extremely slow, so that long boiling, with the consequent necessity of a large excess of acid, is necessary in order to obtain the solution of even a moderate amount of material: *e. g.*, a 1-g. sample was treated with 20 times the required quantity of acid, the mixture heated to boiling, then placed on the steam bath and frequently shaken; after half an hour the residue was filtered off, the filtrate precipitated with oxalic acid, and the oxalates ignited to oxides; this oxide did not exceed more than about 0.05 g. in weight.

Very peculiarly H_2O_2 does not seem to facilitate solution in this case, repeated experiments using large excesses of the peroxide giving no better results than that above noted. As suggested by Dr. W. C. Moore, of the Research Laboratory, this behavior may be due to some reaction taking place between the hydrogen peroxide and the acetic acid itself.

SUMMARY

I—This investigation has shown that the cerium group oxides are fairly readily dissolved by sulfuric, nitric or hydrochloric acid, and especially so when the concentrated acids are used, although in the case of the latter two, considerable dilution still permits of satisfactory results being obtained. However, it is necessary to use a considerable excess of the respective acid, and more particularly so if the sample is small and it is required to dissolve it in concentrated acid.

II—Acetic acid was shown to be a very unsatisfactory solvent.

III—The use of hydrogen peroxide makes rapid dissolving of the oxides by a very small excess of sulfuric, nitric or hydrochloric acid, possible even in quite dilute solution. With acetic acid, however, the use of hydrogen peroxide does not produce this favorable result.

ANALYTICAL LABORATORY, NATIONAL CARBON COMPANY
CLEVELAND, OHIO

A METHOD FOR THE DETERMINATION OF ALCOHOL IN THE PRESENCE OF PHENOL[1]

By J. EHRLICH

Received October 27, 1915

It has been repeatedly observed in this laboratory that the usual method of determining alcohol in the presence of phenol by means of distillation from strongly alkaline solution is by no means exact. Notwithstanding the presence of a large excess of alkali, a bromine test on the distillate invariably indicates that a portion of the alkaline phenate always undergoes hydrolysis, allowing phenol to be carried over.

Inasmuch as tribromphenol or sodium tribromphenate would be expected to have a much higher dissociation constant than phenol or sodium phenate because of the brominated nucleus, it was thought that the conversion of the latter into the former would result in decreased hydrolysis and hence obviate the difficulty referred to above. The method proved to be practicable.

Aqueous solutions (8.6 and 20.0 per cent by volume) of ethyl alcohol were prepared, an accurately standardized bottle pycnometer being used for the determination of specific gravity. Throughout the work solutions were measured and the alcoholic distillates weighed at 25° C. The 50 cc. receiving flask and the 25 cc. and 50 cc. pipettes were found to be relatively correct at 25° C.

---

[1] Published by permission of the Secretary of Agriculture.

When employing the scheme outlined below the following results were obtained:

No.	8.6% alcohol Cc.	Phenol added Grams	Alcohol found Per cent	No.	20.0% alcohol Cc.	Phenol added Grams	Alcohol found Per cent
1	50	1	8.6	4	50	1	20.0
2	50	3	8.6	5	50	3	20.0
3	50	10	8.6	6	50	10	20.0

In testing the method the phenol was dissolved in 50 cc. strong NaOH solution in the distilling flask to which the known alcohol solution was then added.

METHOD

Pipette 50 cc. of sample into a 300 cc. flask containing 30 cc. water. Make strongly alkaline with an excess of strong NaOH solution so that the final volume is about 100 cc. and the odor of phenol is absent. Add glass beads and distil into a 50 cc. graduated flask containing 1 or 2 cc. water. The end of the condenser or adapter should almost touch the surface of the distillate in the receiver, especially at the beginning of a distillation. A drawn-out thistle tube is serviceable in this connection. The flask is lowered as distillation proceeds.

When nearly 50 cc. of distillate have been collected, remove the receiver, dilute with water to mark, shake thoroughly and pipette 25 cc. into another 300 cc. flask containing 30 cc. water. Precipitate the phenol as its tribrom-derivative by adding bromine water, drop by drop, to slight excess while rotating flask. Without delay add normal "hypo" solution (a few drops will be sufficient) to decolorize (*i. e.*, to remove the free bromine excess) and finally add enough strong NaOH solution to dissolve the white tribromphenol as its phenate, and then a decided excess of alkali. The final volume will be less than 100 cc. After the addition of glass beads distil into the 50 cc. flask as before, dilute to mark and determine density by weighing. The percentage of alcohol in this last distillate multiplied by 2 gives the required figure.

For high concentrations of alcohol a 100 cc. receiving flask may be substituted in the above method and 50 cc. of distillate treated and redistilled. For high concentrations of phenol the method is directly applicable since the amount of phenol which passes over during the first distillation is small. If the original phenol content is low, the first distillation may be omitted. In this case the 50 cc. sample plus 30 cc. water in the 300 cc. flask is treated directly with bromine water to slight excess as shown by color; then add "hypo," alkali, etc., as above and distil into a 50 or 100 cc. flask according to alcohol concentration. Samples high in phenol cannot be treated directly in this manner because the bulky precipitate of tribromphenol prevents thorough mixing while adding the bromine water, making it impossible to perceive when an excess of bromine is present.

The hydrobromic acid formed by the action of bromine on the phenol is neutralized and retained by the alkali.

CONCLUSION

The method is seen to be not only accurate in result but extremely simple in manipulation, no filtration or separation being required. The results obtained demonstrate that a low concentration of bromine acting during a short period of time has no appreciable effect on aqueous ethyl alcohol at room temperature.

The behavior of methyl alcohol when present in phenolic ethyl alcohol mixtures will be investigated in the same way.

N. Y. Food and Drug Laboratory
Bureau of Chemistry

THE ANALYSIS OF MAPLE PRODUCTS, VI[1]

A Volumetric Lead Subacetate Test for Purity of Maple Syrup

By J. F. Snell, N. C. MacFarlane and G. J. Van Zoeren

Received August 20, 1915

The fact that lead subacetate produces a heavy precipitate in genuine maple syrup has been utilized in various ways for the detection of adulteration.[2] In the method here communicated a more dilute solution of this reagent than is employed in any of the older methods is gradually added to the diluted syrup from a burette and the end-point of the titration is determined by means of measurements of electrical resistance in the manner suggested by van Suchtelen and Itano.[3] The method in detail is as follows:

SOLUTION

A filtered solution of Horne's lead subacetate of specific gravity 1.033.[4] This solution is to be kept in a bottle connected with a burette and protected from atmospheric carbon dioxide by a soda-lime tube.

METHOD

Dilute the syrup with water, boil until the temperature reaches 219° F., and filter through cotton wool. After cooling, dilute 10 cc. to 100 cc. with distilled water and measure 60 cc. of the diluted syrup into a 100 cc. beaker.

Measure the electrical resistance using a dip electrode.[5] Maintaining the temperature constant, add 1 cc. of the lead subacetate solution from the burette, stir well and again measure the electrical resistance. Continue the addition of the subacetate in this manner, 1 cc. at a time, until 10 cc. have been added. Plot the resistances found against the quantities of subacetate solution used. If the syrup is genuine the results of the plot will be two intersecting straight lines. In the 70 genuine maple syrups,[6] to which the

---

[1] Presented at the 51st Meeting of the American Chemical Society at Seattle, August 31–September 2, 1915. Previous papers of this series: This Journal, **5** (1913), 740, 993; **6** (1914), 216, 301; **8** (1916), 144. An account of the preliminary experiments leading to the volumetric test is given in Paper V, This Journal, **8** (1916), 144.

[2] Hortvet, *J. Am. Chem. Soc.*, **26** (1904), 1543; Bureau of Chem., U. S. Dept. Agric., *Circ.* **23** (1905); Jones, Vermont Agr. Expt. Sta., *18th Ann. Rept.*, **1904–5**, p. 322; Thos. MacFarlane, Laboratory Inland Revenue Dept., Ottawa, *Bull.* **120** (1906); Winton and Kreider, *J. Am. Chem. Soc.*, **28** (1906), 1204; McGill and Valin, Laboratory Inland Revenue Dept., Ottawa, *Bull.* **140** (1907); **228** (1911); Ross, Bureau of Chem., U. S. Dept. Agric., *Circ.* **53** (1910); Department of Inland Revenue, Ottawa, *Circ.* G **994**.

[3] van Suchtelen and Itano, *J. Am. Chem. Soc.*, **36** (1914), 1793.

[4] We make a cold, saturated solution of the subacetate, dilute to approximately the correct density, filter and adjust to exactly 1.033, as measured by a hydrometer.

[5] A suitable form of electrode is described in a paper by Van Zoeren, published in the *Journal of the American Chemical Society*, March, 1916. The rest of the apparatus used by us for the measurements of electrical resistance is described in Paper I of this series (This Journal, **5** (1913), 740).

[6] These syrups were all collected from the makers in the Province of Quebec, 62 in the season of 1915 and 8 in that of 1914.

method has been applied, the intersections have all fallen between 4.8 and 6.6 cc.

SPECIMEN PLOT—The accompanying diagram is a typical specimen of the plots obtained with a pure syrup and with mixtures of the same syrup of equal density made from commercial white sugar.

THE EFFECT OF TEMPERATURE—Measurements at 20°, 25° and 30° C. with five of the syrups indicate that the particular temperature at which the measurement is made is of no consequence as long as the temperature remains constant during the measurements. The resistances were uniformly higher the lower the temperature but the intersection points did not change.

EFFECT OF ADULTERATION WITH SUCROSE SYRUP

Table I gives the results of determinations of, respectively, (1) the "volumetric lead number," *viz.*, the abscissa of the point of intersection of the two straight lines, and (2) the Canadian lead number, upon 20 syrups (10 of which were dark-colored, late-run products) and upon mixtures of these with a syrup of equal density made from commercial granulated sugar. In the table a smooth curve on the plot is represented by the letter "C." Such a curve is given by all but 2 of the mixtures containing 60 per cent of maple syrup and by all but 3 of those containing 70 per cent. The two exceptional 60 per cent mixtures give intersections outside the limits (4.8 to 6.6 cc.) found in genuine syrups.

TABLE I—VOLUMETRIC AND CANADIAN LEAD NUMBERS OF 20 PURE MAPLE SYRUPS AND THEIR MIXTURES WITH CANE SUGAR SYRUP OF EQUAL DENSITY

	1—VOLUMETRIC LEAD NUMBERS					2—CANADIAN LEAD NUMBERS			
No.	100%	90%	80%	70%	60%	100%	80%	70%	60%
1	4.8	4.9	4.8	C	C	5.35	2.85	2.72	2.23
2	4.9	5.9	4.7	C	C	1.94	1.40	1.02	..
3	4.9	5.8	4.8	C	C	2.43	1.44	1.17	..
4	6.0	6.2	5.0	C	C	2.58	1.68	1.35	..
5	6.1	5.3	4.9	C	C	1.96	1.14	0.84	..
6	5.4	5.6	4.7	5.4	4.4	3.25	1.96	1.53	..
7	5.8	6.0	5.5	C	C	2.23	1.45	1.11	..
8	5.6	5.1	5.0	5.0	C	2.67	1.85	1.10	..
15	6.0	5.3	5.7	C	C	1.82	1.38	0.99	..
19	6.0	5.3	4.8	C	C	2.29	1.14	0.99	..
31	5.8	5.8	5.3	C	C	4.27	2.80	2.38	1.6
32	5.8	6.0	5.9	C	C	4.44	2.53	2.06	1.5
33	6.0	6.2	5.5	C	C	3.90	2.46	2.01	1.31
34	5.4	5.5	5.2	C	C	1.72	1.03	0.59	..5
35	5.4	4.8	4.8	C	C	4.11	2.54	2.23	1.79
36	6.2	6.4	5.1	C	C	2.56	1.72	1.18	..
37	5.4	5.1	5.0	C	C	2.21	1.58	0.96	..4
38	5.9	5.9	C	C	4.5	4.76	1.96	1.29	..
39	6.0	5.7	5.9	C	C	3.70	2.59	2.15	1.65
40	5.3	6.0	5.9	5.5	C	2.54	1.95	1.31	..

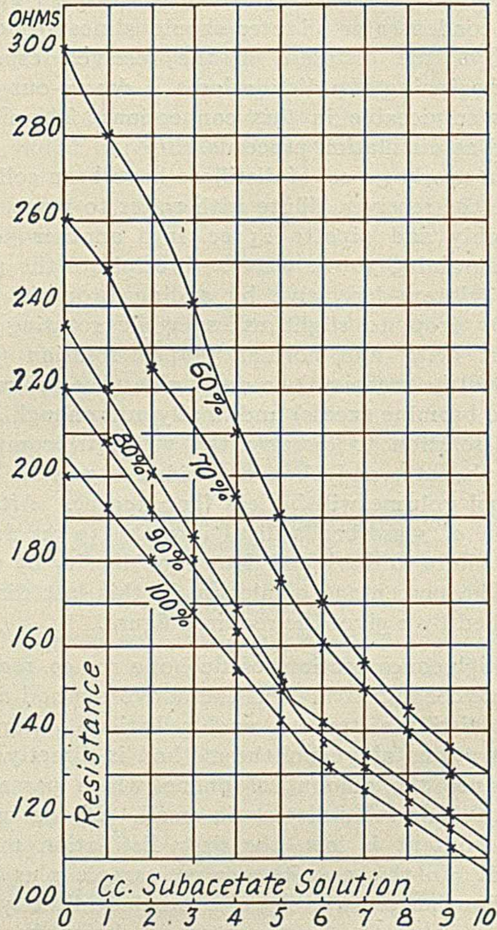
	VOLUMETRIC	CANADIAN
Maximum for pure syrup	6.6	5.35
Minimum for pure syrup	4.8	1.72
Difference	1.8	3.63
Mean for pure syrup	5.64	3.04
Variation, per cent of mean	31.9	113
Variation, per cent of minimum	37.5	211

The Canadian standard (minimum) for Canadian lead number is 1.7. Two of the 62 per cent and 6 of the 70 per cent mixtures attain to this standard.

The results of Snell and Scott[1] show (as well as can be shown by the study of so small a number of syrups) that the Canadian lead method has this advantage over all the other current tests, that its value falls off more rapidly than in proportion to the adulteration with cane sugar syrup. The basis of comparison employed by Snell and Scott in their paper appears scarcely applicable to the volumetric lead subacetate test, inasmuch as the 90 per cent mixture frequently, and the 80 per cent mixture occasionally, gives a higher intersection point than the pure syrup itself. If, however, we assume as a provisional standard for the volumetric lead number the minimum value found in our 70 syrups (*i. e.*, 4.8) it is clear that this test condemns all the 60 and all but 3 of the 70 per cent mixtures, whereas the Canadian lead test, as we have seen, passes 2 of the 60 and 6 of the 70 per cent mixtures and it seems probable from Snell and Scott's work that the other tests, had they been applied, would have made a still poorer showing.

RANGE OF VARIATION IN GENUINE SYRUPS

The range of variation of the volumetric lead number among the 70 syrups (4.8 to 6.6) amounts to only 37.5 per cent of the minimum or 31.9 per cent of the mean (5.64). In the same syrups the conductivity value shows a range of 97 per cent of the minimum or 74 per cent of the mean (125). The volumetric lead number, therefore, appears to have a narrower range than the conductivity value, which, as will be seen by reference to Table V of Paper III, excels all the older analytical values in this respect.



TYPICAL PLOTS FOR A PURE MAPLE SYRUP AND FOR MIXTURES CONTAINING 90 TO 60 PER CENT OF THE SAME WITH CANE SUGAR SYRUP OF EQUAL DENSITY. VARIATIONS IN ELECTRICAL RESISTANCE AS LEAD SUBACETATE SOLUTION IS ADDED

In 28 of the 70 syrups (8 of the season of 1914 and 20 of the season of 1915) the Canadian lead number has been determined. In these 28 samples the three values determined compare as follows:

---

[1] Paper II of this series, THIS JOURNAL, **5** (1913), 993.

	Conductivity Value	Canadian Lead No.	Volumetric Lead No.
Maximum	189	7.55	6.6
Minimum	108	1.72	4.8
Difference	81	5.83	1.8
Mean	134	3.22	5.77
Range, per cent of mean	60	181	31
Range, per cent of minimum	75	339	37.5

MEASUREMENTS ON NON-MAPLE SYRUPS—We have applied the method to 5 of the non-maple and compound maple syrups referred to in Paper I, *viz.*, Nos. 7 and 13 of Table VIII—a golden syrup and a syrup made from a pale brown commercial sugar—the latter of which had given a conductivity value within the limits for maple syrup—and Nos. 11, 31 and 33 of Table IX. All five of these syrups gave smooth curve plots.

A compound syrup, a syrup sold as pure but known to be adulterated, and 5 syrups made from raw cane sugars by dissolving in water, boiling to 219° F., and filtering, gave smooth curves. Two other syrups made from raw cane sugars and a sample of raw beet sugar gave breaks at 3.4, 4.1 and 4.2, respectively,—all outside the limits for maple syrups. Two of these syrups had conductivity values (143 and 210) within the limits found in maple syrups. In 3 samples of cane molasses no material change in the electrical resistance (which, of course, was much lower than with maple syrup) was produced by the addition of the 10 cc. of lead subacetate solution.

TIME REQUIRED FOR THE TEST—The time required to reboil, filter and cool the syrup and to make the test is about half an hour. The time consumed in the test itself is less than 5 minutes.

SUMMARY

I—The volumetric lead subacetate test consists in diluting the syrup to 10 times its original volume and titrating with lead subacetate solution of sp. gr. 1.033, obtaining the end-point by measurements of electrical resistance.

II—The volumetric lead number is the abscissa of the point of intersection of two straight lines on the plot of volumes as abscissae with resistances as ordinates.

III—Seventy genuine Quebec 1914 and 1915 syrups gave volumetric lead numbers ranging from 4.8 to 6.6—a range of 37.5 per cent of the minimum, as compared with 97 per cent for the conductivity value. In 28 of these syrups, the ranges of volumetric lead number, conductivity value and Canadian lead number were, respectively, 37.5, 75 and 339 per cent of the minima.

IV—Seventeen out of 20 syrups containing 30 per cent of sucrose syrup gave smooth curve plots: 18 out of 20 containing 40 per cent sucrose syrup gave smooth curves and the remaining two gave intersections outside the limits for genuine syrups.

V—Of 18 adulterated and non-maple syrups, 12 gave smooth curve plots, 3 gave intersections outside the limits found in genuine syrups and in the remaining 3 (cane molasses) the electrical resistance remained constant.

CONCLUSION

If future work by ourselves and others corroborates our experience of its reliability, we believe that, combining as it does the merits of rapidity, narrow range of values in genuine maple syrup and rapid falling off or early disappearance as the syrup is adulterated with cane sugar syrup, this test will prove the most useful single test for purity of maple products yet proposed.

MACDONALD COLLEGE, PROVINCE OF QUEBEC

COMPARISON OF LIME REQUIREMENT METHODS

By J. W. AMES AND C. J. SCHOLLENBERGER

Received September 17, 1915

The results presented have been obtained in the soil investigations pertaining to the effects of lime treatment being conducted at the Ohio Experiment Station. An estimation of the lime requirement in relation to effectiveness of applications of lime under different conditions of fertilizer treatment has been made, using several of the methods proposed for this determination.

METHODS—The methods used included the Veitch, Hopkins, Hutchinson-MacLennan,[1] MacIntire[2] and Vacuum[3] methods. The Veitch and the Hopkins, which are two of the more generally used methods, are entirely different in principle. The Hutchinson-MacLennan method and that proposed by MacIntire, two of the more recent of the numerous methods which have been published, are somewhat similar, a solution of calcium bicarbonate being the carrier of base in the two latter-mentioned methods. In the Hutchinson method the soil is kept in contact with the bicarbonate solution for 3 hours and a portion of the filtrate is titrated against $N/10$ acid, using methyl orange as indicator, to obtain a figure for the amount of calcium absorbed. The MacIntire method differs in that the bicarbonate solution is evaporated in contact with the soil to a thin paste; after transferring to a suitable flask, the excess of calcium carbonate is determined by addition of acid and estimation of liberated carbon dioxide.

SOILS—These five methods were compared on soils from a number of variously treated plots from one of the fertility sections of the Wooster farm, located on silt loam soil which is largely derived from sandstones and shales. So far as its history is known, it contains no natural supply of calcium carbonate, and each year it becomes increasingly difficult to secure a satisfactory growth of clover unless lime is applied. The west half of the plots had been treated with 1875 lbs. per acre of calcium oxide in 1903, and 2000 lbs. of limestone in 1909. The composition of the lime materials applied was such that the equivalent of 5700 lbs. of calcium carbonate had been applied to the limed halves of the plots previous to the time samples were taken from the plots, which was 3 years after the last treatment with lime.

From determinations of calcium carbonate which

---

[1] *Chem. News*, **110**, No. 2854, Aug. 7, 1914.

[2] *Am. Fert.*, **41**, No. 11, Nov. 28, 1914.

[3] This method was proposed by E. W. Gaither, formerly of this laboratory, and is essentially a modification of the Tacke procedure for estimation of degree of acidity of peat soils. Instead of boiling the mixture of soil and calcium carbonate at 100°, the soil was heated in contact with finely divided calcium carbonate under reduced pressure as in the Marr (*Jour. Agr. Science*, **3**, Part 2, p. 155) procedure for determination of soil carbonates; the carbon dioxide liberated by decomposition of the calcium carbonate by the soil is taken as a measure of the lime requirement.

are available for several of the differently fertilized plots on which lime requirement determinations were made, it is evident that the greater portion of the lime applied has disappeared or no longer exists in the carbonate form.

QUANTITIES OF CALCIUM CARBONATE PRESENT IN THE LIMED HALVES

Plot	FERTILIZER	Lbs. per acre
0	None	150
2	Acid phosphate	225
3	Muriate potash	450
5	Sodium nitrate	575
11	Complete	300
24	Complete, including ammonium sulfate as carrier of nitrogen	None
26	Complete, including bone meal as carrier of phosphorus	250
29	Complete, including basic slag as carrier of phosphorus	300

When tested with litmus paper, all of the soils—the limed soils containing a small amount of lime carbonate residual from application made, as well as the unlimed soils—gave a decided acid reaction. The amounts of $CaCO_3$ required for 2,000,000 lbs. (approximately) per acre 6 in. of soil are stated in Table I.

TABLE I—LBS. $CaCO_3$ INDICATED FOR 2,000,000 LBS. SOIL

Plot	FERTILIZER	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
0	None	3440	2000	3550	2925	7300
	None + Lime	100	Alk.	2250	1700	4900
2	Acid Phosphate	2640	2000	3850	2700	7800
	Acid Phosphate + Lime	80	Alk.	2400	975	3800
3	Muriate Potash	3240	2000	3550	3025	....
	Muriate Potash + Lime	200	Alk.	2650	1600	....
5	Sodium Nitrate	3640	1200	3550	2550	6200
	Sodium Nitrate + Lime	120	Alk.	2500	1250	4225
11	Acid Phos. + Mur. Pot. + Sod. Nitr.	3080	1800	3850	2825	7100
	Acid Phos. + Mur. Pot. + Sod. Nitr. + Lime	80	Alk.	2500	1375	5900
24	Acid Phos. + Mur. Pot. + Amm. Sulf.	4240	3000	4000	2700	8300
	Acid Phos. + Mur. Pot. + Amm. Sulf. + Lime	260	200	2850	1475	5700
26	Bone Meal + Mur. Pot. + Sod. Nitr.	2940	2000	3700	2250	7350
	Bone Meal + Mur. Pot. + Sod. Nitr. + Lime	360	Alk.	2900	1325	4050
29	Basic Slag + Mur. Pot. + Sod. Nitr.	2560	1200	3600	2250	6600
	Basic Slag + Mur. Pot. + Sod. Nitr. + Lime	150	Alk.	2100	1075	4050
18	Manure	2760	2600	4200	3100	8500
	Manure + Lime	120	Alk.	2950	1950	5200

The fact that no residual carbonate is present in the soil, and the poor growth of clover on the plot which received ammonium sulfate as the nitrogen carrier, is in accord with the lime requirement indicated by the Veitch and Hopkins methods, since the figures for the unlimed end of this plot are higher than those obtained for any of the other plots, by either of these methods, while the MacIntire, Hutchinson and Vacuum methods each show the highest lime requirement in the case of the manure-treated plot.

A comparison of the figures for the soils where three different carriers of phosphorus (acid phosphate, bone meal and basic slag) have been used, shows a higher lime requirement for the acid phosphate-treated soil by the Hopkins, MacIntire and Hutchinson methods. The Veitch and Vacuum methods give slightly higher results for the bone meal plot, while the Hutchinson method gives the same figure for both the bone meal and basic slag plots. With this one exception, all the methods indicate a lower requirement for the basic slag plot. The figures by those methods which show a lower requirement for the basic slag and bone plots agree with the growth of clover on the unlimed ends of these plots, since a more satisfactory stand of clover is secured on these plots than on the plot where acid phosphate is the carrier of phosphorus.

The variations shown by several of the methods indicate the possible usefulness of some of these methods for comparative purposes where different soil treatments have been made. For the soils which have been limed, but with amounts which were evidently too small, since the growth of clover on the limed halves of the plots indicates that they will be benefited by additional quantities, the MacIntire, Hutchinson and Vacuum methods have, no doubt, given a better indication of the optimum quantity of lime necessary to make conditions satisfactory for the growth of leguminous plants.

If either the Hopkins or the Veitch test were used to obtain a figure for the limed soil's requirement, the results would lead to erroneous conclusions, because the Veitch method indicates that the limed halves of all the plots are alkaline, excepting the one where ammonium sulfate has been used; and the Hopkins test has shown a very small requirement for the limed halves of the plots, the largest amount of calcium carbonate required, according to this test, being 360 lbs. per acre. The results obtained by the Hutchinson, MacIntire and Vacuum methods are much higher than those by either the Hopkins or Veitch test for the soil which has been limed.

While the figures obtained for the unlimed soil by the several methods do not exhibit the wide variation that is found for the limed soil by the Veitch and Hopkins methods as compared with the other methods, there are appreciable differences indicated. Excepting the ammonium sulfate-treated plot, the results for the unlimed soil are uniformly lower by the Veitch test. In some instances there is a very close agreement between the Hopkins and MacIntire results, although in the majority of cases the Hopkins and Hutchinson methods agree more closely. The results by the Veitch method for Plots 24 and 26, which have received different carriers of phosphorus and nitrogen, correspond to those secured by the Hutchinson method. In the case of the manure-treated soil, the results by the Veitch and Hopkins methods are practically the same.

The Vacuum method shows a much larger amount of lime required than is indicated by the other methods, and it may be that for non-calcareous soils the figures closely approximate the actual amount of calcium carbonate required. However, for many soils naturally supplied with calcium carbonate and which gave an alkaline reaction with litmus, results by this method indicate a further need of lime, the amount required in many cases being considerably in excess of the amount of calcium carbonate present. This would seem to indicate that the results obtained for lime requirement are probably too high and that the method would not be applicable to soils in general.

In Table II the differences between the results obtained for the limed and unlimed soil of the several fertilized plots is expressed in percentages of the figures for the unlimed soil. Considering to what extent the soils lime requirement has been satisfied following the lime treatment, the results obtained by the Hopkins and Veitch methods exhibit a marked uniformity, although the lime requirement for the unlimed soil by the Hopkins test is considerably in excess of the amount shown by the Veitch test. The figures show that the decrease in lime requirement as measured by either the Hopkins or Veitch test is quite uniform for all the plots.

Table II—Percentages of the Original Lime Requirement Satisfied by Lime Treatment

Soil Treatment	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
None	97	100	36	41	32
Acid phosphate	97	100	37	60	51
Muriate of Potash	94	100	25	47	..
Sodium Nitrate	96	100	29	50	31
Acid Phos. + Mur. Pot. + Sod. Nitr.	97	100	35	51	17
Acid Phos. + Mur. Pot. + Amm. Sulf.	94	93	28	45	31
Bone Meal + Mur. Pot. + Sod. Nitr.	87	100	21	41	45
Basic Slag + Mur. Pot. + Sod. Nitr.	94	100	41	52	38
Manure	95	100	29	37	39

The MacIntire and Hutchinson methods exhibit a variation between the soils variously fertilized, the figures by the MacIntire procedure for the majority of the soils showing that a smaller percentage of the lime requirement has been satisfied by the lime treatment previously given the plots.

CHANGES IN LIME REQUIREMENT DURING 16 YEARS

A comparison of the lime requirement figures for soil sampled in 1896 and again in 1912 is of interest in relation to changes which have taken place in soil during a period of 16 years. By inspection of results grouped in Table III, it will be noted that, as measured by the Hopkins method, the requirement of the unlimed soil at the earlier period is markedly lower than that obtained by the other methods, while the same soil at the latter date of sampling has a higher requirement by the Hopkins method than by the other methods, excepting the Vacuum method, and in one case the MacIntire method.

The Veitch results being lower at the latter sampling as compared with the earlier sampling are just the reverse of those by all the other methods which have indicated a decidedly increased lime requirement for the soil after a period of 16 years. Although all the methods excepting the Veitch show an increase in the lime requirement for the soil at the latter date as compared with the earlier sampling, the Hopkins method indicates a much greater increase than the other methods. In direct contrast to the lower results by the Veitch method for the soil at the later date compared with results by the same method for the first sampling, is the fact that for the soil when first sampled, the Veitch method gave higher indications than the Hopkins, MacIntire or Hutchinson methods.

Table III—Comparison of Lime Requirement of Same Soil Sampled in 1896 and 1912

Fertilizer	Sampled	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
Ammonium Sulfate	1896	750	4000	3000	1750	5500
Ammonium Sulfate	1912	4240	3000	4000	2700	8300
Ammonium Sulfate + Lime	1912	260	200	2850	1475	5700
None	1896	625	4000	2700	1575	6100
None	1912	3440	2000	3550	2925	7300
None	1912	100	Alk.	2250	1700	4900

It should be stated that the determinations on the soil collected in 1896 and that in 1912 were made by each of the methods used, at the same time, so that the differences found cannot be attributed to factors introduced by variations in the procedure employed. Many changes have taken place in the soil during 16 years. Following the deeper plowing and better cultivation the soil has received since the 1896 sampling, the physical condition of the soil and its organic content will have been affected to an extent sufficient to cause the variations observed in the lime requirement of the old and new soil by the several methods.

INFLUENCE OF VARIATIONS IN METHOD ON RESULTS

It may be pointed out that these methods for the determination of a "Lime Requirement" are empirical in nature, and comparatively slight variations in procedure affect the results obtained markedly. Thus, the Veitch method is much affected by the degree of clarity of the extract—the clearer the extract the lower the lime requirement, and a method of filtration removing every trace of suspended clay might possibly show a zero requirement in a great number of cases where the usual procedure indicates a considerable lime requirement. On the other hand, all soils do not settle to the same extent when allowed to stand over night, and a comparatively small amount of suspended clay will prevent any appearance of a pink color on boiling, although calcium hydroxide solution in quite measurable quantity is added directly to the boiling solution. For this reason, it was thought best to employ filtration.

Ten grams of soil were weighed into a porcelain dish, wet with sufficient water to give about 50 cc. of liquid after the standard lime water had been added and evaporated on the steam bath as rapidly as possible, stirring once or twice before the mass is dry. It was then washed into a 100 cc. Jena flask with 100 cc. water, shaken occasionally for 15 to 30 minutes, and allowed to stand over night. The contents of the flask were shaken and poured onto an S. & S. 18 cm. folded filter; the first 30 or 40 cc. were rejected, the next 50 cc. collected, a few drops of phenolphthalein added, and immediately boiled down to about 5 cc. in a Jena beaker. A distinct pink color was taken to indicate alkalinity, but in cases where the color was only faint, the result was recorded as doubtful and the experiment repeated.

The Hopkins method will not give the same indications if another salt is substituted for KNO_3. In this work, 100 g. air-dry soil were shaken with 250 cc. N KNO_3 for 3 hours, using a shaking machine, then filtered immediately, 125 cc. pipetted off, boiled and titrated with $N/10$ NaOH, using phenolphthalein. The factor 2.5 was used.

The method proposed by MacIntire is quite sensitive in this respect; the directions call for evaporation "to a thin paste," but higher results are obtained if the evaporation is carried to dryness. The results also vary with the time required for the evaporation, even when it is carried to the same stage (see Table IV).

Table IV—Lime Requirement by MacIntire Method. Lbs. $CaCO_3$ per 2,000,000 Lbs. Soil

G. in 100 cc.	Treatment	$CaCO_3$
10	Evaporated to thin paste immediately	7500
10	Evaporated to dryness immediately	8200
10	To thin paste immediately, to dryness next morning	8900
10	Let stand over night, to dryness next morning	8100
20	Evaporated to thin paste immediately	5750
20	Evaporated to dryness immediately	6300

It should be noted that the soil used in this experiment had a rather high requirement, and that if the requirement as determined when using 10 g. soil to 100 cc. of solution was the correct figure, 20 g. of the soil should be more than sufficient to exhaust 100 cc. of the $Ca(HCO_3)_2$ solution. As a matter of fact, only about three-fourths of the total amount of $CaCO_3$ was decomposed by the 20 g. charge. The soils under investigation showed a requirement of about one-third the total calcium carbonate in 100 cc. bicarbonate solution when 20 g. of soil were used; the evaporations were carried to dryness as rapidly as possible, and stirred several times meanwhile. The residual CO_2 was determined by the Marr method.

The Hutchinson method seems to be affected to some extent by allowing the soil and $Ca(HCO_3)_2$ solution to remain in contact for a period longer than 3 hours. Thus, a determination in which 40 g. soil was shaken with 200 cc. $Ca(HCO_3)_2$ solution for 3 hours indicated a calcium absorption of 3025 lbs. per acre; 100 g. of the same soil shaken with 500 cc. of the same bicarbonate solution for 3 hours, then allowed to stand over night, on titration showed a requirement of 3600 lbs. per acre. The soil used for this experiment was from plot treated with muriate of potash. The bicarbonate extract of the soil showed but a faint trace of chlorine, no potassium, but traces of sodium and magnesium. The calcium in the bicarbonate extract by permanganate titration was only about 0.4 cc. lower than the figure obtained by direct titration with acid, both being on the $N/10$ basis. This shows that with the Hutchinson method interchange of bases plays but a very subordinate part and the chief factor is absorption. The method will sometimes show a lime requirement in the case of a soil which contains a great excess of carbonate.

For this work, 20 g. soil to 200 cc. solution was the rule, the air in the bottle was displaced by CO_2, the bottle securely stoppered, shaken for 3 hours, immediately filtered, and 100 cc. of the filtrate titrated with $N/10$ HCl, using methyl orange; 100 cc. of the original solution was titrated in the same way.

The Vacuum method, it will be noticed, invariably shows the highest figures for the lime requirement; this is doubtless because the conditions of the method are such that the decomposition of $CaCO_3$ by the soil can proceed to a maximum without hindrance.

Ohio Agricultural Experiment Station
Wooster, Ohio

THE ACTIVITY AND AVAILABILITY OF INSOLUBLE NITROGEN IN FERTILIZERS AS SHOWN BY CHEMICAL AND VEGETATION TESTS[1]

By F. R. Pember and Burt L. Hartwell

Received July 30, 1915

Since 1908 the Agricultural Experiment Station of the Rhode Island State College has conducted vegetation tests in pots under greenhouse conditions to ascertain the availability of the water-insoluble nitrogen of certain brands of commercial fertilizers collected in the state, and in various nitrogenous substances, such as Kanona tankage, rape meal, castor pomace, etc.

Until the season of 1910, this station had employed no means, except the vegetation test, for differentiating between the organic nitrogen of one brand of commercial fertilizer and that of another. In March, 1910, the directors of the New York, New Jersey and New England Stations adopted the alkaline permanganate method[1] as a means of distinguishing between the more or less active forms of the water-insoluble organic nitrogen of mixed fertilizers.

The Rhode Island Station, having already secured results by the vegetation method showing a wide variation in the availability of the water-insoluble nitrogen of certain commercial fertilizers, submitted to Mr. C. H. Jones, for activity tests by the alkaline permanganate method, some of the same nitrogenous materials as were used in the vegetation tests and he, without knowing the vegetation results, secured a close agreement.[2]

I—EFFECT OF SEASON ON PLANT GROWTH

In carrying on vegetation tests at different seasons of the year, it was felt that the season and different soil conditions might have a very important influence upon the relative growth of a plant or different kinds of plants. With this in view two experiments were conducted: the *first* from November 11, 1910, to February 15, 1911, and the *second* from February 23, 1911, to May 30, 1911: thus 96 days elapsed between planting and harvesting. In both experiments, 6-inch galvanized iron pots were used, each containing 1 lb. of soil and 6.5 lbs. of a medium fine, fresh-water beach sand. Oat and rye plants were grown in pots having the same mixture of sand and soil, and oats alone were grown in a mixture of the same sand and a different soil: otherwise the treatment of all the pots was the same, with the exception of the nitrogenous material which was added to furnish 0.1 g. of nitrogen per pot except where the amount of blood was doubled. All of the pots received 3 g. of potassium sulfate and 8 g. of acid phosphate. The mixture of sand and soil was changed in each pot for the second experiment so that the two were identical in every way except for the season of year in which they were conducted.

It will be seen from the weights of the dry tops as given in Table I that the plants growing from February 23rd to May 30th made a greater growth in every instance than those growing from November 11th to February 15th under late fall and early winter conditions. The per cent of nitrogen in the dry tops of the first experiment was enough larger, however, than that in those of the second experiment to make the total amount of nitrogen recovered in the tops much alike in the two experiments having the same treatment.

---

[1] Contribution 217 of the Agricultural Experiment Station of the Rhode Island State College.

[1] Report on Nitrogen, C. H. Jones, Referee, Association of Official Agricultural Chemists. Proceedings of the Twenty-seventh Annual Convention, 1910.

[2] "The Availability of Insoluble Nitrogen in Certain Commercial Fertilizers," B. L. Hartwell and F. R. Pember, This Journal, **3** (1911), 584.

Plants having the double amount of blood showed a marked increase in yield and nitrogen recovered over those having half as much, while plants having their nitrogen in the form of garbage tankage, or fertilizer No. 2 were unable to recover in their tops any more nitrogen than those receiving no nitrogen in the manures.

The rye plants were unable to make as great a growth as the oats under the same condition, but the relative growth in comparison with 80, as representing the increase in yield of the plants receiving the smaller amount of blood over those to which no nitrogen was added, was much the same in all.

TABLE I—SHOWING THE RELATIVE AVAILABILITIES OF NITROGEN FOR DIFFERENT PERIODS, CROPS AND SOILS

SOURCE OF NITROGEN	OATS IN SAND AND "STATION SOIL"								OATS IN SAND AND "LARKIN SOIL"								RYE IN SAND AND "LARKIN SOIL"							
	Dry Tops Grams		N in Dry Tops Per cent		N in Dry Tops Gram		Availability		Dry Tops Grams		N in Dry Tops Per cent		N in Dry Tops Gram		Availability		Dry Tops Grams		N in Dry Tops Per cent		N in Dry Tops Gram		Availability	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
None	8.39	9.39	0.89	0.86	0.0746	0.0807	0	0	6.64	9.84	0.84	0.69	0.0557	0.0678	0	0	4.35	6.20	1.23	0.77	0.0535	0.0477	0	0
	8.16	10.92	0.88	0.76	0.0718	0.0829			6.94	9.50	0.92	0.77	0.0638	0.0731			4.50	6.57	1.26	0.81	0.0567	0.0532		
Blood	10.52	13.73	0.85	0.76	0.0894	0.1043	80	80	10.74	13.14	0.86	0.74	0.0923	0.0972	80	80	6.40	8.79	1.30	0.92	0.0832	0.0808	80	80
	8.92	13.65	1.10	0.86	0.0981	0.1173			10.39	13.87	0.95	0.74	0.0987	0.1026			6.91	8.13	1.40	0.88	0.0967	0.0715		
Blood	13.18	16.15	0.99	0.83	0.1304	0.1340	289	109	14.86	17.76	0.88	0.74	0.1307	0.1314	170	169	9.18	11.11	1.30	0.87	0.1193	0.0966	155	173
(doubled)	13.80	13.78	0.92	0.99	0.1269	0.1364			14.76	17.82	0.90	0.77	0.1328	0.1372			8.31	10.60	1.42	0.94	0.1180	0.0996		
Garbage	8.49	10.66	0.91	0.77	0.0772	0.0820			6.59	9.50	0.87	0.73	0.0573	0.0693	0	6	3.59	5.69	1.37	0.89	0.0491	0.0506	—20	—26
tankage	8.65	10.40	0.89	0.79	0.0769	0.0821	16	8	6.95	10.37	0.88	0.73	0.0611	0.0757			4.16	5.72	1.25	0.85	0.0520	0.0486		
Fertilizer	9.49	12.61	0.86	0.79	0.0816	0.0996	93	56	8.50	11.65	0.84	0.73	0.0714	0.0850	44	50	4.94	7.23	1.29	0.86	0.0637	0.0621	28	28
No. 1	10.44	12.64	0.89	0.75	0.0929	0.0948			9.26	12.47	0.82	0.70	0.0759	0.0872			5.49	7.01	1.25	0.91	0.0686	0.0637		
Fertilizer	7.62	9.26	1.08	0.79	0.0822	0.0731	—41	—7	5.97	9.70	0.94	0.79	0.0561	0.0766	—14	13	3.75	6.88	1.31	0.85	0.0491	0.0584	—17	9
No. 2	7.45	10.43	0.96	0.80	0.0715	0.0834			6.26	10.92	0.95	0.74	0.0594	0.0808			4.13	6.38	1.28	0.89	0.0528	0.0567		

II—STANDARD OF COMPARISON FOR NITROGEN AVAILABILITY TESTS

The results in Table II are from vegetation tests conducted in 8-in. Wagner pots containing about 12 lbs. of an air-dry, light, sandy loam soil, which, previous to liming in preparation for the experiment, had been deficient in available nitrogen under field conditions. The water-insoluble nitrogen used, aside from that in the blood, came from brands of commercial fertilizers sold in New England in 1910, which by the alkaline permanganate method showed a wide range in activities.

The oats grew from November 11, 1910, to March 20, 1911. The same pots were replanted June 10th with Japanese millet, which grew until August 25th.

TABLE II—POT TESTS ON SOIL DEFICIENT IN NITROGEN

SOURCE OF NITROGEN	AIR-DRY TOPS Weight in Grams Oats			AIR-DRY TOPS Weight in Grams Millet			Availability for Oats and Millet	Activity by Alkaline Permanganate Method
None	42.0	48.5	44.0	37.5	35.5	35.5	0	..
Fertilizer 517	53.5	48.0		37.5	47.5		50	70
Fertilizer A 2	56.5	54.0		42.0	43.0		65	39
Fertilizer C10	51.0	47.0		41.5	36.0		27	30
Fertilizer C14	57.0	50.0		40.0	41.0		51	34
Fertilizer G 3	49.5	54.0		44.0	41.0		52	37
Dried Blood	50.0	52.0	54.5	48.0	50.5	49.0	80	..
Dried Blood and Extra Phosphorus	53.0	53.0		44.0	46.5		..	..
Dried Blood, doubled	55.0	57.0		61.0	61.0		..	..
Nitrate of Soda	61.0	54.0		49.0	52.0		..	..

Before each planting all of the pots received optimum amounts of potassium and phosphorus in sulfate of potash, Thomas slag and acid phosphate. The accompanying nitrogen application was 0.1 g. of nitrogen per pot. The soil proved to be only slightly deficient in nitrogen with the first crop, oats, for the average weight of dry tops from the no-nitrogen pots was 44.8 g., and from those receiving blood, 52.2 g., a difference of only 7.4 g. The millet made a fair growth in all of the pots. The average weight from the no-nitrogen pots was 36.2 g. of dry tops as compared with 49.2 g. from those receiving blood, or a difference of 13 g.

Since there was very little lack of nitrogen in the soil, as shown by the oat crop, and as the millet had the benefit of any nitrogenous residues left by the oats, together with a like nitrogen application as in the first experiment, the weights of the two crops are taken together in calculating the relative availability of the water-insoluble nitrogen in the various fertilizers. This is based arbitrarily on 80 as representing the increase in growth caused by the dried blood (when nitrate of soda is used as the standard of comparison the increase caused by it is usually considered as 100).

It will be seen readily that by this method of expressing the availability of the water-insoluble nitrogen in the various nitrogenous substances, the greater the difference in growth between the plants receiving no nitrogen and those receiving dried blood, the less the effect of small differences in growth will be upon the degree of availability. When the difference is just 80 g., then a variation of 10 g. in growth would change the availability only 10 points while with a difference of only 40 g., a variation of 10 g. in yield would change the availability 20 points.

As might be expected, considering that the plants were grown in soil in which there was no marked deficiency of nitrogen, the activity values (per cent of the insoluble nitrogen which is "active" or is liberated by the alkaline permanganate method from the water-insoluble nitrogen) for the fertilizers were not in close accord with the vegetation results.

III—VEGETATION TESTS OF FERTILIZERS SOLD IN RHODE ISLAND

Vegetation experiments have been conducted during the last four winters, using one or more brands of commercial fertilizer from most of the different companies doing business in the state of Rhode Island, to test the availability of the water-insoluble nitrogen as compared with nitrogen in blood, and also to show to what extent the availability as shown by the oat crop agreed with the activity obtained by the alkaline permanganate or neutral permanganate method. Most of the fertilizers chosen for the tests were those containing at least 0.75 per cent water-insoluble nitrogen having an activity of less than 65 by the alkaline permanganate method. The fertilizers were ground fine enough to pass through a 1 mm. sieve and washed free of water-soluble nitrogen. The washing at first was by decantation but finally all of the material was placed on the filter and washed until 15 cc. of distilled water per gram of the original material had been used. After the washed material had been allowed to dry at a low temperature, it was resifted and analyzed for nitrogen. Dried blood, the same as used for the standard, was subjected to the same grinding and washings as the fertilizers; another sample of blood was also included for comparison with the first. Two pots having aluminum nitride were included in the experiment.

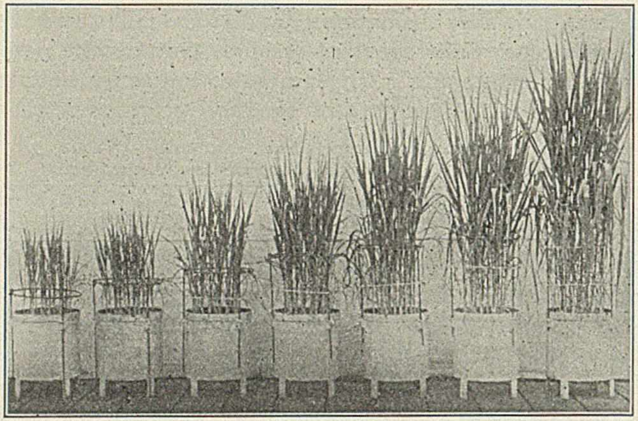


FIG. I—GROWTH OF OATS WITHOUT NITROGEN, AND WITH EQUAL AMOUNTS OF NITROGEN IN THE INSOLUBLE PART OF CERTAIN FERTILIZERS AND IN OTHER UNEXTRACTED MATERIALS

Eight-inch Wagner pots were used for these tests. The soil medium was composed of about 15 lbs. of fine, dry sand, and 3 lbs. of dry soil which under field conditions was deficient in nitrogen. Optimum amounts of potassium and phosphorus were provided in sulfate and muriate of potash, potassium magnesium carbonate, acid phosphate and Thomas slag. For the first three winters each pot received 20 g. of well-rotted, finely chopped hay. In 1911 the sand and soil were inoculated with 250 cc. of a garden soil extract and the nitrogen application was 0.3 g. per pot.

Oats were planted in all of the pots December 27, 1911, and harvested April 9, 1912, just as the best plants were ready to put out heads. Fig. I shows the general condition of the plants the week before they were harvested.

The results of the tests appear in Table III. In selecting the 1911 brands for repetition in 1912, those showing in most cases a rather marked difference between the availability as determined by the oat plant and the activity by the alkaline permanganate method, were chosen. The 1912 crop was allowed to mature and produce grain.

It will be seen by Table III that the relative availability as shown by the two vegetation tests agrees quite closely; that the addition of the extra phosphorus was not needed and that the nitrogen in the water-extracted blood was just as available as that in the unextracted. Aluminum nitride proved to be utterly worthless.

The relative amounts of nitrogen determined in the dry tops correspond very closely with the relative availability obtained from the weights of the dry tops. The amount of nitrogen in the dry tops of the 1912 oats grown with fertilizer No. 17 was found to be 0.9594 g., representing a relative availability of 63. In securing the relative availability based upon the nitrogen in the 1912 oat plants, the amounts given in Table V for the plants receiving blood and no nitrogen respectively were used.

For purposes of comparison an availability for the oat plant of less than 45 as related to one of 80 for dried blood is in the present paper considered as representing inferior water-insoluble nitrogen. Likewise an activity of less than 80 by the neutral, and less than 55 by the alkaline method is herein considered as indicating inferior material. With these bases of comparison it will be seen in Table III that 7 of the 18 fertilizers were shown by the oat plant to have inferior insoluble nitrogen, of which 4 were also detected by the alkaline method and 5 by the neutral method. The alkaline method rated fertilizer 51 as poor with an activity of 50 while the availability was only 46; and the neutral method rated fertilizer 53 as poor, with an activity of 79 while the availability was 49.

TABLE III—VEGETATION TESTS ON FERTILIZERS SOLD IN RHODE ISLAND

SOURCE OF NITROGEN	Weight of Air-Dry Oat-Tops Grams			Nitrogen in Dry Tops Gram	Relative Amount of Nitrogen Recovered	Repeats (1912) Dry Tops Grams		Availability of Nitrogen for Oats		Activity by Permanganate Methods	
								1911	1912	Alkaline	Neutral
None	6.5	7.0	6.0	0.1016	0	....		0	0	..	..
Fertilizer 85	21	21		....	..	....		66	..	69	86
Fertilizer 36	21	23		....	..	....		70	..	71	92
Fertilizer 988	15	16.5		0.2125	40	60.5	61.5	42	52	79	87
Fertilizer 34	26.5	23.5		....	..	93	88	84	97	71	93
Fertilizer 936	23	22.5		....	..	....		74	..	77	90
Fertilizer 75	19	19.5		0.2902	60	....		58	..	72	92
Fertilizer 958	16.5	17.5		....	..	....		48	..	66	83
Fertilizer 67	16	18.5		....	..	....		49	..	67	80
Fertilizer 26	15	15.5		0.2532	51	....		40	..	65	83
Fertilizer 17	17	21		....	..	70	67	57	63	59	81
Fertilizer 982	11.5	12		....	..	40	41	24	20	60	77
Fertilizer 997	8.5	8		0.1102	12	33	34.5	8	9	58	70
Fertilizer 72	13	13		....	..	....		29	..	52	80
Fertilizer 28	14	13		....	..	....		32	..	50	79
Fertilizer 51	17	15		0.2198	42	60.5	55.5	44	47	50	81
Fertilizer 77	13.5	11.5		....	..	....		27	..	49	70
Fertilizer 50	8	9.5		0.1176	14	35.5	34.5	10	11	45	55
Fertilizer 53	18	16.5		....	..	....		49	..	60	79
Aluminum Nitride	5.5	7		....	..	....		—1	..	..	..
Dried Blood	25.5	23	24	....	80	....		80	80	..	..
Dried Blood + extra Phosphorus	25	24		....	..	....		81	..	..	..
Dried Blood, water-extracted	24	25.5		....	..	....		82	..	..	..
Dried Blood, triple amount	61.5	60.5		....	..	....		246	..	..	..
Dried Blood, another sample	30.5	27.5		....	..	....		102	..	..	..
Nitrate of Soda	43.5	39.5		....	..	....		158	..	..	..

Table IV gives the activities secured by the alkaline and neutral permanganate methods,[1] and, with certain modifications of the latter by Mr. R. A. Lichtenthaeler, on the water-insoluble nitrogen in the commercial fertilizers used in the previous vegetation tests. The modifications of the neutral permanganate method consisted of changes in the reaction of the solution by the addition of Na_2CO_3, $CaCO_3$ or H_2SO_4 and in the time and temperature of digestion. All of the activities obtained by means of the different modifications were lower than those obtained by the unmodified method; in most cases they were much lower.

---

[1] J. P. Street, "Note on the Neutral Permanganate Method for the Availability of Organic Nitrogen," THIS JOURNAL, 4 (1912), 437.

Digesting for 18 hours at 25° C. with Na_2CO_3 present gave the highest activities of the various modifications but the average of the activities was 19 points lower than those secured by the unmodified method of digesting at the temperature of boiling water for half an hour, while digesting for 30 minutes at 40° C. reduced the average of the activities 26 points, and digesting for 30 minutes at 60° C. without Na_2CO_3 present reduced the average of the activities 37 points. Substituting $CaCO_3$ for Na_2CO_3 and digesting for 30 minutes at 40° C. reduced the average of the activities 32 points, or 6 points lower than where Na_2CO_3 was used under otherwise like conditions. Acidifying the solutions to $N/100$ with H_2SO_4 and digesting for 30 minutes at 40° C. gave the lowest activities of any of the modifications, while digesting for 18 hours at 25° C., otherwise under like conditions, raised the average of the activities more than 10 points.

IV—SECOND TESTS OF TANKAGES, ETC.

After the vegetation results of the water-insoluble nitrogen in certain fertilizers sold in the state in 1911 had been obtained, the manufacturers were informed of such result as concerned them individually, and in certain cases, where the availability was very low, the manufacturer sent a sample of tankage direct from his factory, claiming such sample was the basis of his 1911 goods. These, with tankages collected in the state in 1912, and also samples of castor pomace, rape meal, and Kanona tankage, were subjected to the same treatment as the commercial fertilizers. Blood from the same lot as used in 1911 for the standard was again used, and pots receiving their nitrogen in calcium nitrate and American Calcium Cyanamid were included. The nitrogen application was 0.6 g. per pot except where the extra amount of blood was used. Two of the pots to which dried blood was applied each received 7.22 g. C. P. $CaCO_3$ to ascertain whether the effect of the Calcium Cyanamid might be attributable in part to its calcium, and two others received a half more than the regular application of potassium and phosphorus. Oats were planted in all of the pots on January 20, 1913, and were allowed to mature seed.

TABLE IV—ACTIVITY DETERMINATIONS OF THE WATER-INSOLUBLE NITROGEN IN CERTAIN COMMERCIAL FERTILIZERS, BY THE NEUTRAL PERMANGANATE METHOD WITH CERTAIN MODIFICATIONS: DIGESTION WITH $KMnO_4$ SOLUTION

Fertilizer No.	Permanganate Method		With Na_2CO_3		Without Na_2CO_3	With $N/100$ H_2SO_4		With $CaCO_3$
	Alk.	Neut.	40° C. 1/2 hr.	25° C. 18 hrs.	25° C. 1/2 hr.	40° C. 1/2 hr.	25° C. 18 hrs.	40° C. 1/2 hr.
85	69	86	53	64	50	10	25	14
36	71	92	67	..	57	..	..	..
988	79	87	59	83	..	20	42	37
34	71	93	64	73	40	—2	17	14
936	77	90	57	66	44	16	29	23
75	72	92	60	57	48	19	29	23
958	66	83	47	56	41	13	20	13
67	67	80	59	68	52	23	35	27
26	65	83	52	63	44	12	22	16
17	59	81	57	60	38	14	20	14
982	60	77	47	70	36	17	23	47
997	58	70	58	54	32	27	24	21
72	52	80	43	..	40	..	..	..
28	50	79	46	49	56	21	26	22
51	50	81	64	..	55	..	..	..
77	49	70	50	61	52	26	39	30
50	45	55	40	36	16	12	..	12
53	60	79	61	..	..	..	..	..

It will be seen in Table V that the plants receiving their nitrogen in ordinary tankage, castor pomace, rape meal or some of the fertilizers were as good, if not better, than those receiving it in blood. The amount of nitrogen in the dry tops was determined in certain cases. Here again the amount of nitrogen found in each case bore about the same relation to the standard as the weight of the dry tops. Plants dependent upon Kanona tankage for their nitrogen were unable to make a very satisfactory growth, showing an availability of 39 compared with 80 for blood. The 0.6 g. of nitrogen per pot in American Calcium Cyanamid proved quite injurious to the young plants, but they were able to recover sufficiently to make a fair growth.

Accepting the same arbitrary standard as used in the preceding experiment for classifying the water-insoluble nitrogen in fertilizers, we find that of the 18 fertilizers tested by the oat plant as given in Table V, 6 were shown to have inferior insoluble nitrogen. The alkaline method detected 3 of the poor ones and condemned 2 more with availabilities of 54 and 50. The neutral method detected the 6 poor ones, and also condemned 4 more which had availabilities of 81, 74, 54 and 50, respectively.

In conducting the vegetation availability test of the water-insoluble nitrogen in some of the fertilizers collected in 1913, 5 g. of corn meal was added to each pot with the regular fertilizer application and rotted hay, except that two of the pots to which the standard amount of blood was added, received neither the corn meal nor the hay. The addition of corn meal was made after considering the results obtained in the preceding experiment, in which plants having their nitrogen in the form of rape meal or castor pomace made larger growths than with any other form of organic nitrogen used. It seemed probable that the increase in growth was due to the greater amount of carbonaceous material rather than because the nitrogen was in the form of vegetable instead of animal matter.

TABLE V—SECOND SERIES OF TESTS ON TANKAGES, ETC.

Source of Nitrogen	Weight of Air-Dry Oat Tops Grams			Nitrogen in Dry Tops Gram	Relative Amount of Nitrogen Recovered	Availability of N for Oats	Activity by Permanganate Methods	
							Alk.	Neut.
None	27.5	26	30	0.2045	0	0	..	..
Fertilizer 222	75	76.5		....	..	74	64	85
Fertilizer 155	61.5	59.5		....	..	51	64	84
Fertilizer 235	75.5	74		....	..	73	63	86
Fertilizer 177	51.5	47.5		....	..	34	63	68
Fertilizer 182	76.5	77		....	..	76	62	81
Fertilizer 157	78.5	81.5		1.1299	81	81	62	84
Fertilizer 147	89	89.5		....	..	95	61	90
Fertilizer 163	53	56.5		0.8088	45	42	61	68
Fertilizer 179	80.5	79.0		....	..	81	60	75
Fertilizer 218	36.5	32		....	..	10	60	51
Fertilizer 263	71.5	70.5		....	..	67	59	83
Fertilizer 230	69.5	65.5		....	..	62	58	83
Fertilizer 240	77.5	73.5		....	..	74	56	77
Fertilizer 211	47.5	43		....	..	27	54	77
Fertilizer 210	33	32.5		0.5115	12	8	53	59
Fertilizer 212	63	62.5		....	..	54	51	71
Fertilizer 215	59.5	61		0.8523	50	50	41	66
Fertilizer 189	29.5	30.5		....	..	3	28	67
Tankage 19	82	85.5		....	..	87	..	..
Tankage 20	78	76		....	..	76	..	..
Tankage 21	84.5	92		....	..	94	..	..
Tankage 22	85	78		....	..	83	..	..
Castor Pomace	96.5	94		....	..	105	..	..
Rape meal	88.5	93.5		....	..	98	..	..
Kanona Tankage	52	53.5		....	..	39	..	..
Dried Blood	78	81.5	78.5	0.5561(*a*)	..	80	..	..
Dried Blood + extra Lime	80	78.5		....	..	79	..	..
Dried Blood + extra Potassium + Phosphorus	83.5	75.5		....	..	81	..	..
Dried Blood (triple amount)	116.5			....	..	..	..	..
Calcium Nitrate	104	111.5		....	..	..	..	..
American Cyanamid	70.5	72.0		....	..	..	..	..

(*a*) Tops from one pot.

For some unexplained reason the oat plants having the standard application of blood together with rotted hay and corn meal made the very unsatisfactory growth of 49 grams of dry tops per pot while under like conditions, but without the rotted hay and corn meal, the weight was 67 grams per pot, which is nearly the normal weight for oat plants having that amount of nitrogen in blood when grown under like conditions for the same period, as shown by the preceding and succeeding experiments. Although the plants having extra blood made a good increase over those having the standard amount, namely 82 compared to 49 grams dry tops per pot, the growth was about half the usual amount. Plants receiving their nitrogen in nitrate of soda made a normal growth.

In Table VI are given the weights of the dried tops cut May 11, 1914, and their relative availabilities, also the activities by the alkaline permanganate method. Inasmuch as the standard blood plants having rotted hay and corn meal mixed with the soil made such a poor growth, those grown with the same amount of blood but without the rotted hay and corn meal were taken as the standard.

TABLE VI—TESTS ON 1913 FERTILIZERS, ETC.

SOURCE OF NITROGEN	Weight of Air-Dry Oat-Tops Grams		Availability of Nitrogen for Oats	Activity by Alkaline Permanganate Method
None	24	19.5	0	..
Fertilizer 310	60.5	62.5	70	68
Fertilizer 319	48	52.5	50	56
Fertilizer 426	24	26.5	6	48
Fertilizer 328	63.5	55.5	66	63
Fertilizer 329	51.5	54.5	55	48
Fertilizer 341	38	37	28	52
Fertilizer 350	38	31.5	23	53
Fertilizer 355	48.5	50	48	59
Fertilizer 356	46	50	46	59
Fertilizer 367	63.5	58.5	69	61
Fertilizer 371	58.5	61	67	75
Fertilizer 373	50	48.5	48	57
Fertilizer 382	42.4	43.5	37	66
Fertilizer 391	41.5	43.5	36	54
Fertilizer 397	47	44	42	66
1146 Mass.	53.5	46.5	50	54
Dried Blood	49	49	48	..
Dried Blood + extra Potash and Phosphorus	52.5	52.5	54	..
Dried Blood without corn meal or hay	67	67.5	80	..
Dried Blood (triple amount)	85	78.5	106	..
Nitrate of Soda	91.5	98.5	129	..

On the bases stated previously, the oat plant condemned 6 of the 16 fertilizers tested as having inferior water-insoluble nitrogen. The alkaline method rated 4 of the 6 as poor, and condemned 2 more with activities of 48 and 54 which had availabilities of 55 and 50. It is interesting to note that the latter had an availability of 49 when tested at the Massachusetts Agricultural Experiment Station.

V—TESTS OF 1914 FERTILIZERS, ETC.

In conducting the vegetation test for the availability of the water-insoluble nitrogen in certain of the fertilizers collected in 1914, the use of rotted hay and corn meal was dispensed with, except where used in certain pots to determine their toxic effect, if any. Four of the fertilizers tested in 1913, Nos. 310, 328, 356 and 426, were included, in order to ascertain to what extent the growth of the oat plants was influenced in the last experiment by the addition of rotted hay and corn meal. Dr. R. N. Brackett, Clemson College, S. C., A. O. A. C. referee on nitrogen, kindly furnished us with samples of tartar pomace, Nos. 5 and 6 nitrogenous manures and beet root manure, from the same materials as furnished the different stations in 1914 for nitrogen determinations and activities by the alkaline and neutral permanganate methods. All of these materials were given the same laboratory treatment as the fertilizers. Two pots were included having oxamide, $C_2O_2N_2H_4$, prepared by Dr. John E. Bucher, Brown University; likewise two with soot for use in plant growing, an English importation.

The fertilizing materials with $CaCO_3$ at the rate of two tons per acre were added to the soil medium December 31, 1913, and the oats planted January 13, 1914. The weights of the dry oat tops and relative availabilities are given in Table VII, also the activities by the alkaline and neutral permanganate methods. The activities for the material received from Dr. Brackett were obtained by averaging those reported from the different stations. Fig. II shows the growth of oats without nitrogen and with an equal amount of nitrogen in blood and in the water-insoluble part of the A. O. A. C. material.

It will be seen by the weights of the dry tops that the addition of the extra potassium and phosphorus to the standard blood pots did not change the growth of the plants, while the addition of rotted hay increased the growth of the dry tops about 10 g. per pot, and rotted hay and corn meal nearly as much. Where a triple amount of the corn meal (15 g.) was used without any rotted hay, the growth was depressed about 10 g. per pot. Furthermore, by comparing the weights of the dry tops for fertilizers Nos. 310, 328, 356 and 426 in Table VII with those in Table VI it appears that with only one exception, fertilizer No. 328, the combined weights of the dry tops for the two pots were a little larger in the first trial. It is interesting to note that oxamide, which is insoluble in water, ranks between blood and nitrate of soda as a source of nitrogen for the oat plant.

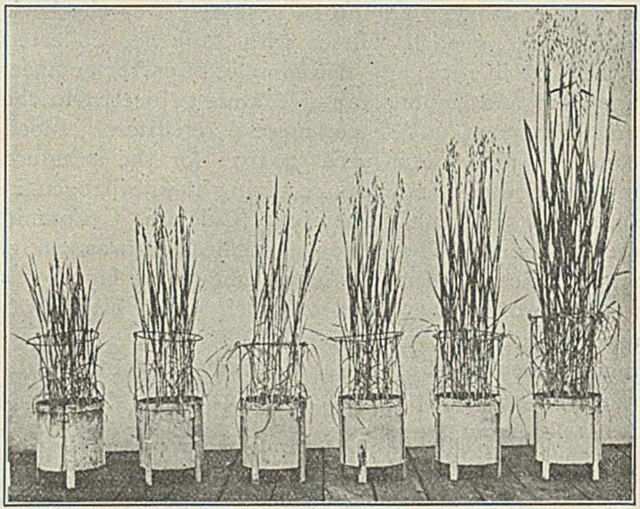


FIG. II—GROWTH OF OATS WITHOUT NITROGEN AND WITH AN EQUAL AMOUNT OF NITROGEN IN BLOOL AND IN THE INSOLUBLE PART OF OTHER MATERIALS

On the bases previously stated, it will be seen in Table VII that of the 20 fertilizers tested by the oat plant, 11 were found to contain inferior insoluble nitrogen. Of these the alkaline method detected 6 and failed on 2 more by only two points or less either way.

The neutral method detected 8 of the 11 poor ones and rated 1 good one as poor. The oat plant showed the nitrogen in the material from Dr. Brackett to be of very inferior quality: the alkaline method rated 3 as having inferior nitrogen, while the neutral method condemned but 1.

TABLE VII—TESTS OF 1914 FERTILIZERS, ETC.

SOURCE OF NITROGEN	Weight of Air-Dry Oat-Tops Grams		Availability of N	Activity by Permanganate Methods	
				Alk.	Neut.
None	12.5	10	0	..	..
Fertilizer 506	41	48	43	56	76
Fertilizer 512	35	32	29	70	87
Fertilizer 513	20	21	12	50	73
Fertilizer 525	47	51.5	49	63	89
Fertilizer 536	60	59.5	63	55	86
Fertilizer 547	73.5	69	77	70	86
Fertilizer 548	20.5	17	10	44	74
Fertilizer 575	37.5	42.5	37	55	89
Fertilizer 584	43	47	44	55	88
Fertilizer 591	63	59	64	58	88
Fertilizer 592	41.5	44	41	50	74
Fertilizer 598	19	20.5	11	40	74
Fertilizer 605	57.5	54	51	65	88
Fertilizer 606	32	34	28	50	65
Fertilizer 310	57.5	59.5	61	68	89
Fertilizer 426	23.5	22.5	15	48	77
Fertilizer 328	63	64.5	68	63	64
Fertilizer 356	42.0	48.5	44	59	78
Tartar Pomace	11.5	13	1	35	60
No. 5 Nitrogenous Manure	28	35	26	57	86
No. 6 Nitrogenous Manure	16	16	6	49	80
Beet Root Manure	11.5	10.5	0	23	85
Soot	57	52	56	..	..
Oxamide, $C_2O_2N_2H_4$	91.5	91.5	104	..	..
Dried Blood	70	76.5	80	..	..
Dried Blood + extra Potassium and Phosphorus	72	74	80	..	..
Dried Blood + Rotted Hay	83	84	93	..	..
Dried Blood + Rotted Hay + 5 g. Corn Meal	81.5	82	91	..	..
Dried Blood + 15 g. Corn Meal	63	65.5	68	..	..
Dried Blood (triple amount)	161	158	191	..	..
Nitrate of Soda	100	105	118	..	..

SUMMARY

1—Rye and oat plants grown during late fall and early winter conditions did not make as large a growth as those grown after midwinter for the same period under otherwise the same conditions, but the amount of nitrogen removed in the tops of the plants was much the same in both experiments.

2—Although the rye plants did not make as large a growth as the oat plants, the relative growth was much the same with those having like treatment.

3—Plants having their nitrogen added in the form of garbage tankage or aluminum nitride made no larger growth than those to which no nitrogen was added.

4—Nitrogen in water-extracted blood proved just as available to the oat plant as that in the unwashed blood.

5—Plants securing their water-insoluble nitrogen in animal tankage made fully as large a growth as those receiving it in blood.

6—The water-insoluble nitrogen in castor pomace and rape meal proved excellent sources of nitrogen for the growth of oat plants while Kanona tankage proved to be quite an inferior source of nitrogen.

7—An application of 0.6 g. nitrogen in Cyanamid (165 lbs. of nitrogen per acre) proved toxic to the young plants but they were able to overcome the toxicity and make a fair growth.

8—All the water-insoluble nitrogen in the material received from Dr. Brackett, A. O. A. C. referee on nitrogen, proved to be of inferior value when subjected to the plant test.

9—The nitrogen in soot had an availability of 56 compared with that in blood at 80.

10—Nitrogen in oxamide produced plant growth about equal to the average produced by that in blood and in nitrate of soda.

11—Lower activities, secured by modifications of the neutral permanganate method, in general agree no better with the availabilities than those secured by the unmodified method.

12—Of the 56 fertilizers tested, not only by the oat plant but also by the alkaline and neutral permanganate methods, 24 were found to contain water-insoluble nitrogen having an availability of less than 45 as compared with blood nitrogen at 80; of these, 13 were actually classed as inferior by having an activity of less than 55 by the alkaline permanganate method, and 3 more were practically so classed, their activities being only one to two points higher: 2 having availabilities of only 54 and 50 were condemned by activities of 51 and 41. None was condemned by the alkaline method which proved to have a high availability.

13—The neutral method, on the basis of activities of less than 80, detected 19 of the 24 inferior ones and three more having availabilities of only 54, 50 and 49, but unfortunately condemned three with the satisfactory availabilities of 81, 74 and 68.

14—Concerning the A. O. A. C. inferior nitrogenous material, distributed for coöperative work in 1914, the inferiority of 3 of the 4 samples was detected by the alkaline method, whereas only 1 of them was detected by the neutral method.

15—It will be seen that about the same percentage of the inferior samples was detected by the two methods, but that the neutral method condemned some samples which proved to have satisfactory availabilities according to the vegetation tests.

16—The percentage of the insoluble nitrogen attacked by the potassium permanganate solution agrees much closer with the relative availability by vegetation test, in case of the alkaline than of the neutral method.

AGRICULTURAL EXPERIMENT STATION
RHODE ISLAND STATE COLLEGE
KINGSTON, R. I.

A PROPOSED NEW METHOD FOR CITRATE-INSOLUBLE PHOSPHORIC ACID

By CHAS. H. HUNT

Received September 24, 1915

There is, perhaps, no other point in the chemistry of fertilizers which has called forth so much discussion and difference of opinion as the method for the determination of citrate-soluble or reverted phosphoric acid by means of neutral ammonium citrate. The present arbitrary method for this determination is unsatisfactory and also unscientific, since the same substance frequently gives different results in the hands of different analysts. If a method could be found that would measure the amount of citrate-insoluble P_2O_5 and, indirectly, the amount of citrate-soluble P_2O_5, in which there are not so many factors that influence the results, it would be of great aid to the fertilizer chemist. It is believed that the method proposed below will, in a way, help solve the problem.

It has been known for some time that lime,[1] limestone and other forms of calcium[2] added as a filler or as an essential ingredient in fertilizers, decreases the available P_2O_5, or, in other words, increases the citrate-insoluble P_2O_5, and also, that the rate of increase in the amount of citrate-insoluble P_2O_5 is proportional to the amount of added calcium. This fact has been further confirmed in this laboratory. It is believed that the explanation for this is that the calcium, in whatever form it may be, reacts with the mono- and dicalcium phosphate, in the ammonium citrate medium, and changes them into the tricalcium phosphate, a form which is supposed to be insoluble in neutral ammonium citrate, according to the following equations:

$$CaH_4(PO_4)_2 + 2CaO = Ca_3(PO_4)_2 + 2H_2O$$

$$Ca_2H_2(PO_4)_2 + CaO = Ca_3(PO_4)_2 + H_2O$$

Whether a similar reaction takes place in those fertilizers containing no added lime or other forms of calcium the writer is not able to say just now, but it has been noticed that there is a fairly constant ratio between the amount of calcium oxide, determined as such, both in those fertilizers that do and those that do not contain added calcium compounds, and the citrate-insoluble P_2O_5, as is shown in Table I. The proposed method is based upon some of these facts.

TABLE I

FERTILIZER	Per cent citrate-insoluble P_2O_5	Per cent calcium oxide	Ratio citrate-insoluble P_2O_5 to calcium oxide
Tankage	8.55	20.00	1 : 2.34
Tankage	4.85	11.72	1 : 2.41
Tankage	4.83	11.50	1 : 2.38
Bone meal	16.65	31.80	1 : 1.91
Fish fertilizer	1.80	4.06	1 : 2.25
Complete(*a*)	10.80	27.34	1 : 2.53
Complete(*a*)	6.25	13.78	1 : 2.20
Complete(*a*)	8.45	19.35	1 : 2.29

(*a*) Contains added calcium compounds.

METHOD

The fertilizer is digested as in the Official method[3] for total phosphoric acid and made up to a definite volume. An aliquot is then taken and an excess of ammonia is added whereupon a white precipitate of tricalcium phosphate is formed.[4] It is then filtered and washed thoroughly with water. The precipitate is dissolved on the filter paper with nitric acid and the phosphoric acid determined in the filtrate according to the volumetric optional method.[5]

From this investigation it has been found that the phosphoric acid is in excess of the calcium that is necessary to combine with it to form tricalcium phosphate, or that all of the phosphoric acid is not precipitated with ammonia. Now the amount of tricalcium phosphate precipitated with ammonia depends upon the amount of calcium present in the fertilizer. Also the amount of citrate-insoluble P_2O_5 depends upon the amount of calcium as has already been pointed out. Now if the amount of calcium governs these two factors then there must be some definite ratio between the factors themselves. This ratio is shown in Table II.

TABLE II

FERTILIZER	Per cent P_2O_5 precipitated with ammonia	Per cent(*a*) citrate-insoluble P_2O_5	Ratio of citrate-insoluble P_2O_5 to P_2O_5 precipitated with ammonia
Meat and bone	22.45	17.39	1 : 1.29
Concentrated fertilizer	19.75	10.80	1 : 1.82
Vegetable	19.00	13.02	1 : 1.46
Meat and bone	15.35	9.10	1 : 1.68
Rose lawn	20.90	12.60	1 : 1.68
Lawn fertilizer	14.15	9.43	1 : 1.67
Concentrated	13.60	9.06	1 : 1.52
Bone meal	22.35	16.03	1 : 1.39
Bone meal	19.70	14.07	1 : 1.40
Blood and bone	14.90	10.04	1 : 1.48
Fish fertilizer	8.85	6.47	1 : 1.37

(*a*) Determined by Official method.

It is seen that the ratio between the citrate-insoluble P_2O_5 and that precipitated with ammonia is about 1 : 1.50. Hence, by dividing the amount precipitated with ammonia by 1.50 we obtain a figure which is approximately equal to the citrate-insoluble P_2O_5 as obtained by the Official method. This ratio varies in some cases. The proposed method does not seem applicable to superphosphates, perhaps due to the fact that a large part of the calcium has been removed as water-soluble P_2O_5. Also, since the amount of citrate-insoluble P_2O_5 in a fertilizer depends upon the amount of material digested,[1] we can readily account for the low results in the case of those fertilizers containing a large amount of water-soluble P_2O_5, because the amount of material treated has been con-

TABLE III

No.	Fertilizer	Per cent N	Per cent total P_2O_5	Per cent water-soluble P_2O_5	Per cent citrate-insoluble P_2O_5	Per cent P_2O_5 New method	Diff.
1413	Bone meal	2.98	23.63	..	17.39	14.96	—2.43
1595	Bone meal	3.02	26.20	..	18.07	15.36	—2.71
1518	Bone meal	0.94	33.75	..	27.40	21.53	—5.87
1540	Bone meal	3.73	23.29	..	15.50	12.70	—2.80
1530	Bone meal	4.08	24.60	..	16.03	14.90	—1.13
1281	Bone meal	3.94	19.80	..	14.07	13.13	—0.94
1314	Bone meal	3.98	23.85	..	16.65	12.27	—4.38
1619	Bone meal	4.06	20.10	..	11.40	13.26	+1.86
1716	Bone meal	3.66	26.20	..	18.55	17.06	—1.49
1730	Bone meal	4.07	20.20	..	15.15	13.00	—2.15
1774	Bone meal	2.63	25.85	..	15.25	17.00	+1.75
1791	Bone meal	4.31	24.22	..	16.60	15.70	—0.90
1669	Bone meal	3.85	21.98	..	13.55	14.40	+0.85
1687	Bone meal	4.08	22.69	..	16.57	14.80	—1.77
1511	Tankage	4.37	16.10	..	8.55	10.63	+2.08
1545	Tankage	7.23	10.20	..	4.85	6.63	+1.78
1515	Tankage	7.07	11.27	..	4.83	5.63	+0.80
1668	Tankage	7.05	5.19	..	1.90	2.24	+0.34
1672	Tankage	5.58	16.48	..	5.29	8.13	+2.84
1673	Tankage	5.27	13.86	..	9.20	9.10	—0.10
1676	Tankage	7.13	7.20	..	2.70	4.26	+1.56
1688	Tankage	8.47	3.23	..	0.79	0.53	—0.26
1731	Tankage	4.72	14.20	..	8.30	9.56	+1.26
1767	Tankage	7.93	15.13	..	7.80	9.66	+1.86
1788	Tankage	3.38	19.70	..	12.35	13.17	+0.82
1267	Bone and blood	4.05	14.98	..	10.04	9.93	—0.11
1596	Meat and bone	6.48	15.90	..	9.10	10.23	+1.13
1728	Meat and bone	2.64	24.80	..	16.90	16.13	—0.77
1737	Meat and bone	7.18	12.65	..	8.25	8.46	+0.21
1475	Fish guano	13.60	4.50	..	1.80	1.40	—0.40
1278	Fish guano	7.11	8.97	..	6.47	5.90	—0.57
1772	Fish guano	9.34	6.15	..	2.23	3.60	+1.37
1670	Sheep guano	3.77	1.93	..	0.62	0.82	+0.20
1671	Sheep guano	4.48	3.83	..	1.37	1.38	+0.01
1522	Complete fertilizer	2.95	15.30	0.18	11.35	9.70	—1.65
1523	Complete fertilizer	2.70	20.03	2.95	10.80	13.16	+2.36
1516	Complete fertilizer	2.44	19.08	0.08	13.02	12.66	—0.36
1581	Complete fertilizer	3.90	11.85	3.10	6.25	7.76	+1.51
1576	Complete fertilizer	5.61	21.65	..	12.60	13.93	+1.33
1564	Complete fertilizer	3.02	13.60	2.45	8.50	8.85	+0.35
1541	Complete fertilizer	4.45	14.35	0.71	8.45	9.43	+0.98
1542	Complete fertilizer	3.99	14.10	1.40	8.95	9.06	+0.11
1616	Complete fertilizer	3.19	10.60	2.26	6.30	6.13	—0.17
1618	Complete fertilizer	1.98	12.40	3.45	6.25	7.60	+1.35
1622	Complete fertilizer	2.05	14.35	5.25	6.60	8.93	+2.23
1625	Complete fertilizer	3.08	16.40	4.65	8.15	10.50	+2.35
1679	Complete fertilizer	4.60	11.75	0.96	6.30	7.17	+0.87
1712	Complete fertilizer	7.17	10.70	..	6.20	6.70	+0.50
1727	Complete fertilizer	3.32	16.10	..	12.05	10.40	—1.65
1781	Complete fertilizer	3.48	8.25	2.58	4.05	5.17	+1.12

---

[1] Wash. Agric. Exp. Station, *Bull.* **116**.

[2] THIS JOURNAL, **6** (1914), 20; also **5** (1913), 933.

[3] U. S. Dept. Agric., *Bull.* **107**, Rev. Ed., p. 2.

[4] Perkin, "Qualitative Chemical Analyses," p. 86, foot-note. If iron is present it will be precipitated here.

[5] U. S. Dept. Agric., *Bull.* **107**, Rev. Ed., p. 4.

[1] Wiley, "Principles and Practice of Agricultural Anal.," Vol. II, p. 136.

siderably decreased from the amount supposed to be used in making the determination. If the amount of citrate-insoluble P_2O_5 depends upon the weight of material digested, is it not illogical to determine the amount of citrate-insoluble P_2O_5 on a 2 gram sample in the case of bone meal or tankage and make the same determination on the residue of a 2 gram sample, after the water-soluble P_2O_5 has been removed, which, in many cases is much less than 2 grams, in the analysis of a mixed fertilizer containing superphosphate? Results obtained, on the same sample, by the Official method and the proposed new method are given in Table III. While these results vary somewhat, there is yet a degree of uniformity in the variations. Those obtained by precipitation with ammonia are usually lower than those by the Official method in the case of bone meal and generally higher in the case of tankage and complete fertilizers. The plus and minus errors for all classes of fertilizers reported are nearly equal to each other, which fact seems to suggest a possibility of using a different factor for different types of fertilizers. Again, it is noticeable that the differences between those obtained by the Official and proposed methods are, in most cases, no greater than the variations in those obtained by different analysts working upon the same sample, when the Official method is used.

SUMMARY AND CONCLUSIONS

I—Lime, limestone and other calcium compounds, added as a filler or as an essential ingredient increases the citrate-insoluble P_2O_5.

II—The ratio between the calcium oxide, determined as such, and the citrate-insoluble P_2O_5 is fairly constant both in those that do and those that do not contain added calcium compounds.

III—In the proposed method the fertilizer is digested as for total P_2O_5. An aliquot is made alkaline with ammonia and the P_2O_5 is determined in the precipitate thus formed.

IV—The ratio between the citrate-insoluble P_2O_5 and the P_2O_5 precipitated with ammonia is about 1 : 1.50.

V—By dividing the amount of P_2O_5 precipitated with ammonia by 1.50 we obtain a figure which is approximately equal to the citrate-insoluble P_2O_5 determined by the Official method.

VI—The plus and minus errors in the final results nearly balance each other. The fact that the errors for bone meal are nearly the same and that for tankage and complete fertilizers are also nearly the same but of opposite quantity, seems to suggest a possibility of using a different factor for different types of fertilizers.

VII—The difference between the results obtained by the Official and proposed methods are no greater than the differences in the results obtained by different analysts working on the same sample when the Official method is used.

VIII—The proposed method claims to be much shorter and less expensive, doing away with the use and preparation of neutral ammonium citrate.

State College Food and Fertilizer Laboratory,
Pullman, Washington

LABORATORY NOTES ON THE STANDARDIZATION OF THE MERCURIALS

By Donald K. Strickland

Received September 7, 1915

Six methods for the estimation of mercury were submitted for study,[1] by the committee on quantitative methods of the division of pharmaceutical chemistry of the American Chemical Society. These included: (1) the Hempel volumetric method for mercurous chloride, bromide and iodide, involving the use of iodine and sodium thiosulfate solutions; (2) a modification of the method of Rupp, in which the metallic precipitate is redissolved in nitric acid and reprecipitate as mercuric iodate, which at length is determined volumetrically by the use of sodium thiosulfate; (3) an electrolytic method;[2] (4) the well-known Rupp[3] formaldehyde method for mercuric salts; (5) a method in which mercuric arsenate is weighed; and (6) a gravimetric estimation as mercurous chloride. These methods were studied with the object of devising methods which might be used as pharmacopoeial methods, where a standard of purity for mercury salts has been required, without offering an official method of examination.

The methods in use to-day for establishing the standard of purity of these chemicals are no doubt quite uniform and the best methods have long since been established in practice. These were pointed out by C. E. Smith.[4] The Hempel method serves best for the analysis of calomel and mercurous iodide, while mercuric chloride, iodide, and ammoniated mercury are analyzed by the method of Rupp. For oxide of mercury the method most serviceable is that of R. Cohn[5] simplified by Rupp and Kraus,[6] which is found in the German Pharmacopoeia.

Recently the effort has been made, not only to determine the purity of these salts as they enter into the manufacturing processes, but also to standardize the finished products, especially in tablets and pills. L. F. Kebler[7] reported the results obtained upon analysis of 30 samples of calomel and of calomel and sodium bicarbonate tablets, 12 of which (or 40 per cent) varied more than 10 per cent from the claim on the label as to the calomel content. In this they were slightly more inaccurate than the average of the samples of tablets on the American market at that time. It was found in this investigation that 36.7 per cent of all the tablets varied more than 10 per cent from the standard claimed. At the same time, 5 tablets of corrosive sublimate, out of 17 examined, were found to vary 10 per cent or more from the declaration on the label. Two antiseptic mercuric chloride tablets were examined, both of which were inaccurate by more than 10 per cent. In this important contribution to pharmaceutical chemistry there are recommended for the estimation of calomel

---

[1] *Am. Jour. Pharm.*, **83** (1911), 186.
[2] Smith, "Electro-Analysis," 90–94.
[3] *Ber.*, **39** (1906), 3702.
[4] *Am. Jour. Pharm.*, **83** (1911), 311.
[5] *Ber.*, **34** (1901), 3502.
[6] *Ibid.*, **35** (1902), 2015.
[7] *J. Am. Pharm. Assoc.*, **3** (1914), 1069.

three methods: (1) the Hempel, (2) a gravimetric, and (3) a volumetric method, in which the calomel is decomposed with normal sodium hydroxide and the chloride ion is titrated with silver nitrate by the Volhard method. For the corrosive sublimate tablets there was utilized: (1) the Rupp formaldehyde method, (2) precipitation of mercuric sulfide and (3) a method[1] involving the conversion of mercuric chloride into the undissociated mercuric cyanide and the titration of the hydrochloric acid.

J. W. Marden[2] has pointed out the many difficulties arising in the assay of calomel tablets in control work. In part at least, these difficulties are due to the fact that gum acacia, confection of rose, etc., are used in the process of manufacture. A. W. Bender[3] notes similar difficulties in the assay of mercuric iodide tablets. The general result of these difficulties in the assay of mercurial preparations, so far as tablets and pills are concerned, has given rise to numerous proposed methods for their assay, many of which are based upon the fundamental idea of removing by oxidation[4] the sugar which interferes.

R. M. Chapin[5] in a paper on the assay of mercuric chloride tablets points out the difficulties involved in using the Rupp method in the presence of ammonium chloride and gives a modification of the Rupp method to apply to tablets of the Wilson formula.

In the work of standardizing mercurial preparations a very considerable experience has demonstrated that a perfect calomel tablet is prepared by using lactose as the diluent, a 10 per cent solution of cane sugar in distilled water as granulating material and avoiding all use of gums, confections, etc., so that the finished tablet contains only 0.9 per cent lubricant and 1.5 per cent chalk besides the granulation. Tablets made by this method were assayed for some time by the simple method of Hempel, just as if they consisted of mercurous chloride alone. The recent literature above quoted, which shows discrepancies in results obtained in assaying tablets by the Hempel method, has caused me to analyze in the routine work the same samples of calomel products by three methods, given in detail in the experimental part. Since the first method must be correct, the comparison with the other quicker and more commonly used methods is interesting in indicating the error caused by the presence of lactose. The writer is strongly inclined to the view that a tablet which must be boiled with aqua regia to dissolve the calomel, does not represent a suitable product. The results given in Table III show that, for tablets made as stated above, the Hempel method is accurate, and that the method involving the titration of the chloride ion had a tendency to low results.

We have never had cause to doubt the accuracy of the Hempel method when used on mercury protiodide tablets and pills.

For the determination of mercuric chloride, the hydrogen sulfide method is used for the tablet of Wilson's formula thus avoiding the difficulty presented by possible secondary reactions between ammonium chloride and formaldehyde. The Rupp method is used for all other mercuric chloride tablets. The tablet made according to the Wilson formula is a compressed tablet and by assaying the granulation before compression a closer approach to the desired strength is possible than in the moulded tablet made according to the Bernay formula. In fact this large moulded tablet of brittle nature is very difficult to bring to the same degree of accuracy as is possible for most other tablets: here accuracy is sacrificed for the sake of speedy solubility.

I took occasion before utilizing the Rupp method for standardizing mercuric iodide products to see if the presence of lactose even to the extent of 25 times the weight of the mercuric iodide present caused any interference with the method, but noted none. Provided the alkalinity of the solution is sufficient and the length of time given to the reduction is ample, the estimation proves to be exquisitely accurate.

There is appended, in the experimental part, the methods used with expediency for the various mercury ointments. Our attention was directed to these by the paper of Smith.[1]

EXPERIMENTAL

The methods used for obtaining the results upon calomel tabulated are as follows:

I—DETERMINATION OF CALOMEL IN SIMPLE GRANULATIONS, TABLETS AND PILLS

(*A*)—A quantity of material containing 0.324 g. (5 grains) calomel is treated with warm water during a period of about 30 minutes. Filter the undissolved calomel upon a weighed, previously ignited Gooch crucible, wash with water, finally with alcohol, and dry at 100° C., cool in desiccator, and weigh. Heat the Gooch crucible in a Bunsen flame sufficiently to volatilize completely the calomel. The difference in weight represents calomel. In the case of calomel and sodium bicarbonate tablets, the sodium bicarbonate may be estimated volumetrically in the filtrate.

(*B*)—A quantity of the granulation or a number of the finished tablets or pills containing 0.324 g. (5 grains)[2] of calomel is placed in a glass stoppered Erlenmeyer flask. Add 1 gram of potassium iodide and 5 to 10 cc. water. Rotate the flask a few times and add 30 cc. of $N/10$ iodine solution. Stopper the flask and shake until the mercury has dissolved. Remove the stopper, rinsing it so that the washings flow into the flask and titrate the excess of iodine with $N/10$ sodium thiosulfate solution, using starch solution as an indicator, until the blue color disappears, and lastly with $N/10$ iodine solution until the blue color returns. 1 cc. $N/10$ iodine = 0.02361 g. calomel.

(*C*)[3]—The material in amount sufficient to contain 0.324 g. of calomel is first disintegrated with 30 cc.

---

[1] *Apoth. Ztg.*, **24** (1909), 939.

[2] *Am. Jour. Pharm.*, **86** (1914), 511.

[3] THIS JOURNAL, **7** (1914), 753.

[4] A. W. Bender, *Loc. cit.*, and R. I. Grantham, *J. Am. Pharm. Assoc.*, **4** (1915), 442.

[5] *Am. Jour. Pharm.*, **86** (1914), 1.

[1] *Loc. cit.*

[2] In the case of tablets, etc., containing large quantities such as 1 grain, 20 tablets were weighed and powdered and an aliquot weight equivalent to 5 grains of calomel was taken.

[3] J. W. Marden and O. E. Cushman, *Loc. cit.*

TABLE I—ASSAY OF GRANULATIONS OF CALOMEL AND MILK SUGAR BY THE HEMPEL METHOD

(These data are given as indicating the nature of the results. The method was used on 37 products. The average error of the calomel in granulation is 2.23 per cent, while in the finished tablet the average error is 2.3 per cent.)

Lot No.	Weight Taken Grams	Calomel per Prospective Tablet Found	Calomel per Tablet Required	ERROR Per cent Calomel	Calomel in Finished Tablet	ERROR Per cent Calomel
20134	5.0	0.006433	0.00648	—0.7	....	...
20229	5.0	0.0063	0.00648	—2.8	....	...
20271	5.0	0.00632	0.00648	—2.5	....	...
20329	5.0	0.006499	0.00648	+0.3	....	...
20480	5.0	0.006455	0.00648	—0.4	0.006575	+1.5
20556	5.0	0.00632	0.00648	—2.5	0.006272	—3.2
20884	5.0	0.00649	0.00648	+0.15	0.00662	+2.2
20889	5.0	0.00628	0.00648	—3.1	0.006358	—1.9
21248	6.5	0.00633	0.00648	—2.3	....	...
20005	2.5	0.01584	0.0162	—2.2	....	...
20535	1.5	0.0156	0.0162	—3.7	0.0156	—3.7
20600	2.0	0.01584	0.0162	—2.2	0.01568	—3.2
20833	2.0	0.0161	0.0162	—0.6	0.0161	—0.6
21510	2.0	0.0156	0.0162	—3.7	0.01588	—2.0
20583	6.0	0.003213	0.00324	—0.8	0.00312	—3.7
20415	4.0	0.00783	0.0081	—3.3	0.008133	+0.4
20799	0.5	0.03178	0.0324	—1.9	....	...
20816	1.0	0.0312	0.0324	—3.7	0.0311	—4.0
20062	0.8	0.0633	0.0648	—2.3	0.06351	—2.0
20254	0.7	0.06163	0.0648	—4.9	0.06374	—1.6
20774	0.5	0.06214	0.0648	—4.1	....	...
20926	0.5	0.1283	0.1296	—1.0	....	...

TABLE II—ASSAY OF CALOMEL PILLS BY HEMPEL METHOD

Lot No.	No. of Pills Used	CALOMEL PER PILL Found	CALOMEL PER PILL Required	ERROR Per cent Calomel
24736	20	0.01612	0.0162	—0.5
24812	5	0.06559	0.0648	+1.2
25842	50	0.00647	0.00648	—0.1
24828	50	0.006445	0.00648	—0.5
24460	10	0.03152	0.0324	—2.7
AVERAGE ERROR OF CALOMEL IN PILLS...........				1.0

TABLE III—COMPARISON OF RESULTS OBTAINED UPON ASSAYING CALOMEL PREPARATIONS BY GRAVIMETRIC, HEMPEL AND CHLORIDE TITRATION METHODS

Lot No.	METHOD (See text)	CALOMEL PER TABLET Found	CALOMEL PER TABLET Required	ERROR Per cent Calomel	Calomel in Tablet	FINAL ERROR Per cent Calomel
21845	A	0.0631	0.0648	—2.6	...	..
	B	0.06186	0.0648	—4.5	0.06384	— 1.4
	C	0.06044	0.0648	—6.7	...	..
21849	A	0.00642	0.00648	—1.0	Not det.	..
	B	0.00640	0.00648	—1.2	Not det.	..
	C	....	0.00648	...	Not det.	..
21854	A	0.00654	0.00648	+0.9	Not det.	..
	B	0.006516	0.00648	+0.5	Not det.	..
	C	0.006044	0.00648	—6.7	Not det.	..
21749	A	0.03153	0.0324	—2.7	...	..
	B	0.03168	0.0324	—2.2	0.03197	— 1.3
	C	0.03017	0.0324	—6.8	...	..
21835	A	0.1859	0.1944	—4.3	...	..
	B	0.1866	0.1944	—4.0	0.1816	— 6.6
	C	0.1821	0.1944	—6.3	...	..
21601	A	....	0.1620	...	0.1561	— 3.6
	B	....	0.1620	...	0.157	— 3.1
	C	....	0.1620	...	0.1428	—11.8
21580	A	....	0.0162	...	0.01624	+ 0.2
	B	....	0.0162	...	0.01662	+ 2.6
	C	....	0.0162	...	0.01639	+ 1.2

water and made slightly acid to litmus with dilute nitric acid; sodium peroxide is added a little at a time, with stirring, until the metallic mercury separates out: about 1 gram of sodium peroxide is added in excess. After warming for a very few minutes, the precipitated mercury is filtered onto a Gooch crucible and washed with water. The filtrate is rendered acid with nitric acid, $N/10$ silver nitrate is added in excess, and the excess of silver nitrate is titrated with $N/10$ ammonium sulfocyanate, using ferric alum as an indicator. 1 cc. $N/10$ $AgNO_3$ solution = 0.02361 g. calomel.

II—ASSAY OF CALOMEL AND SODIUM BICARBONATE TABLETS AND GRANULATIONS

(1) DETERMINATION OF SODIUM BICARBONATE—A quantity of the granulation or of the powdered tablets equivalent to 5 to 10 grains of sodium bicarbonate is transferred to a covered beaker and about 10 cc. of water are added. Now add a quantity of standard sulfuric acid solution which is in excess of the required amount.

$$1 \text{ cc. } N/20\ H_2SO_4 = 0.0042 \text{ g. } NaHCO_3.$$

For example, if 10 tablets of 0.5 grain (=0.324 g.) $NaHCO_3$ is used, then 0.324/0.0042 or 77.2 $N/20$ acid is required. Now add a volume in excess of the calculated quantity. After effervescence has stopped, transfer by filtration to a 100 cc. graduated flask and wash the beaker and filter paper containing the insoluble calomel with cold water, finally bringing up to the mark.

The excess of acid is titrated in an aliquot of the filtrate. Methyl orange may be used as an indicator for direct titration. If the filtrate is light pink the solution may be boiled and cooled and quite accurately titrated with phenolphthalein.

(2) DETERMINATION OF CALOMEL—Transfer the filter paper containing the calomel to a glass stoppered Erlenmeyer flask and proceed as described above under determination of calomel (Method *B*).

III—ASSAY OF CALOMEL AND BISMUTH SUBNITRATE PRODUCTS

Transfer a quantity of the material sufficient to contain 5 grains of calomel to a glass stoppered Erlenmeyer flask. Add sufficient dilute hydrochloric acid to dissolve the bismuth subnitrate and then filter through a hardened filter, retaining as much of the calomel in the flask as possible. Repeat washing by decantation, using dilute hydrochloric acid to remove the bismuth subnitrate, and finally remove the acid by washing with water. Return the filter paper to the flask and proceed with the determination of calomel as outlined above (Method *B*).

TABLE IV—ASSAY OF GRANULATIONS AND TABLETS OF CALOMEL AND SODIUM BICARBONATE (HEMPEL METHOD)

(Forty assays of these formulae gave the same average error as here recorded)

Lot No.	Grams Taken for Assay	GRAM CALOMEL PER PROSPECTIVE TABLET Found	GRAM CALOMEL PER PROSPECTIVE TABLET Required	ERROR Per cent Calomel	GRAM SODIUM BICARBONATE PER PROSPECTIVE TABLET Found	GRAM SODIUM BICARBONATE PER PROSPECTIVE TABLET Required	ERROR Per cent Soda	GRAM ACTUALLY IN FINISHED TABLET Calomel	GRAM ACTUALLY IN FINISHED TABLET Soda	ERROR PER CENT CALOMEL	ERROR PER CENT SODA
20681	2.5	0.00644	0.00648	—0.6	0.0637	0.0648	—1.7	0.0064	0.0648	—1.2	0.0
20776	2.5	0.00658	0.00648	—1.5	0.0642	0.0648	—0.9	0.00635	0.06233	—2.0	—3.8
21478	5.0	0.00633	0.00648	—2.3	0.0633	0.0648	—2.3	0.00623	0.0634	—4.0	—2.0
21555	5.0	0.00634	0.00648	—2.1	0.0607	0.0648	—6.3	0.00634	0.06065	—2.2	—6.4
20242	2.5	0.0164	0.0162	+1.2	0.0659	0.0648	+1.7	...	...	...	...
20277	2.0	0.01564	0.0162	—3.4	0.01644	0.0162	+1.5	0.0157	0.0163	—3.1	+0.6
20572	1.5	0.0151	0.0162	—6.8	0.0640	0.0648	—1.2	0.1626	0.0642	+0.4	—1.0
20584	1.5	0.0156	0.0162	—3.7	0.060	0.0648	—7.4	0.160	0.0637	—1.2(*a*)	—1.7(*a*)
20456	1.0	0.0618	0.0162	—4.6	0.0617	0.0648	—4.6	0.0637	0.0648	—1.7(*b*)	—0.0(*b*)
20852	1.0	0.0644	0.0162	—0.6	0.0623	0.0648	—4.0	0.0626	0.0652	—3.4	+0.6
Average error in calomel and sodium bicarbonate granulations..........										2.68	3.16
Average error in calomel and sodium bicarbonate tablets or pills..........										2.13	1.80

(*a*) It was estimated that a correction of 3 per cent of the weight of the tablet should be added to the weight calculated in the tablet manufacturing department.

(*b*) Was raised 2 per cent. This tablet is made by mixing dry granulations and the mixture is assayed before compression.

TABLE V—ASSAY OF CALOMEL AND BISMUTH TABLETS FOR CALOMEL

Lot No.	No. of Tablets Used	CALOMEL PER TABLET Found	Required	ERROR Per cent Calomel
21905	50	0.00646	0.00648	0.3
20356	25	0.00648	0.00648	0.0
20775	50	0.00627	0.00648	—3.2
21579	50	0.00645	0.00648	—0.5

IV—DETERMINATION OF MERCURY PROTIODIDE (YELLOW) IN GRANULATIONS, TABLETS AND PILLS

The method of analysis used is practically identical with the method described above for calomel.

1 cc. $N/10$ iodine = 0.032752 g. HgI.

TABLE VI—ASSAY OF MERCURY PROTIODIDE PRODUCTS
(This method gave similar results with 27 products)

Lot No	Taken for Assay		Gram HgI per Prospective Tablet or Pills Found	Required	ERROR Per cent HgI	Gram HgI in Finished Tablet or Pill	ERROR Per cent HgI
20015	40	Tablets	...	0.0081	...	0.00818	+1.0
20353	2.5	Grams	0.01617	0.0162	—0.2	...	..
20361	4.0	Grams	0.01045	0.0108	—3.2	0.01044	—3.3
20709	0.5	Gram	0.03174	0.0324	—2.0	...	..
21324	3.0	Grams	0.01216	0.01296	—6.2	0.01268	—2.1
24730	20	Pills		0.0162		0.01637	+1.0
24536	10	Pills		0.0324		0.03183	—1.75
24758	24	Pills		0.0081		0.00812	+0.2
24870	20	Pills		0.0162		0.01626	+0.4
25232	20	Pills		0.0162		0.01588	—1.9
25302	10	Pills		0.0324		0.03201	—1.2
25414	40	Pills		0.0081		0.00801	—1.1
25464	25	Pills	0.01218	0.01296	—6.0	0.01262	—2.6

AVERAGE ERROR FOR HgI IN GRANULATIONS............. 2.9
AVERAGE ERROR FOR HgI IN TABLETS................. 2.1
AVERAGE ERROR FOR HgI IN PILLS.................... 1.27

V—DETERMINATION OF MERCURIC CHLORIDE

(*A*) METHOD OF RUPP—For hypodermatic tablets, compressed tablets and pills, introduce a quantity equivalent to 2 to 4 grains of mercuric chloride, accurately weighed, into a 250 cc. Erlenmeyer flask, dissolve in 25 cc. water, add 2.5 grams of potassium iodide (dissolved in 5 cc. of water), 30 cc. of N sodium hydroxide solution (above the quantity required to make the solution alkaline in the first place), and 3 cc. of a 37 per cent formaldehyde solution. Mix thoroughly and set aside for 15 to 30 minutes with occasional shaking. Render the solution acid with 18 per cent acetic acid and mix. Finally add 25 to 50 cc. of $N/10$ iodine solution, stopper the flask and shake vigorously until all the mercury has been dissolved. Titrate the excess of $N/10$ iodine solution with $N/10$ sodium thiosulfate solution using starch as an indicator.

1 cc. $N/10$ iodine solution = 0.01385 g. $HgCl_2$.

For the assay of antiseptic tablets of the Bernay and Wilson formula, we have used the above method for the former product and have occasionally checked it by the following method. The tablet made according to Wilson's formula is also assayed as outlined below.

TABLE VII—ASSAY OF MERCURIC CHLORIDE PRODUCTS

Lot No.	Kind of Tablet	Method Used	GRAM MERCURIC CHLORIDE Found	Required	ERROR Per cent $HgCl_2$
21225	Bernay (small)	V(A)	0.1135	0.1179	—3.7
21225	Bernay (small)	V(B)	0.1133	0.1179	—3.8
21933	Bernay (small)	V(A)	0.1133	0.1179	—3.8
21933	Bernay (small)	V(B)	0.1190	0.1199	+1.0
21725	Wilson (large) (*a*)	V(A)	0.4728	0.4730	0.0
21725	Wilson (large) (*a*)	V(B)	0.4810	0.4730	+1.7
21682	Wilson (large) (*a*)	V(A)	0.4698	0.4730	—0.7
21682	Wilson (large) (*a*)	V(B)	0.47705	0.473	+0.8
18706	Wilson (large) (*a*)	V(A)	0.4842	0.47304	+2.4
18706	Wilson (large) (*a*)	V(B)	0.46694	0.47304	+1.3
21409	Triturate	V(A)	0.00214	0.00216	—0.9
21936	Bernay (large)	V(A)	0.4622	0.473	—2.2
21936	Bernay (large)	V(B)	0.4736	0.4730	+0.1

(*a*) Compressed tablet.

(*B*) DETERMINATION BY WEIGHING THE SULFIDE—The smaller tablet (Bernay, small) contains 1.82 grains and the larger (Bernay and Wilson) contains 7.3 grains of corrosive sublimate. Of the smaller, dissolve 15 in 500 cc. Take an aliquot of 100 cc. for analysis. Of the larger, take 5 tablets in 500 cc. and remove 100 cc. for analysis. Acidify the solution with dilute hydrochloric acid, precipitate mercuric sulfide with hydrogen sulfide and filter on a weighed Gooch. Wash with water, alcohol (10 cc.) and finally with carbon disulfide until all the free sulfur has been removed. Dry at 100° and weigh. Mercuric sulfide multiplied by 1.1756 = corrosive sublimate. It is seen from Table VII that the methods check but that the mercuric sulfide method has a tendency to give high results.

VI—DETERMINATION OF MERCURIC IODIDE

The method described under V(*A*) was successfully used for the determination of mercuric biniodide. Before applying it to various products it was tried out upon known quantities in the presence of varied amounts of sugar of milk. It was found that the sugar did not affect the result. Other factors in the reaction were varied. Thus it was observed that the time which the solution stood after alkali and formaldehyde were added was important. The most important factor, however, is the alkalinity of the solution. Unless there is a considerable excess of alkali present the mercury is not precipitated quantitatively: 30 minutes is the time required.

TABLE VIII—INFLUENCE OF VARIOUS FACTORS ON RUPP METHOD FOR MERCURIC IODIDE

Gram HgI_2 Taken	Grams Lactose Taken	Cc. N Alkali Added	Time Min.	Cc. $N/10$ Iodine Used	Grams HgI_2 Recovered	Error Per cent HgI_2
0.2	3.5	0.5	10	0.38	0.0086	—95.7
0.2	3.5	0.5	40	0.45	0.0102	—94.9
0.2	3.5	13.0	80	7.99	0.1815	— 9.2
0.2	3.5	25.0	10–15	8.69	0.1974	— 1.3
0.2	3.0	30.0	10–15	8.7	0.1976	— 1.2
0.2	5.0	30.0	40	8.8	0.1999	— 0.05
0.1	3.0	30.0	30	4.42	0.1004	+ 0.4
0.1	5.0	30.0	30	4.39	0.0997	— 0.3
0.25	1.0	30.0	30	11.06	0.2512	+ 0.5
0.2	3.5	30.0	30	8.83	0.2006	+ 0.3
0.2	4.0	30.0	30	8.75	0.1998	— 0.1
0.2	5.0	60.0	10	8.8	0.1999	— 0.05
0.2	5.0	60.0	20	8.8	0.1999	— 0.05
0.2	5.0	60.0	30	8.82	0.2004	+ 0.2

TABLE IX—ASSAY OF MERCURY BINIODIDE PRODUCTS BY RUPP PROCESS

Lot No.	Taken for Assay	Grams HgI_2 per Prospective Tablet Found	Required	Error Per cent HgI_2	Grams HgI_2 in Finished Tablet or Pill	Error Per cent HgI_2
20527	4 grams	0.003104	0.00324	—4.2	0.003205	—1.0(*a*)
21199	5 grams	0.003882	0.00405	—4.1	0.00387	—4.4
21265	1.25 grams	0.01571	0.0162	—3.0	....	...
25196	24 pills	....	0.0081	...	0.00804	—0.7
21476	2.5 grams	0.00804	0.0081	—0.7	0.008122	+0.2

(*a*) Was raised 2 per cent.

1 cc. $N/10$ iodine = 0.02272 g. HgI_2.

VII—VOLUMETRIC DETERMINATION OF MERCURY IN OINTMENTS

(*A*) OINTMENT OF AMMONIATED MERCURY[1]—Heat about 5 grams of the ointment accurately weighed, in a small flask upon a water bath with 25 cc. of 12.5 per cent hydrochloric acid, for 30 minutes. Pour the acid liquid through a small plugget of cotton into a 100 cc. graduated flask. Warm the fat once more with 20 cc. of diluted hydrochloric acid and then twice more with 20 cc. portions of water, and add these

---

[1] This method is readily adapted to the assay of ammoniated mercury itself.

rinsings to the solution already in the flask. Make the volume up to 100 cc., mix thoroughly and transfer an aliquot of 25 cc. to a 250 cc. glass stoppered Erlenmeyer flask. Proceed as in the assay of mercuric chloride tablets, using 15 cc. 2 *N* sodium hydroxide solution after first rendering the strongly acid solution alkaline.

1 cc. *N*/10 iodine solution = 0.01257 g. ammoniated mercury.

(*B*) ASSAY OF MERCURIAL OINTMENT[1]—Heat under a reflux condenser about 2 grams of the ointment (accurately weighed into a small flask) with 20 cc. nitric acid until all the mercury has dissolved. Pour the acid solution through a plugget of cotton into a 100 cc. graduated flask, and rinse the fat in the flask on the water bath two or three times more, first with a small quantity of diluted nitric acid and then with 20 cc. portions of water. To this solution, add a 3 per cent potassium permanganate solution until the former is permanently pink or until brown flakes separate. Decolorize with a 3 per cent solution of ferrous sulfate and finally make the volume up to 100 cc. To an aliquot of this solution, add a few drops of ferric alum solution, and add an excess of *N*/10 KSCN solution. Titrate the excess with *N*/10 $HgNO_3$ solution, and finally complete the titration with *N*/10 KSCN. 1 cc. KSCN solution = 0.01 g. mercury.

(*C*) OINTMENT OF RED MERCURIC OXIDE[2]—This is assayed by the above method using five grams of the ointment.

1 cc. *N*/10 KSCN = 0.0108 g. mercuric oxide.

(*D*) OINTMENT OF MERCURIC NITRATE is assayed as above described, using 10 grams.

In conclusion, the author wishes to thank Dr. Frederick W. Heyl at whose suggestion the work of reviewing the standardization of these preparations was taken up.

THE UPJOHN COMPANY
KALAMAZOO, MICHIGAN

ELECTROLYTIC DETERMINATION OF MERCURY IN MERCURY OLEATES

By B. L. MURRAY

Received September 13, 1915

Owing to the greasy nature of the numerous oleates of mercury the determination of mercury in them by the older methods of analysis presents some difficulties. The necessary separation and removal of the oleic acid together with the tedious determination of mercury by the usual precipitation methods may perhaps have deterred some from assaying the oleates heretofore. The tendency has been to take the oleates mostly on faith. In our experience, however, an effort has been made to get away from routine and endeavor to make a new application of the electrolytic determination of mercury, already found so useful and satisfactory on other pharmaceutical products.

The method that is given below has been in use in its present form about two or three years and in our hands proves accurate. One would hardly believe quantitative results could be obtained if the mixture is observed just before the electrolysis. The apparatus, a cathode beaker, contains metallic mercury, toluene, hydrochloric acid 10 per cent, and the oleate of mercury. Upon turning on the electric current, however, and almost as if by magic, this heterogeneous mixture readjusts itself into orderly arrangement, and in a short time the mercury that was combined in the greasy oleate lies shining and bright on the bottom of the cathode beaker ready to be weighed.

METHOD—About 0.7 to 1.0 gram of the oleate is weighed directly into a mercury cathode cup (such as a small beaker, capacity 50 to 75 cc.). To this sample there are added 15 to 20 cc. of 10 per cent hydrochloric acid and 15 cc. of toluene. The cathode cup with its contents is placed within a somewhat larger crystallizing dish or beaker which later can be filled with cold water to keep the temperature of the reaction down as desired. After attaching the anode and making the connections in the customary way, electrolysis of this non-uniform mixture is begun, gradually and slowly increasing the current up to 3 amperes, using about 10 minutes to do it. The current (3 to 3.5 amperes at about 8 volts) is then maintained for about 30 minutes, the anode rotating at about 800 revolutions per minute. As the electrolysis continues, the contents of the cup become heated nearly to the boiling point of some of the constituents, thus melting the mercury oleate. It is essential that the mercury oleate should melt. If the liquid in the cathode cup becomes too hot and appears apt to boil over, it should be cooled down by pouring water into the crystallizing dish or other surrounding vessel, but it should not be cooled down below 60° C. When the mercury is all deposited the cathode cup is washed out by siphonation in the customary way with water, after which the metallic mercury is washed with alcohol, dried with ether and finally weighed.

LABORATORY OF MERCK & COMPANY
RAHWAY, N. J.

ELECTROLYTIC DETERMINATION OF BISMUTH IN BISMUTH β-NAPHTHOL

By B. L. MURRAY

Received September 13, 1915

Another useful application of the electric current in analytic work has been found in the determination of bismuth in bismuth β-naphthol. Aside from the electrolytic portion it is only necessary to ignite the compound in order to remove organic matter and dissolve the bismuth oxide and metal thus formed in nitric acid. The resulting bismuth nitrate is then electrolyzed.

METHOD—A sample of 0.3 gram is weighed into a porcelain crucible and heated very gently to decomposition of the β-naphthol. The crucible is finally heated to the full red heat of a Meker burner for 3 minutes to burn off the last traces of carbon. The residue resulting is yellow in color and is composed chiefly of bismuth oxide together with a small quantity of metallic bismuth. The crucible is placed in a

---

[1] This method is not as practical as the one given in the U. S. P.

[2] In assaying an ointment of yellow oxide of mercury which contains only 0.8 per cent of the mercurial, it was found necessary first to remove the base with ether. It was then possible to obtain results approximately correct; *i. e.*, 0.75 per cent.

small beaker and a mixture of 4 cc. of nitric acid (sp. gr. 1.4) and 5 cc. of water is added, after which it is heated on a steam bath to complete solution. The solution is washed with distilled water into a mercury cathode cup, keeping the volume down to 20 cc. The cathode cup is conveniently made from a 50 cc. Erlenmeyer flask. The 20 cc. solution is then electrolyzed under the following conditions:

CURRENT (maximum), 4.5 amperes at 6 volts.
REVOLUTIONS PER MINUTE, 1000. TIME, 45 minutes.

The initial application of the current is 1 ampere and this is followed by a gradual increase to 4.5 amperes. Some black masses are seen to form, but rapid rotation of the anode prevents the formation of a large quantity and all disappear. When the black masses have entirely disappeared the rotation of the anode is stopped and the cathode is washed with distilled water by siphonation while the full strength of current is on. The electrolyte should be tested for bismuth with hydrogen sulfide. After 2 to 3 washings with water, followed by alcohol, and then by ether, the mercury cathode is weighed. The increase in the weight of the mercury cathode is due to the bismuth which has been deposited on and amalgamated with the mercury.

LABORATORY OF MERCK & COMPANY
RAHWAY, N. J.

ELECTROLYTIC DETERMINATION OF MERCURY IN MERCURY SALICYLATES

By B. L. MURRAY

Received September 13, 1915

A rapid and convenient method of determining mercury in mercury salicylates is herewith presented. It consists in a new application of the already well and favorably known electrolytic deposition of mercury. The method here given as used on salicylates of mercury has been in use about two years and has proved reliable.

About 0.3 gram is weighed into the mercury cathode dish and dissolved in 10 cc. of sodium sulfide solution (sp. gr. about 1.18). To this solution are added 20 cc. of 10 per cent potassium hydroxide solution. The mixture is now electrolyzed using a current of 1 ampere at 7 volts until the mercury is completely deposited, usually about one-half hour being required. The anode should rotate about 500 revolutions per minute. After the deposition the electrolyte is decanted, the mercury is washed with water until free from alkalinity, then with alcohol, finally with ether, and then weighed.

LABORATORY OF MERCK & COMPANY
RAHWAY, N. J.

LABORATORY AND PLANT

DETERMINATION OF SULFUR DIOXIDE AND SULFUR TRIOXIDE IN FLUE GASES

By R. J. NESTELL AND E. ANDERSON

Received January 15, 1916

In carrying on some experimental work recently on the gases issuing from the roasting furnaces at one of the large Arizona copper smelters, a rapid, accurate and convenient method for the quantitative estimation of SO_2 and SO_3 was of primary importance. The conditions of the work in hand demanded:

1—That the determination of both sulfur oxides should be made upon the same sample of gas.

2—That the time necessary for such determinations should be as short as possible in order that any change in the composition of the gases given off in consequence of varying conditions in the operation of the furnaces might be rapidly and continuously determined by one or two operators.

3—That the apparatus required should not be too fragile or unwieldy in character but capable of convenient transportation to any point of the smelter construction.

4—That the analytical operations necessary should be of such a nature as to admit of ready performance in the field.

In considering the various methods, applicable to this problem, previously proposed or employed by other workers and of which we have found any record, it was evident that no one of them fulfilled all the requirements of the present case.

A scheme proposed by Hawley[1] for separating SO_3 from SO_2 seemed to be the most promising. This consists of humidizing the gases with H_2O vapor to convert any SO_3 into the white fog of H_2SO_4 and then passing them through a double filter paper held between the large ends of two funnels. This mechanically retains the H_2SO_4 and allows the SO_2 to pass through. The H_2SO_4 so caught is then determined by placing the filters in a small beaker with about 50 cc. of water, adding a drop of methyl orange and titrating with standard alkali.

In support of the accuracy of this method Hawley gives the following data of tests made by him in which known amounts of H_2SO_4 were heated in a hard glass tube and the fume, mixed with air, passed through the filter and the acid so caught determined:

	1	2	3
Grams H_2SO_4 taken	0.064	0.050	0.034
Grams H_2SO_4 found	0.060	0.047	0.032
Per cent found	93.7	94.0	94.1

We have made a series of similar tests in which accurately weighed amounts of H_2SO_4 were heated in a √‾ shaped hard glass tube and the volatilized acid drawn with a current of air through the "Hawley" filter. The H_2SO_4 remaining in the tube and also that caught on the filter were then determined. This gave exactly the amount of acid volatilized and recovered. The following data were obtained:

	1	2	3	4	5
Grams SO_3 taken	0.572	0.0989	0.0708	0.0230	0.0482
Grams SO_3 found	0.564	0.0976	0.0692	0.0228	0.0481
Per cent found	98.6	98.7	97.7	99.1	99.8

These figures show a considerably higher efficiency for the method than do Hawley's and demonstrate it to be sufficiently accurate for general application.

To apply this method then to our work it was necessary to provide only for the estimation of the SO_2

---

[1] *Eng. Min. Jour.*, Nov. 23, 1912, p. 987.

passing the "Hawley" filter. This might be done by bubbling the gas through a measured excess of standard iodine solution, containing sufficient $NaHCO_3$ to neutralize the HI and H_2SO_4 formed in the reaction between the SO_2, I_2 and H_2O, and titrating back with $Na_2S_2O_3$.

There were certain disadvantages in using this method such as: (1) the necessity of employing two different standard solutions than were required for the SO_3 estimation; (2) the danger and the necessity of providing against loss of iodine by volatilization on passing hot gases through the solution; (3) the possible presence of reducing gases other than SO_2; (4) the loss of iodine by air oxidation during aspiration (this latter loss is slight).

The iodine method was therefore dismissed from consideration and it was decided to use standard Na_2CO_3 as the medium for absorbing the SO_2, using a measured excess and titrating back with standard acid. This method presents no difficulties if note is taken of one fact, *viz.:*

The reaction between the Na_2CO_3 and the SO_2, where the former is in excess, proceeds according to the equation

$$(1)\ Na_2CO_3 + SO_2 \longrightarrow Na_2SO_3 + CO_2.$$

When the solution, then, containing Na_2SO_3 and the excess of Na_2CO_3, is titrated with standard acid, using methyl orange as indicator, the two following reactions take place:

$$(2)\ Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

and

$$(3)\ Na_2SO_3 + HCl \longrightarrow NaHSO_3 + NaCl$$

$NaHSO_3$ being neutral to methyl orange, this indicator does not show acidity until the two reactions stated here have been carried to completion. The amount of HCl used in this titration is therefore not only a measure of the Na_2CO_3 remaining unused, but also of the $NaHSO_3$ formed in the titration which must be borne in mind when calculating the results.

When, however, a solution of Na_2SO_3 is exposed to air, or slightly agitated during titration, and particularly if the air be actually drawn through such a solution, as must be done in these determinations in order to displace all the SO_2 from the apparatus, some of the Na_2SO_3 is oxidized to Na_2SO_4. The sulfate thus formed does not react with the HCl in the titration to form an acid salt, and the amount of SO_2 calculated will be high to that extent.

For this reason all of the Na_2SO_3 formed was oxidized, before titration, with H_2O_2—this being first made neutral to methyl orange—the reaction taking place being as follows:

$$(4)\ Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$$

The acid then used in the titration is therefore a measure of the excess sodium carbonate, only, from Equation 1 where the normal salt is formed.

In the usual method of determining the excess of alkali by titration with acid in the presence of the sulfite and with methyl orange as indicator leading to the formation of the acid sulfite, it is evident, from the equation, that each cc. of $N/10$ alkali consumed is equivalent to 0.0064 g. SO_2, while in the modification we have employed, where the sulfite is first oxidized to sulfate, each cc. of $N/10$ alkali = 0.0032 g. SO_2.

The following tests were made which illustrate clearly the influence of air oxidation above mentioned, a solution of SO_2 in water being used.

(1)—20 cc. of the SO_2 solution were titrated with $N/10$ iodine of which 24.3 cc. were required, showing the SO_2 content of the solution to be 0.00389 gram per cc.

(2)—20 cc. of the SO_2 solution were added to a mixture of 25 cc. $N/10$ Na_2CO_3 and 5 cc. neutral H_2O_2. Methyl orange was then added and the excess alkali determined with $N/10$ HCl. Of this latter 0.65 cc. was required, showing 24.35 cc. $N/10$ Na_2CO_3 used up by the SO_2. A repetition of this test under parallel conditions gave 24.38 cc. alkali consumed, showing SO_2 content of the solution to be 0.0039 g. per cc.

(3)—20 cc. of the SO_2 solution were added to 25 cc. $N/10$ Na_2CO_3 and, without the addition of H_2O_2 or any further aeration than was caused by mixing the two solutions, titrated with $N/10$ HCl: 12.2 cc. of the latter were required, using methyl orange. This shows 12.8 cc. of the Na_2CO_3 to have been used up and, as each cc. thereof is equivalent to 0.0064 g. SO_2, it would indicate an SO_2 content of 0.0041 g. per cc. This apparently too high value is readily accounted for by the fact that part of the Na_2SO_3 formed in the reaction between the SO_2 and the Na_2CO_3 had been oxidized to Na_2SO_4 either previous to or during the titration with the $N/10$ HCl and in consequence thereof less HCl was required to react with the Na_2SO_3 to form $NaHSO_3$ thus giving, indirectly, a higher value for the amount of Na_2CO_3 consumed.

(4)—20 cc. of the SO_2 solution were added to 25 cc. $N/10$ Na_2CO_3 and then 2000 cc. of air were bubbled through the mixture, requiring 15 minutes for the aspiration. The solution was then titrated with $N/10$ HCl, of which only 9.45 cc. were required, indicating an SO_2 content of 0.00497 g. per cc. Of course the same explanation applies here as in (3) above.

It is evident, therefore, that in titrating the residual alkalinity of solutions containing Na_2SO_3, where the possibility of air oxidation of this compound exists, due precaution must be taken to guard against the error introduced by this factor.

The use of H_2O_2 eliminated this difficulty and has been proved to render the method accurate, simple and readily applicable to field work. The addition of the H_2O_2 may be made after aspiration is completed and just prior to the titration with standard acid.

For practical work in the field the apparatus shown in Fig. I was employed.

The joints between the several members of the outfit are close and made tight by short lengths of rubber tubing. *B*, *C* and *D* are held in a small, open-top wooden box about 18 in. long, 5 in. wide and 4 in. high with partitions to support and prevent motion of *B* and *D* when carried about. The whole apparatus, without the aspirating bottles, ready for a determination, weighs less than 5 lbs. Two of these outfits can be easily carried under each arm.

In making a test the sampling tube *A* is connected to *B* and inserted at any particular point of the furnace or stack; the aspirator *E* is connected to *D* and aspiration started at the desired rate by loosening the pinchcock *G*.

Throughout our work 2000 cc. in each case was the volume of gas aspirated through the apparatus and determined by noting when the water in *F* had reached a mark showing that volume to have passed over.

The tube *A* is then withdrawn from the furnace and, while still attached to *B*, a further volume of 1000 cc. of air aspirated. This was found sufficient to remove completely the last trace of SO_2 from all parts of the apparatus in front of *D*. *A* is then disconnected, the outside wiped off with a cloth or damp sponge, and the inside thoroughly washed down into a small beaker with distilled water. This point is very important, for it was found that in many cases approximately 50 per cent of the SO_3 had condensed and been retained in *A*.

The contents of *B* are next added to the washings from *A* and this tube also thoroughly washed out. The two funnels carrying the filters are then disconnected, the filter papers placed in the beaker containing the washings from *A* and *B*, and the funnel which has been next to *B* also washed and the washings added to the same beaker.

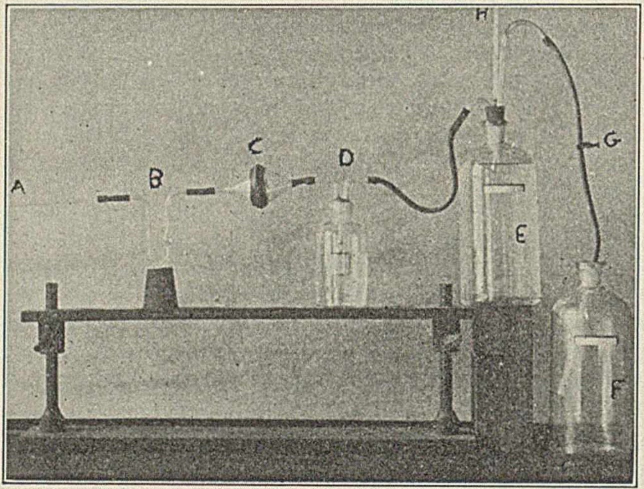


FIG. I

A—Hard glass or quartz sampling tube, 1/4" diameter, 3' long.
B—Humidizing bulb containing just enough water to seal the bend.
C—Double S. & S. No. 589 or Munktell No. 0 filters held between the large ends of two funnels by a section of rubber tubing such as is used for holding Gooch crucibles.
D—Double-action Allihn gas wash-bottle containing *N*/10 Na_2CO_3 and H_2O_2.
E, F—Syphon aspirating bottles holding about 3 liters each.
G—Pinch-cock to regulate flow of syphon water.
H—Thermometer.

A drop of methyl orange is added to the contents of the beaker and the H_2SO_4 present titrated with *N*/10 Na_2CO_3.

To determine the SO_2 caught, methyl orange is added to *D* and the excess of Na_2CO_3 determined by titration with *N*/10 HCl. The volume of the *N*/10 Na_2CO_3 used up during the aspiration of the gases is a measure of the amount of SO_2 present.

It was found by repeated trials that the one absorption bottle *D* was sufficient to retain all SO_2 even when the gases were aspirated at the rate of 2000 cc. in 4 minutes. An important source of error in determinations of this kind is the catalytic action of the walls of the sampling tube and also of dust particles which may collect in the tube. When the temperature of the aspirated gases is sufficiently high, appreciable amounts of SO_2 are oxidized to SO_3 on contact with the hot dust and walls of the tube. If, then, the gases be drawn through slowly this will introduce large errors.

In a number of instances when the gases were aspirated from the hottest hearths of the roasting furnaces, the temperature being between 600° C. and 700° C., the ratio of SO_3 to SO_2 found was 1 : 10 when the aspiration rate was 300 cc. per minute, while when the gases were drawn through at 45 cc. per minute the ratio was 1 : 6. With an aspiration of approximately 1000 cc. per second, obtained by allowing the gases to rush into a partially exhausted 2 liter bottle and then drawing this gas through the apparatus, the ratio of SO_3 to SO_2 was 1 : 12. With a temperature less than 450° C. this catalytic action is very slight and can probably be neglected, but with hotter gases it is necessary either to aspirate with sufficient rapidity or to cool the sampling tube by means of a water jacket.

TABLE I—TYPICAL ANALYSES OF FLUE GAS FOR SO_3 AND SO_2
Temperature of flue gases in each case averaged about 400° C.
Volume of gas taken, 2000 cc. Pressure, 655 mm.

Temperature in aspiration bottle	Aspiration time Minutes	Cc. *N*/10-Na_2CO_3 for		Gram found		Volume Per cent		Ratio of SO_3 to SO_2
		SO_3	SO_2	SO_3	SO_2	SO_3	SO_2	
38	5	5.4	78.4	0.0216	0.2508	0.40	5.82	1 : 14.55
60	5	3.5	50.1	0.0140	0.1632	0.28	4.05	1 : 14.45
38	20	4.1	67.8	0.0164	0.2170	0.30	5.02	1 : 16.73
49	15	4.15	48.0	0.0166	0.1539	0.32	3.70	1 : 11.56

Table I shows analyses of gases taken from the outlet flue of a multiple hearth roasting furnace which are typical of a large number in which the method here described was employed.

LABORATORIES WESTERN PRECIPITATION COMPANY
LOS ANGELES, CALIFORNIA

BOILING AND CONDENSING POINTS OF ALCOHOL-WATER MIXTURES[1]

By P. N. EVANS

Received December 22, 1915

The boiling points of alcohol-water mixtures depend on the proportions of the constituents, and range from about 78° C. for pure ethyl alcohol to 100° C. for pure water. Except at a concentration of 96 per cent alcohol by weight (97.5 per cent by volume) any mixture of alcohol and water when boiled gives off a vapor of different composition from that of the liquid, the vapor being richer or poorer in alcohol than the liquid when the latter contains respectively less or more than about 96 per cent of alcohol. The vapor has, of course, a condensing point identical with the true boiling point of the liquid from which it is given off.

The purpose of the work here reported was to ascertain experimentally the relation between the boiling point (or condensing point) and the composition of both the liquid and *vapor* phases, that with the information so obtained it might be possible by observation of the corrected boiling point to learn the com-

---

[1] Abstracted by author from Indiana Academy of Science Report for 1913.

position of the boiling liquid and that of the vapor being evolved at any moment during distillation.

The relation between the boiling point and the composition of the liquid phase was determined for low percentages of alcohol by J. J. Pohl,[1] and for all concentrations by Dupré and Page,[2] and by Gröning,[3] but the results were very discordant. H. W. Wiley[4] gives a rule for calculating the strength of alcohol-water mixtures containing not over 5 per cent of alcohol. W. A. Noyes and R. R. Warfel[5] determined the relation between boiling point and composition over the whole range, with special reference to the minimum boiling point, which they found to be 78.74° C. for 96 per cent alcohol by weight, and mention is made by them of the determination by J. K. Haywood[6] of boiling points of mixtures containing less than 85 per cent of alcohol. So far as known to the writer the relation between the composition and condensing point of the *vapor* phase has not been previously determined.

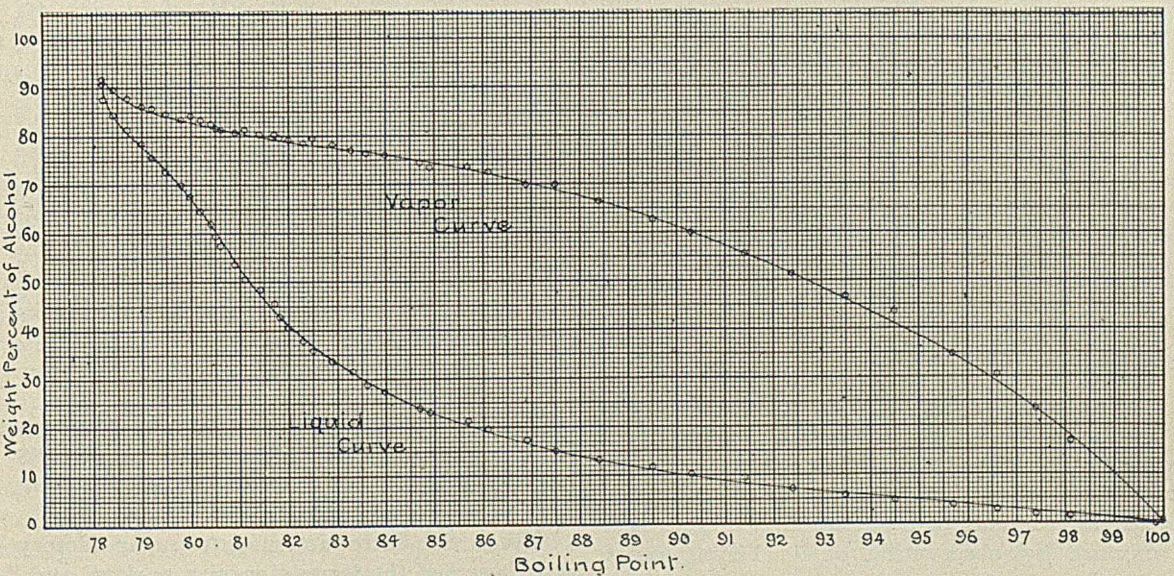


Fig. I

PROCEDURE

The gravity and temperature of a strong alcohol were determined with a Westphal balance and the weight per cent of alcohol calculated by means of Mendelejeff's table.[7] Five hundred cubic centimeters were placed in a one liter distilling flask with an accurate thermometer graduated in tenths of a degree inserted with its bulb just below the side-neck. The liquid was then slowly distilled at a uniform rate of about one drop per second until 15 cc. had passed over, the distilling temperature being read when 7.5 cc. had collected in the graduated receiver. The per cent of alcohol in the distillate and that in the residue were determined from the gravities as already stated. The average of the percentages found in the liquid in the flask before and after distillation was taken as that of the liquid phase, and the percentage in the distillate as represented in the vapor phase at the time when the boiling point was observed half-way through the distillation.

The original volume of the liquid in the flask was restored by the addition of 15 cc. of water, and the slightly more dilute mixture so obtained was used for the next experiment. In this way 43 mixtures were examined, ranging from 91 to 0 per cent alcohol.

Corrections were introduced in the temperature readings for the barometric pressure and for the exposed mercury column, as follows: Regnault and Claassen[1] have shown that the effect of such variations of pressure as may be due to atmospheric conditions is practically the same on the boiling point of water and that of alcohol, so it seemed justifiable to use Landolt's correction for these mixtures and add 0.043 to the observed reading for each millimeter below 760 shown by the barometer. The observed temperature reading was also corrected for the exposed mercury column by adding $N(T - t)$ 0.000154, in which N is the length of the exposed column in degrees, T the observed boiling point, and t the room temperature.

The thermometer used was compared throughout the range of observations with a similar instrument calibrated by the Reichsanstalt. The corrections in no case exceeded 0.1° and were disregarded, as only this degree of accuracy was aimed at. The temperature results are probably accurate within 0.2 degree, and the concentrations within 2 per cent (in most cases within 1 per cent).

RESULTS

The results obtained are given in Table I. The relations existing between the boiling point or con-

---

[1] *Jahresber.*, **1850**, p. 455.

[2] *Phil. Trans.*, **1869**, p. 591.

[3] Watts' "Dict. Chem.," **1872**, I, p. 95.

[4] *Jour. Am. Chem. Soc.*, **18** (1896), 1063.

[5] *Ibid.*, **23** (1901), 463.

[6] *J. Phys. Chem.*, **3** (1899), 318.

[7] Biedermann's "Chem. Kal.," **1914**, I, p. 296.

[1] Biedermann's "Chem. Kal.," **1914**, II, pp. 112, 113.

Table I—Values Obtained by Experiment

No.	Specific gravity before distillation	Temperature during gravity determination	Per cent alcohol before distillation	Specific gravity of residue	Temperature during gravity determination	Per cent alcohol in residue	Average per cent alcohol in liquid	Specific gravity of distillate	Temperature during gravity determination	Per cent alcohol in distillate	Observed temperature of distillation	Barometer reading mm.	Barometer correction in boiling point	Room temperature	Correction for exposed mercury column	Corrected boiling point
1	0.815	20	91.1	0.812	23	91.1	91.1	0.811	22	91.8	77.2	750	0.4	23	0.6	78.2
2	0.822	22	87.7	0.821	23	87.7	87.7	0.815	23	90.0	77.2	750	0.4	22	0.6	78.2
3	0.829	23	84.6	0.829	23	84.6	84.6	0.819	22	89.6	77.4	750	0.4	22	0.6	78.4
4	0.836	24	81.5	0.838	22	81.5	81.5	0.823	22	88.0	77.6	748	0.5	22	0.6	78.7
5	0.845	22	78.7	0.843	25	78.8	78.8	0.825	22	86.5	77.7	743	0.7	22	0.6	79.0
6	0.852	22	75.8	0.851	23	75.8	75.8	0.827	22	85.8	77.8	740	0.8	22	0.6	79.2
7	0.857	24	72.9	0.860	21	72.9	72.9	0.829	23	84.6	78.1	741	0.8	22	0.6	79.5
8	0.864	23	70.4	0.866	23	69.6	70.0	0.832	22	83.8	78.4	741	0.8	23	0.6	79.8
9	0.873	21	67.5	0.873	21	67.5	67.5	0.833	20	84.2	78.6	743	0.7	21	0.6	79.9
10	0.879	21	65.0	0.880	21	64.6	64.8	0.835	20	83.5	78.9	743	0.7	21	0.6	80.2
11	0.884	21	62.7	0.885	23	61.4	62.0	0.838	19	82.7	79.1	743	0.7	21	0.6	80.4
12	0.891	22	59.2	0.893	20	59.2	59.2	0.839	20	81.9	79.5	750	0.4	21	0.6	80.5
13	0.898	20	57.1	0.899	21	57.5	57.3	0.839	21	81.5	79.6	750	0.4	21	0.6	80.6
14	0.904	21	54.1	0.904	23	53.2	53.6	0.839	23	80.8	80.2	757	0.1	23	0.6	80.9
15	0.908	23	51.4	0.910	22	51.0	51.2	0.840	21	81.2	80.3	756	0.2	22	0.6	81.1
16	0.915	22	48.6	0.916	22	48.2	48.4	0.842	21	80.4	80.5	756	0.2	22	0.6	81.4
17	0.920	22	46.4	0.923	22	45.0	45.7	0.843	20	80.4	80.8	756	0.2	22	0.6	81.7
18	0.926	23	43.8	0.928	22	42.5	43.1	0.844	21	79.6	81.0	756	0.2	22	0.6	81.8
19	0.933	22	40.5	0.932	25	40.0	40.2	0.845	20	79.6	81.2	755	0.2	19	0.6	82.0
20	0.936	24	38.0	0.938	23	37.5	37.7	0.848	19	78.8	81.5	755	0.2	20	0.6	82.3
21	0.940	24	36.0	0.942	23	35.5	35.7	0.846	20	79.2	81.6	755	0.2	20	0.7	82.5
22	0.945	23	33.9	0.947	22	33.3	33.6	0.849	19	78.3	82.0	755	0.2	20	0.7	82.9
23	0.949	23	31.7	0.950	23	31.1	31.4	0.851	20	77.1	82.4	755	0.2	21	0.7	83.3
24	0.952	24	30.0	0.955	23	28.1	29.0	0.853	20	76.2	82.7	756	0.2	21	0.7	83.6
25	0.956	23	27.5	0.956	25	26.9	27.2	0.853	21	75.8	82.5	748	0.5	20	0.7	84.0
26	0.958	24	26.2	0.961	22	24.7	25.4	0.856	22	74.2	83.4	748	0.5	22	0.8	84.7
27	0.962	23	23.7	0.964	23	22.3	23.0	0.858	19	73.7	83.7	750	0.4	21	0.8	84.9
28	0.965	23	21.7	0.966	23	21.0	21.3	0.859	20	73.7	84.3	750	0.4	21	0.8	85.7
29	0.966	23	21.0	0.969	23	18.9	19.9	0.860	22	72.5	84.8	747	0.5	22	0.8	86.1
30	0.970	23	17.9	0.972	22	16.7	17.3	0.866	22	70.0	85.5	745	0.6	23	0.8	86.9
31	0.973	22	15.8	0.974	24	14.4	15.1	0.865	23	70.0	86.2	747	0.5	23	0.8	87.5
32	0.975	24	13.3	0.977	25	12.3	12.8	0.873	23	66.7	86.9	756	0.6	24	0.9	88.4
33	0.977	25	12.3	0.979	25	11.0	11.6	0.882	24	62.5	88.1	748	0.5	25	0.9	89.5
34	0.980	22	11.0	0.982	23	9.3	10.1	0.891	21	60.0	89.1	750	0.4	22	0.9	90.3
35	0.982	23	11.0	0.984	24	7.9	9.4	0.901	20	55.8	90.1	750	0.4	22	0.9	91.4
36	0.985	22	7.9	0.987	22	6.4	7.1	0.910	22	51.4	91.1	750	0.4	22	0.9	92.4
37	0.987	22	6.4	0.989	20	5.0	5.7	0.919	22	46.8	92.2	750	0.4	23	0.9	93.5
38	0.990	21	4.4	0.991	23	3.9	4.1	0.927	22	43.7	93.1	747	0.5	21	0.9	94.5
39	0.991	23	3.9	0.992	24	2.8	3.3	0.947	21	33.5	94.3	747	0.5	22	0.9	95.7
40	0.992	24	2.8	0.994	22	2.2	2.5	0.953	21	30.6	95.2	747	0.5	22	0.9	96.6
41	0.995	22	1.7	0.996	21	1.1	1.4	0.964	21	23.6	96.0	747	0.5	22	0.9	97.4
42	0.996	22	1.1	0.996	23	0.9	1.0	0.972	22	16.7	96.8	751	0.4	22	0.9	98.1
43(a)	0.998	25	—0.5	0.999	22	—0.3	—0.4	0.999	21	—0.1	98.7	753	0.3	22	0.9	99.9

(a) This experiment was with water only.

densing point and the composition of the liquid and vapor phases are shown clearly by the plot in Fig. I. A convenient table of results estimated from the curves appears in Table II, which enables one to determine quickly the approximate concentration of any alcohol-water mixture by observation of its boiling point, with corrections for barometric pressure and exposed mercury column. It is also possible to tell the approximate composition of both liquid and vapor (or distillate) at any moment during the distillation of a mixture. The accuracy is, of course, less than by the usual and more difficult analytical method of distillation and the determination of the gravity of the distillate with a pycnometer.

Table II—Values Estimated from Curves in Fig. I

Boiling point ° C.	Weight per cent alcohol in liquid	Weight per cent alcohol in vapor	Boiling point ° C.	Weight per cent alcohol in liquid	Weight per cent alcohol in vapor	Boiling point ° C.	Weight per cent alcohol in liquid	Weight per cent alcohol in vapor
78.2	91	92	82.0	41	79	91.5	8	55
78.4	85	89	82.5	36	78	92.0	8	53
78.6	82	88	83.0	33	78	92.5	7	51
78.8	80	87	83.5	30	77	93.0	6	49
79.0	78	86	84.0	27	76	93.5	6	46
79.2	76	85	84.5	25	75	94.0	5	44
79.4	74	85	85.0	23	74	94.5	5	42
79.6	72	84	85.5	21	73	95.0	4	39
79.8	69	84	86.0	20	72	95.5	4	36
80.0	67	83	86.5	18	71	96.0	3	33
80.2	64	83	87.0	17	70	96.5	3	30
80.4	62	82	87.5	16	69	97.0	2	27
80.6	59	82	88.0	15	68	97.5	2	23
80.8	56	81	88.5	13	67	98.0	1	19
81.0	53	81	89.0	12	65	98.5	1	15
81.2	50	80	89.5	11	63	99.0	0	10
81.4	47	80	90.0	10	61	99.5	0	5
81.6	45	80	90.5	10	59	100.0	0	0
81.8	43	79	91.0	9	57			

Purdue University
Lafayette Indiana

A RAPID PYCNOMETRIC METHOD FOR "GRAVITY SOLIDS" IN CANE-SUGAR FACTORIES

By Herbert S. Walker

Received September 13, 1915

Since the introduction into sugar factory control by Deerr[1] of the terms "gravity purity" and "gravity solids," and his demonstration that the determination of total solids by the Brix spindle, while not absolutely accurate except in pure sucrose solutions, when applied to juices, sugars, and molasses at approximately the same dilution (about 15° Brix) yielded, in consequence of consistent error, results fully as valuable for factory control work as the more tedious process of drying to more or less constant weight, this latter method has been entirely abandoned in many factories.

The principal objection to the substitution of densimetric for direct drying methods has been the lack of even relative accuracy in Brix spindle readings; this, as regards accuracy of reading the graduations on the stem of the spindle, has been somewhat improved by several devices suggested in recent years, but there still remain certain inherent errors in the method, due to variable viscosity and surface tension of liquids, which are very difficult to eliminate.

The pycnometer is generally conceded to be an exceedingly accurate means of determining specific gravities, but has thus far found little favor in cane-

---

[1] *Bull.* **41**, Agr. and Chem. Series, H. S. P. A. Expt. Station.

sugar factories, owing probably to real or fancied difficulty of manipulation and to the extra calculation involved. By means of a few simple modifications, however, a pycnometer determination may be made almost as easily as an ordinary Brix test, and with no calculation other than looking up the Brix in a specific gravity table.

A 100 cc. pycnometer with ground-in thermometer and capillary side arm is used; since all determinations are made at room temperature, the cap of the side arm is thrown away and the arm itself cut off two or three millimeters above the graduation mark, thus facilitating rapid filling to a definite volume.

All calculations could be eliminated by making a pycnometer to contain exactly 100 g. water at a given standard temperature, such as 17.5°, 20°, 27.5° (weighed in air), or 4° (weighed in vacuum), according to the tables one intends to use. The weight of the liquid in the pycnometer would then be 100 times its density as compared with water at that temperature, and if a tare were made to just balance the empty pycnometer, then the weights required to balance the pycnometer filled with sugar solution would indicate the density of that solution without calculation; Brix could then be obtained from the tables, applying the same correction used for Brix spindles in case the determination were not made at exactly standard temperature.

It is, unfortunately, difficult to obtain a pycnometer of exactly a desired capacity; one a little too large may be reduced by grinding in the thermometer with emery powder, a rather tedious though not difficult process; but a bottle of too small capacity is difficult to enlarge with accuracy.

In such cases it is easiest so to regulate the tare that the additional weights required to balance the pycnometer full of water at standard temperature shall be exactly 100 g., irrespective of the true volume of the pycnometer, *i. e.*, if pycnometer contains 101 g. water at standard temperature and weight of tare equals weight of pycnometer, then

Pycnometer + water = tare + 101 g.

Increasing weight of tare by 1 g.,

Pycnometer + water = tare + 100 g.,

and with pure water this pycnometer and tare will always indicate a density by direct weighing of 1.0000.

With dilute sugar solutions, a pycnometer as much as 1 cc. "off" in capacity will give densities with very little error, but when working with more concentrated solutions a small correction must be made to the observed weights, since the 1 cc. excess capacity which, in the case of pure water, was compensated for by the 1 g. heavier tare, will now weigh more than 1 g. In the above case of a 101 cc. pycnometer with tare adjusted for pure water, if it be used with a solution of 1.3000 density, the extra 1 cc. weighs of course 1.30 grams, while only 1 g. has been compensated for by the excess weight of tare.

Knowing the capacity of a pycnometer, it is a simple matter to make a table of corrections to be applied at different densities. Such a table for a pycnometer containing 101 cc. (a cc. here being considered to be the volume occupied by 1 g. of water at the temperature taken as a standard for the density tables it is desired to use) would be as follows:

Weights used—grams....	100	101	105	110	120	130
Cor. to wts. (subtract)....	0.00	0.01	0.05	0.10	0.20	0.30 g.

According to the amount of change in tare needed to give a weight of 100 g. with pure water, a table such as the above can be easily constructed for any pycnometer; thus, if it contain 100.30 g. water at standard temperature, make tare equal weight of pycnometer + 0.30 g., and the correction table for different densities is the one given above multiplied by 0.30. The following is an example of pycnometer calibration:

Weight of Pycnometer................................	47.40 grams
Weight of Pycnometer + water at 29° C................	146.93
Weight of water......................................	99.53 grams

Assuming that this pycnometer is to be used with 17.5°/17.5° tables, and that the average temperature at which it is to be used approximates that of calibration, the change of volume due to expansion of glass may be neglected and the weight of water contained at 17.5° (or its volume in terms of "17.5° cc.") may be considered to be 99.53 × (density aq. 17.5° ÷ density aq. 29°) or 99.53 × (0.99872/0.99598) = 99.80. If a tare is then made to equal weight of pycnometer *minus* 0.20 g., or 47.20 g., the weights needed to balance pycnometer full of water at 17.5° will be 100 g., thus giving density direct. The correction for densities greater than 1.0000 will be:

Weights used....	100	101	105	110	115	120	125	130 g.
Correction (add)..	0.00	0.002	0.01	0.02	0.03	0.04	0.05	0.06 g.

After looking up the Brix corresponding to any density, the customary Brix correction for temperature of observation must of course be made.

In case the laboratory temperature prevailing were as high as that just noted, it would perhaps be more convenient to use tables calculated for 17.5°/27.5°, in which case the calculation of tare and correction table would be the following:

Weight water content at 27.5° = 99.53 × (0.99641/0.99598) = 99.57 g.
Weight tare should be 47.40 — 0.43 = 46.97 g.

Wts. used..	100	101	102	105	110	115	120	125	130 g.
Cor. (add)	0.00	0.004	0.009	0.02	0.04	0.06	0.09	0.11	0.13 g.

Where it is desired to use a pycnometer for juices or solutions of always the same approximate density, the correction for this density may be incorporated in the tare. In case the above pycnometer were to be used solely with solutions of about 15° Brix or 1.06 density, the correction could be added automatically by making tare 0.02 g. *lighter* than for pure water, *i. e.*, 46.95 g. instead of 46.97 g. Densities around 15° Brix would then be obtained by direct weighing, with absolutely no correction other than that for temperature subsequently applied to the Brix reading.

The calibration of a new pycnometer, including adjustment of a tare (best made from a small bottle weighted with shot) and construction of a correction table, can easily be done in less than an hour; the calibration of a new Brix spindle at three points on the stem, which is just as necessary, takes considerably more time than this.

An ordinary determination of density of a juice or diluted molasses consists simply of filling the pycnometer to the mark and weighing the centigrams on any ordinary sugar balance, which requires from 3 to 5 minutes, hardly more time than is needed for an *accurate* determination by means of the Brix spindle.

As regards accuracy, an error of more than 0.01 gram in weighing is unusual; this, at 15° Brix, corresponds to 0.023° Brix, or about one-fourth the average error in reading a Brix spindle.

Department of Sugar Technology
College of Hawaii, Honolulu, Hawaii

SEED ANALYSIS

By Nahum E. Katz

Received August 30, 1915

The chemical analysis of cotton seed is of interest and value to oil mill operators only when accompanied by a table showing the available yield of products that may be expected from each ton of seed.

The following formulae are offered as a method for calculating the theoretical yield of products per ton of seed, based on the results of a chemical analysis of the seed. As the derivation of the formulae is rather lengthy, it is omitted.

Let a = per cent kernels in whole seed
b = hulls in whole seed
f = per cent oil in whole seed
g = per cent ammonia in whole seed
l = per cent oil lost in the hulls, as made in the mill, due to imperfect separation
p = lbs. of oil left in cake
L = lbs. of lint removed in delinting
V = lbs. of waste due to mots, dirt, loss in moisture, etc.
A = per cent ammonia desired in the cake
0.2 per cent be assumed to be the average per cent of oil naturally found in the hulls as made in the mill
0.3 per cent be assumed to be the average per cent of ammonia naturally found in the hulls as made in the mill
r = lbs. of hulls, which are necessary to mix with the kernels in order to dilute the cake to the desired per cent of ammonia
z = per cent of r in the uncooked and unextracted meats.
H = lbs. of hulls to be made to the ton of seed
O = lbs. of oil to be pressed out per ton of seed
C = lbs. of cake to be made to the ton of seed

Then:

$$H = \frac{A(2000 - 20f + p + 0.04b - 1.002L) - 2000g}{1.002A - l(0.01A - 0.01) - g/a(3.33l - 0.67) - 0.3} \cdot \left(1 - \frac{V}{2000 - L}\right)$$

$$O = \left[(20f - 0.04b - p + 0.002L) . \left(1 - \frac{V}{2000 - L}\right)\right] - H(0.01l - 0.002)$$

$$C = 2000 - (H + O + L + V)$$

$$r = b\left(20 - \frac{V}{100}\right) - L - H(1.0067 - 0.0333l)$$

$$z = \frac{100r}{2000 - V - L - H}$$

C may also be calculated by the formula

$$C = \left[(2000 - 20f + p + 0.04b - 1.002L) . \left(1 - \frac{V}{2000 - L}\right)\right] - H(1.002 - 0.01l)$$

If it be agreed to consider the numerical values 0.7 per cent for l, 75 lbs. for L, and 57 lbs. for p, as standard values, then the above given formulae may be considerably simplified. They then appear as follows:

$$H = \frac{A(1981.85 - 20f + 0.04b) - 2000g}{0.995A - 1.66g/a - 0.3} . \left(1 - \frac{V}{1925}\right)$$

$$O = \left[(20f - 0.04b - 56.85) . \left(1 - \frac{V}{1925}\right)\right] - 0.005H$$

$$C = 1925 - (H + O + V)$$

$$\text{or} \quad C = \left[(1981.85 - 20f + 0.04b) . \left(1 - \frac{V}{1925}\right)\right] - 0.995\,H$$

$$r = b\left(20 - \frac{V}{100}\right) - 75 - 0.983H$$

$$z = \frac{100r}{1925 - H - V}$$

The formulae for r and z are especially valuable to the superintendent. Knowing the percentage of hulls which should be mixed with the kernels, and comparing it with the percentage obtained by an actual test on the meats, he is enabled to tell whether the proportions of kernels and hulls in the meats are correct or not, before the meats are carried to the crushing rolls.

Chemical Laboratory, Eagle Cotton Oil Company
Meridian, Mississippi

ADDRESSES

THE USE OF DIAGRAMS IN CHEMICAL CALCULATIONS

By Horace G. Deming

Received May 15, 1915

The use of charts or diagrams for the solution of arithmetical problems is well known to the engineering profession, and several books have been written on the subject.[1] Thus we have the graphical representation of forces and moments, Kutter's formula for the flow of water, indicator diagrams for steam engines, and vector diagrams for the diagrammatic representation or graphical solution of problems in alternating current theory. In metallurgy we have diagrams for the representation of the composition of slags; in chemistry the familiar rectangular and triangular diagrams for the representation of the phase relations between the members of two-component and three-component systems; and, in chemical technology, diagrams for the calculation of mixtures for the manufacture of cement.

In spite of such scattering instances of the use of graphical methods in industrial chemistry, it appears that chemists do not in general take advantage of the really remarkable opportunities that the use of diagrams presents for the quick solution of chemical problems met in every-day work; and but little systematic study of the possibilities of the graphical method in chemistry has ever been published.[1] The diagrams that are here presented are selected from among a large number devised by the writer with a view to illustrating some of the principal computations that may be solved by graphical means; they indicate at the same time what a great variety of problems are susceptible to such treatment, and what diverse types of diagrams may be used. It is hoped that those presented may suggest others better adapted to the individual needs of the readers of This Journal; for this reason it will be necessary to mention the mathematical principles on which the construction of the different types of charts is based; but, since we are concerned rather with general principles than with details of execution, we can do no more than refer to many interesting charts that differ from those here given in but a few particulars.

---

[1] d'Ocagne, "Traité de Nomographie," Paris: Gauthier-Villars; Peddle, "The Construction of Graphical Charts," New York: The McGraw-Hill Book Co.; Turner, "Graphical Methods in Applied Mathematics," London: Macmillan and Co.

[1] But see a series of articles by Nickel, *Z. physik. Chem.*, Vols. 10 to 14. Of somewhat different scope is Kremann, "Leitfaden der graphischen Chemie," Berlin: Geb. Borntraeger, 1910.

It is evident that any relation capable of exact mathematical expression may be given in graphical form. There are, in fact, many methods that might be used in any particular case. Considerations of ease of construction and accuracy of reading must determine which of the different possible charts is the one to be employed; or whether the desired result may not be most easily obtained by calculation with a slide-rule or by direct reading from a table.

The ordinary slide-rule is accurate to within about 1 part in 500, and the ordinary chart to within about 1 part in 250. The graphical method has the advantage that it can cover many complicated formulas involving operations impossible with a slide-rule; and a combination of slide-rule and chart will in many cases effect the greatest saving of time. For problems that demand a degree of precision not to be reached by the use of graphical methods, the latter often still afford a quick and convenient means of checking results, a fact which will lead us to consider one or two charts that we should otherwise regard as of little practical use.

RADIAL CHARTS

The familiar type of diagram, in which two variables are laid off along perpendicular axes on cross-section paper and the relation between them expressed by means of a curve, serves principally for the graphical representation of experimental results, presenting to the eye in an easily comprehensible form a collection of data that could not be so easily interpreted if given in a table. But, as a means of computation, charts of this form are of rather limited use, for the reason that the relation between two variables may generally be expressed most conveniently and accurately in the form of a table. It is only where the precise mathematical relation between two variables is unknown or very complicated, or where more than two variables enter that it may be worth while to construct a diagram to save a part of the labor involved in drawing up a table.

As an example of the simplest chart of this description let us consider the conversion of a temperature reading in Centigrade degrees into degrees of the Fahrenheit scale, according to the equation

$$F = 9/5C + 32.$$

This relation may be expressed as a straight line inclined to the horizontal axis at an angle whose tangent is 9/5, and cutting the vertical axis 32 units above the origin. This chart is shown in Fig. 1, its use being self-explanatory. It is evident that any other relation between two variables that can be put into the form

$$y = ax + b$$

can be expressed in a diagram of this type. In practice such a chart is best constructed by locating two points by calculation, then passing through them a straight line of indefinite length. The best sort of cross-section paper to use is that having heavily ruled square-centimeter divisions, with square-millimeter subdivisions (the so-called standard millimeter cross-section paper).

When the constant b in the above equation becomes zero we have a simple proportionality between the two variables. Problems of this sort are best solved with a slide-rule, where the quantity a is a real constant, invariable from problem to problem. But where a may have different values we make use of one of the types of charts illustrated in Figs. 2 and 3, which will be called *radial charts*, because they are characterized by a series of axes and construction lines that radiate from the lower left-hand corner.

In Fig. 2 we have a chart for the conversion of a given weight of one compound into the equivalent weight of another. In constructing this chart distances were first measured to the right along the horizontal axis, each equal (in centimeters) to one-fifth the molecular weight of some definite compound. From the points thus located vertical axes were erected and labeled with the formulas of the compound or elements to which they correspond. Thus the axis for magnesium oxide is placed $1/5 \times 40.32 = 8.06$ cm. to the right of the vertical axis; along the left side of the chart is laid down a scale of weights, each cm. being equivalent to 10 mg.

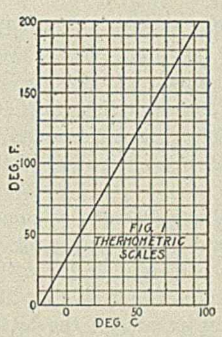


FIG. 1 THERMOMETRIC SCALES

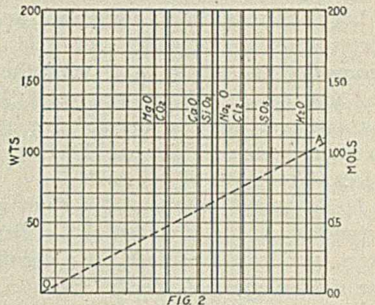


FIG. 2 CHEMICAL EQUIVALENTS

If it be required to convert 100 mg. of potash into its equivalent weight of carbon dioxide, locate a point A on the K_2O axis, corresponding to 100 mg. wt. Connect this point with the origin of O. Notice that the CO_2 axis is crossed at an elevation corresponding to 47 mg., the equivalent of 100 mg. of potash.

An axis at the right-hand margin of the chart, *20 centimeters from the origin*, gives the number of millimols of the substances concerned. Thus, in the problem we have just been considering, the dotted construction line cuts this axis at 1.06, the molecular equivalent of 100 mg. of potash or 47 mg. of carbon dioxide. It is apparent that the construction line OA need not actually be drawn, it being sufficient to lay a transparent straight-edge on the chart to connect the points A and O.

A chart of this kind might be used for calculating the weight of oxygen needed to burn a fuel of a given composition, the weight of silica necessary for combination with a mixture of basic oxides, or in general the weight of any one substance needed to react with definite weights of one or several others. Since the volume occupied by a given weight of a gas is inversely proportional to its molecular weight, we may use the same chart in calculating the volumes corresponding to definite weights of different gases, an additional axis in this case being erected 22.38 cm. to the right of the origin, since the gm.-mol. volume of gases is 22.38 l., and the oz.-mol. volume (by a happy accident) is very closely 22.38 cu. ft. If the weight of the gases be expressed in grams, their volume, read from the volume-axis, will be given in liters; if their weight be given in ounces their volume will be in cubic feet. Each centimeter of distance along the volume-axis will represent 2 units of volume, this being dependent on the scale-units used in graduating the horizontal and vertical axes. A chart derived from that just discussed may be used for converting solutions of one strength of specific gravity into equivalent weights or volumes of another strength. In Fig. 3 weights in lbs. or kg. are plotted along a

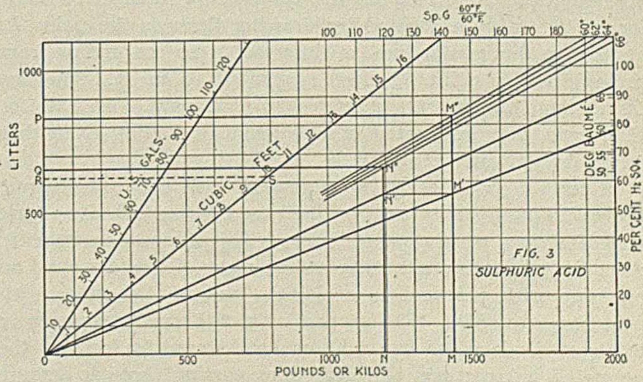


FIG. 3 SULPHURIC ACID

horizontal axis, and percentages of sulfuric acid along a vertical axis at the right-hand edge of the diagram. Specific gravities or degrees Baumé may conveniently be laid off along the vertical scale as well.

Let it be required to find what weight of acid of 66° B., corresponds to 1430 lbs. of acid of 60° B. Draw lines connecting the origin at *O* with the points corresponding to 60° and 66° B. From the point *M* corresponding to 1430 lbs. pass vertically to the 60° line at *M′*, thence horizontally to intersect the 66° line at *N′*, thence downward to *N*, where we read 1190 lbs. of 66° acid.

A slight modification of this chart will enable us to calculate volumes. At the left edge of the diagram lay down a scale of liters, and from the tenth main division of this scale lay off to the right a scale of specific gravities, in such a way that the slopes of straight lines drawn to connect points on the latter scale with the origin will in all cases be equal to the reciprocal of the specific gravity. In the figure, four such lines have been drawn, namely those passing through points on the specific gravity scale corresponding to 60°, 62°, 64° and 66° B.

Let it now be required to convert 1190 kg. of acid of 66° B. into liters. From 1190 on the horizontal scale (which in this case must be read in kg. instead of in lbs.) we pass upward to *N″* on the line drawn through the gravity corresponding to 66° B., thence horizontally to *Q*, where we read 650 liters, *Ans.*

Let us consider one more problem, in which 650 liters of acid of 66° B., are to be converted into liters of acid of 60° B. From the point corresponding to 650 liters, at *Q* on the vertical scale, pass horizontally to intersect the 66° gravity line at *N″*, thence vertically downward to intersect the 66° weight line at *N′*, thence horizontally to the 60° weight line at *M′*, thence upward to the corresponding gravity line at *M″*, thence horizontally to *P*, where we read 830 liters, *Ans.*

If weights of acid are not to be considered, but volumes alone, as in the last example, the chart as just described may be made to read in other units than those of the metric system, the vertical scale at the left being simply relabeled gallons or cubic feet. But if weights of acid are to be used in the calculation, it will be necessary to graduate new axes for the U. S. gallons or cubic feet. If the horizontal axis be read in lbs. the vertical axis will give the number of lbs. of water occupying the same volume at 60° F. Since 623 lbs. of water = 10 cu. ft., an axis for cu. ft. may be located by drawing through the point *R*, at 623, a horizontal line to intersect a 10 cm. radius from the origin at a point *S*, which is marked 10 cu. ft. The line *OS* is then drawn and graduated to that scale. An axis for U. S. gals. may be located in a similar way, having given that 833.7 lbs. of water at 60° F. = 100 U. S. gals.

In certain problems we have to deal with two constituents. For example, we may need to find the SO_3 content of sulfuric acid of a given percentage of H_2SO_4. This is most conveniently done by graduating the scale at the right of the diagram, on one side with percentages of H_2SO_4, and on the other with percentages of SO_3. The vertical axis of Baumé degrees is in this case displaced to the right, and graduated by locating the points of intersections of radial lines passing through definite percentages. With such a chart we can calculate the amount of water to be added by fuming acid in order to convert it into commercial acid of any desired strength.

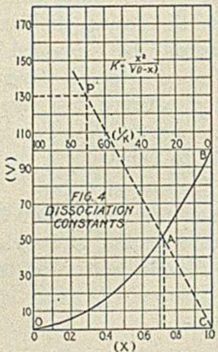
This type of chart might be used to calculate the amount of water to be added to a solution of definite strength to produce a solution of another strength, for the difference between equivalent weights of two solutions must represent the weight of water to be added to the stronger one. Charts of this type have also been devised for calculating the amount of filler to be added to a fertilizer to reduce it to a desired percentage of a single element; for determining the amount of water to be removed by evaporation during the concentration of a solution from a lower to a higher density; and for calculating the proportions in which two raw materials need to be mixed in order to produce a mixture containing a given percentage of some one constituent. But, since problems of this sort may be solved somewhat more conveniently by means of other charts to be described later, no description of these diagrams need be given.

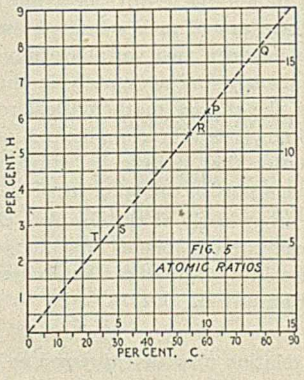
It is worth while noting that radial charts, such as those described above and illustrated in Figs. 2 and 3, may be used for the solution of any problem, in which the relation

$$x/a = x'/a'$$

obtains, x and x' being distances along the horizontal axis, and $1/a$ and $1/a'$ being constants proportional to the slopes of the radiating lines. The constants a and a' should have unchanging values in all the problems that are to be solved by the use of a given chart, since in this case we may draw the radiating lines once for all when the chart is first constructed. If a and a' are variables, we are forced to draw new lines with slopes respectively proportional to $1/a$ and $1/a'$ for each problem to be solved, or to draw in the beginning a great number of radiating lines, and afterward resort to interpolation. For this reason a set of computations in which the constants a and a' vary from problem to problem is best carried out by a modification of the "figure-four" chart to be described later.

The principles involved in the preceding diagrams may frequently be applied in the solution of rather complex formulas.





As an example, let us consider that for the constant of dissociation of a gas yielding two gaseous products of dissociation:

$$k = \frac{x^2}{(1-x)V}.$$

In Fig. 4 the values of x are laid down along the horizontal axis and the curve *OAB* drawn through the calculated values of x^2. The values of V are then laid down along the vertical axes and the values of the *reciprocal of k* from right to left along a horizontal axis. Given 72 per cent dissociation and a volume of 130 calculate the constant of dissociation. Enter the diagram at 72 on the base-line, pass upward to cross the curve at the point *A*. Connect *A* with *C* and produce the line thus obtained until it cuts the horizontal line passing through 130 units of volume, at *P*. Passing downward we read the value of $1/k$, *viz.*, 70, from which $k = 0.143$. *Vice versa*, if we have a volume of 130 units and know that the value of $1/k$ is 70, we locate the point *P* corresponding to these data and draw the line *PC*; from the point *A* where this line cuts the curve, we pass vertically to the base line, where we read 72 per cent dissociation.

Of course in practice it is unnecessary to draw the construction lines in this and similar diagrams. If the edge of a transparent triangle is passed through the desired points or, better yet, a straight line scratched on the under side of a sheet of celluloid, it will be possible to make readings directly. The horizontal scale through the middle of the diagram might also have been graduated directly in values of k, instead of in reciprocal values, by laying down graduations proportional to the reciprocal of the numbers that appear in Fig. 4; but scales of reciprocals have the disadvantage that their divisions are not equal, hence there is a loss of accuracy in interpolation. For this reason it is better to read the values of $1/k$ directly, and convert them into values of k by means of a slide-rule or table of reciprocals.

RECTANGULAR COÖRDINATE CHARTS

Closely related to the preceding type of chart is one in which the composition of a compound or mixture is expressed by the rectangular coordinates of a point in a plane or in space. As an example, let us take a chart for the determination of the ratio of the number of atoms of carbon and hydrogen in an organic compound, having given the percentage of each of these elements (Fig. 5).

Along the vertical axis of the diagram is laid down a scale of hydrogen, in such a way that the percentages of that element in the compounds to be considered fall within the limits of the chart. Along the horizontal axis is laid down a scale of percentages of carbon, in such a way that 11.9 per cent of carbon is the same linear distance as 1 per cent of hydrogen, since the atomic weight of carbon is 11.9 (on a basis of $H = 1$). The horizontal and vertical divisions of the chart are also marked 5, 10, 15, etc., to indicate the relative number of atoms of each element.

Let us suppose that a given compound contains 60.0 per cent of carbon and 6.1 per cent of hydrogen. Locate the point P corresponding to this composition and lay a straight edge through OP. Where this line happens to pass through the corner of a square may be read the atomic ratio. It will be seen that there are four corners, Q, R, S, and T, which very nearly coincide with the given line. Q corresponds with the ratio $C_{13}H_{16}$, R with C_9H_{11}, S with C_5H_6, and T with C_4H_5. Which of these formulas is the correct one will of course need to be determined from other considerations; for the errors of organic combustion methods are of such a magnitude as to leave the matter of a formula more or less in doubt, unless the percentages of the elements other than carbon and hydrogen be taken into consideration.

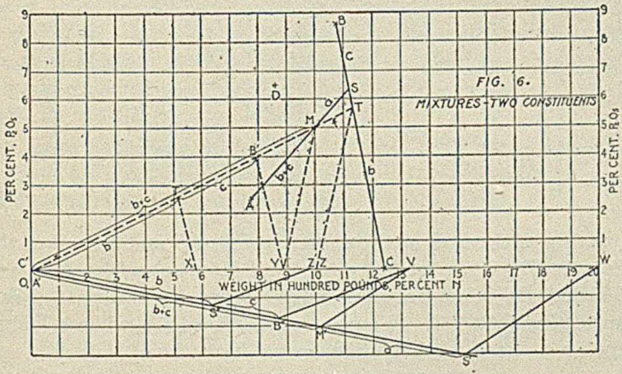


FIG. 6. MIXTURES—TWO CONSTITUENTS

Another method of working this same problem is to convert the percentage of hydrogen found into its equivalent percentage of carbon by means of the radial diagram of Fig. 2. The ratio between this number and that giving the percentage of carbon actually found is then taken by means of a slide-rule. The chart just described may of course be modified for use with any other pair of elements.

In Fig. 6 we have a diagram for the adjustment of various raw materials to give a mixed fertilizer containing desired percentages of nitrogen and phosphorus. Percentages of nitrogen are laid off along the horizontal axis, and percentages of phosphoric acid (P_2O_5) along a vertical axis. Suppose that we have to prepare a mixed fertilizer containing 10 per cent nitrogen and 5 per cent P_2O_5 (point M) and that there are available for the purpose the four fertilizers whose compositions are expressed by the four points, A, B, C and D, together with filler, which, since it contains zero per cent of the elements of plant food, is of course represented by the point O. It will first be noticed that the point M, representing the required composition of the mixed fertilizer, lies within a triangle formed by connecting up the points A, B and C; this means that it is possible to secure the desired mixture by a combination of these three raw materials. On the other hand, a triangle obtained by connecting the points A, C and D does not include the point M; it is therefore impossible to produce the desired mixture by any combination of these three raw materials alone, in spite of the fact that some of the raw materials contain *more* and others *less* nitrogen or phosphoric acid than the mixture. The first use of the chart we have constructed is therefore to tell us which of the various raw materials placed at out disposal may be used in making up a mixture of the desired composition.

Now suppose that it is desired to make up 1000 lbs. of the mixture having the composition denoted by the point M, using for the purpose the raw materials B and C and filler. Connect B and C, and draw from the point O, representing filler, a line passing through M, which is produced until it cuts the line BC at T. From T draw the line TZ to the point representing 1000 lbs., the weight of mixture to be made. Draw the line MY parallel to TZ to intersect the base line at Y.

That portion of the line BC *most distant* from B is marked b, and that most distant from C is marked c; in the same way that portion of OT most distant from O (filler) is marked f, while that most distant from B and C is marked $b + c$. The distances OB' and OT' are laid off equal to CB and CT, respectively and the segments thus found are marked b and c according to the portion of BC to which they correspond. Next connect B' with the point Y, previously located, and draw $T'X$ parallel to $B'Y$. The distance OX, lying under the segment b of the line OT, is the amount of raw material B needed to make up the fertilizer; the distance XY, lying under the segment c, is the amount of C to be taken; while the distance YZ, lying under the segment f, is the amount of filler needed.

If for any reason it had been decided to make up the mixed fertilizer from A, B and C, without using any filler, the construction lines needed would have been those shown full length in the diagram to distinguish them from the broken construction lines of the preceding problem. Draw the line AM through M, the point representing the composition of the desired mixture, and produce it to intersect BC at S. Since the line AS does not pass through O, it will be necessary in this case to draw an auxiliary line $A'S'$ making any convenient angle with the base line. Along this line take $A'M'$ any convenient multiple of AM (say three times AM), and $A'S'$ that same multiple of AS. If 2000 lbs. are to be made, connect S' with the point W representing that weight, and draw $M'V$ parallel to $S'W$. The segments MS and $M'S'$ are labelled a, and the segments AM and $A'M'$ are labelled $b + c$. The distances CS and CB are transferred to OS'' and OB'', and the construction finished by drawing the parallel lines $B''V$ and $S''Z'$. The distance OZ', under the segment b of the line $C'S'$, represents the amount of raw material B to be taken; the distance $Z'V$ represents the amount of C; and the distance VW represents the amount of A that will be needed.

The preceding chart may be adopted very readily to the preparation of mixtures of any sort in which definite precentages of two different components are to be secured. If three different components are to be considered, the same chart may be used provided that the sum of the three adds up to 100 per cent; or a slight modification of the chart, which cannot be presented here, will serve for more complex cases. If each of the raw materials contains but a single one of the constituents to be considered in the final mixture, the problem becomes simply one in inverse proportion, and may be most simply solved by means of a slide-rule. It is worth mentioning that another modification of the chart last described will permit one to calculate the proportions in which feeding-stuffs need to be mixed in order to form a standard ration according to any one of the several systems in use.

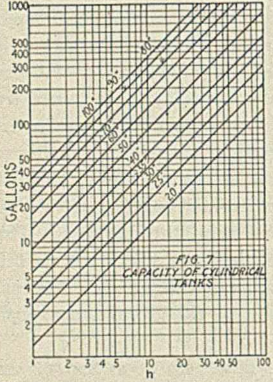


FIG. 7
CAPACITY OF CYLINDRICAL TANKS

LOGARITHMIC CROSS-SECTION CHARTS

Our next class of charts includes those plotted on logarithmic cross-section paper, namely, on that in which the graduations along the perpendicular axes are proportional to the logarithms of the variables, instead of to the variables themselves. This paper may be obtained from dealers in draftman's supplies.

Since the equations

$$y = ax \quad \text{and} \quad x/a = x'/a'$$

may be put in the logarithmic form

$$\log y = \log a + \log x, \text{ and, } \log x - \log a = \log x' - \log a',$$

it is possible to construct logarithmic cross-section charts to solve the same problems as the radial charts of Figs. 2 and 3. There is, however, nothing important to be gained by such a procedure, and there is even some loss of accuracy in so doing, since interpolations are less easily made on logarithmic cross-section paper.

The most important use of the logarithmic charts is in the solution of equations of the general form

$$y = a^m x^n;$$

but in equations in which several factors are to be multiplied together such charts are very convenient, providing that a reading to the nearest 2 or 3 per cent is accurate enough for the purposes in hand. In Fig. 7 is a chart for the capacity of cylindrical tanks in U. S. gallons, the diameter of the tanks and the depth of the liquid being given in inches. In this case the formula used is

$$C = \frac{\pi d^2 h}{4 \times 231},$$

where d is the diameter of the tank in inches, and h is the depth of the liquid it contains. Putting this into the logarithmic form we have

$$\log C = \log \frac{\pi d^2}{924} + \log h.$$

Note that all the constants in the equation are combined with a single variable d, the variable h, representing the depth of liquid in the tank, being kept free of constants.

To construct the chart work out the values of $\frac{\pi d^2}{924}$ by means of a slide-rule for all the values of d that are likely to be used, and lay off the results along the vertical logarithmic scale. From the points thus located draw a series of lines sloping upward toward the right at an angle of 45° with the horizontal, and label each with that value of d to which it corresponds. Along the horizontal axis lay down a logarithmic scale of depths (values of h, in inches) and graduate the vertical axis in gallons.

Logarithmic cross-section paper is very useful in recording results that would extend over too great a range if plotted on ordinary cross-section paper; for example, in the plotting of absorption spectra, the coördinates representing respectively logarithms of vibration frequencies and millimeters length of the absorbing layer of solution. In certain work experimental results plotted on logarithmic cross-section paper fall very nearly on a straight line, where ordinary cross-section paper would give a curve; this happens, for example, in a study of the volumes of filtrate delivered by a filter-press in varying periods of time. If an empirical equation exists connecting the variables in such a set of experimental data, a logarithmic chart will frequently reveal its form and the values of some of the constants that appear in it much more readily than they may be obtained in any other way.

FIGURE-FOUR CHART

An equation of the general form

$$ax + by = u/v$$

may be treated by means of a chart we are about to discuss, which has two parallel axes intersected by a third in such a way as to remind one of a "figure-four."

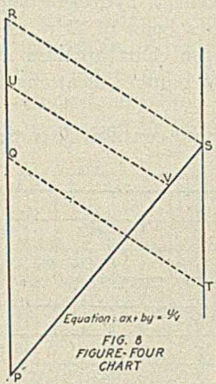


FIG. 8
FIGURE-FOUR CHART

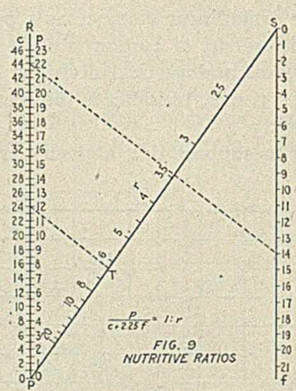


FIG. 9
NUTRITIVE RATIOS

In Fig. 8 the axes of the chart are PR, PS and ST. Let the distance $PQ = ax$; let $TS = by$; let $PU = u$; and let $PV = v$, UV and RS being drawn through U and S parallel to a line connecting Q and T. We have then $QR = TS$, whence $PR = ax + by$. From similar triangles we have then

$$PR : PS = PU : PV;$$

that is,

$$ax + by = u/v,$$

if the distance PS be taken as unity.

As a first example of the application of this chart let us consider the equation for finding the nutritive ratio of a foodstuff, *e. g.*,

$$\frac{p}{c + 2.25f} = \frac{1}{r}.$$

Putting this in the standard form for the type of chart we are discussing, we have

$$c + 2.25\,f = \frac{p}{1/r}.$$

To construct this chart (Fig. 9) lay down a scale of percentages of digestible carbohydrates along the axis PR, in such a way that the highest percentage met will fall within the limits of the chart. Draw an inclined axis making any convenient angle with the axis just drawn, and take PS a measured distance equal to, say, 30 centimeters. From S lay down a scale of percentages of digestible fat, and graduate it downward, using a scale unit 22.25 times that used in graduating the scale of digestible carbohydrates.

On the opposite side of the axis PR from the graduations representing percentages of digestible carbohydrates, lay down a scale of digestible protein. If the unit of this scale be taken as n times the unit of the carbohydrate scale, then unit distance along the inclined axis will be n times the distance PS. In this particular case it will be convenient to have the divisions of the protein scale twice as long as those of the carbohydrate scale; the unit distance along PS will then be $2 \times 30 = 60$ cm. Now since the quantity $1/r$ appears in the equation above in place of the variable v in the general equation of this type of chart, we must take the reciprocals of the various values of r, thus getting a series of fractions 1/3, 1/4, 1/5, etc. Since the unit distance along PS is 60 cm. the point corresponding to the fraction 1/3 will be 20 cm. from the left end of the inclined axis. This point is marked with the value of r, which is of course 3, since $1/r$ is 1/3. In a similar way locate other points corresponding to other values of $1/r$ and mark them with the values of r. A skillful combination of slide-rule and engineer's scale will enable any one to graduate this part of the chart in a few minutes.

To use the chart lay down the edge of a draftsman's triangle to connect the percentages of digestible carbohydrates and fat (say 44 and 14 per cents, respectively). Slide the triangle along the edge of another triangle until its ruling edge passes through the percentage of digestible protein (say 12 per cent). The place where this edge of the triangle cuts the inclined axis (at T) gives the second term of the nutritive ratio, which in this case is read 1 : 6.3.

Another way to use this chart is to construct it on paper thin enough to be transparent to a series of heavily ruled parallel lines on a sheet placed beneath it. The chart is moved until one of these parallel lines, seen through the transparent paper of the chart, connects the percentages of carbohydrate and fat; then another parallel line, passing through the percentage of protein, is followed up until it intersects the inclined axis, where the nutritive ratio is read.

A chart very similar to that just described might be constructed for calculating the rate of transfer of heat from circulating hot water to iron, according to the equation

$$\frac{H}{t} = \frac{1.67 + \sqrt{v}}{0.02},$$

where H is the number of calories of heat transferred in one second to a square meter of surface, t is the temperature difference between water and metal (degrees C.), and v is the velocity of the water in centimeters per second.

In Fig. 10 we have a chart for converting specific gravities greater than unity into degrees of the Baumé scale. In this case the inclined axis of the chart has been made horizontal, though this need not necessarily be done. A point P is located on the left axis 145 units above the horizontal axis; the right-hand axis is graduated in the same scale units as those used in locating P; while the horizontal axis is graduated in specific gravities, the distance between the two vertical axes being taken as unity. A line connecting the point P with the observed specific gravity will intersect the vertical axis in the corresponding number of the Baumé scale. The equation for this chart is

$$145 - b = 145/g,$$

the values of b being laid off *upward* along the right-hand axis, because of the negative sign of b in the equation.

The equation for the constant of a unimolecular reaction may be put into the form

$$\log a - \log (a - x) = \frac{t}{1/k},$$

which is evidently one capable of being solved with the help of a chart of the kind we have been considering. In Fig. 11 the scales for a and $a - x$ are logarithmic, while those for t and $1/k$ are not. Of course the values of k corresponding to the different values of $1/k$ might have been calculated and laid down on the chart, but in practice it will be found more convenient to convert values of $1/k$ read from the chart into values of k by the use of a slide-rule or table of reciprocals. The equation for the constant of a bimolecular reaction may be worked out with this same chart, the values of $a(b - x)$ and $b(a - x)$ being read from a slide-rule before the chart is entered.

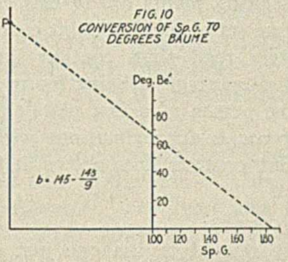


FIG. 10
CONVERSION OF Sp.G. TO DEGREES BAUME

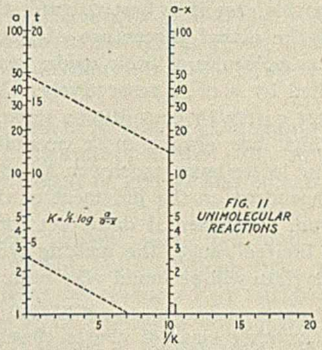


FIG. 11
UNIMOLECULAR REACTIONS

A diagram of this sort is probably the quickest means of determining the order of a reaction being investigated for the first time.

As a final example of a chart of this class, consider that in Fig. 12 for the representation of the composition of furnace slags. This chart is constructed on cross-section paper, each main (centimeter) division of the cross-sectioning representing 2 per cent silica in the slag, or some equally convenient figure. A scale of percentages of silica is plotted just within the left-hand border of the chart.

Just outside the scale of silica lay down a scale of lime, such that the point corresponding to 30.15 per cent silica ($SiO_2 \div 2 = 30.15$) coincides with the point corresponding to 28.04 per cent lime ($CaO \div 2 = 28.04$). At the right-hand side of the chart construct a scale of ferrous oxide, letting 35.92 per cent FeO occupy the same linear distance as 30.15 per cent SiO_2.

As an example of the use of the chart let us suppose that a slag is found to have the percentage composition FeO, 44; CaO, 17; SiO_2, 37; other substances, 2. Required its chemical formula and approximate melting point. Connect the point M, representing the ferrous oxide, with the point N, representing the lime; at P, where the inclined axis is crossed, we read "33 molecules of CaO in the slag for 100 molecules of (FeO + CaO)." From a point, S, representing the silica in the slag, draw a line, ST, parallel to MN. The point T, where the inclined axis is crossed, will give the number of molecules of SiO_2 for 100 molecules of (CaO + FeO). In the present case there are 33 molecules of lime, 67 molecules of ferrous oxide, and 67 molecules of silica for 100 molecules of basic oxides, hence the formula of the slag is very closely

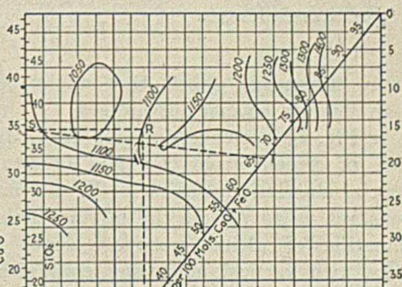


FIG. 12
SLAGS

$$CaO.2FeO.2SiO_2.$$

This chart gives also the melting points of slags of various compositions. Thus, if we pass vertically upward from P to meet the horizontal from S at the point R, we find ourselves on the contour line marked 1100°, the melting point of the slag in question. The diagram shows, moreover, that a slight increase in the percentages of ferrous oxide and silica at the expense of the lime would result in a slag of lower melting point.

In the case of highly acid slags the point *T* will lie so far to the right as to fall entirely without the limits of the diagram. In this case it is best to enter the chart with half or one-fifth of the actual percentage of silica, the molecules of silica per 100 molecules of basic oxides read from the chart being multiplied by 2 or 5, respectively. Melting points are in this case best gotten by consulting a separate set of melting-point curves, which are always more accurately read than contour lines. The latter have, moreover, the disadvantage of being too much dependent on the judgment of the person who first plots them from experimental data; yet for rough approximations within a limited range, the melting point contour lines shown in the diagram will be found very useful.

MIXTURE CHARTS

Another class of charts closely related to the one just described is that for dealing with mixtures. Many special cases occur, according to whether the composition of the final mixture or either of its constituents is constant or variable in composition; according to whether results are to be calculated to a basis of a fixed weight of mixture or of one of its constituents; and according to whether or not different ingredients are to be reduced to a basis of chemically equivalent quantities, etc. Lack of space prevents us from giving more than three of the many interesting charts that might be presented here, each with its own special advantages.

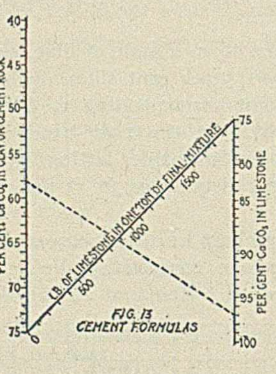


FIG. 13
CEMENT FORMULAS

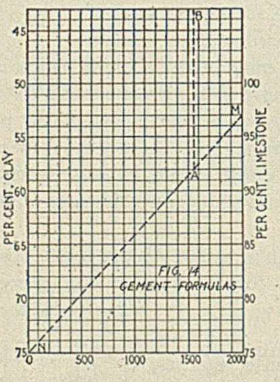


FIG. 14
CEMENT FORMULAS

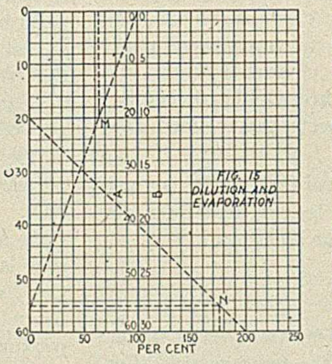


FIG. 15
DILUTION AND EVAPORATION

In Fig. 13 is a chart for preparing mixtures for the manufacture of cement from clay and limestone, assuming the content of alumina and silica in the raw materials to be so nearly constant as to permit the mixture being controlled by determinations of calcium carbonate alone. To construct this chart draw two vertical axes, any convenient distance apart, and graduate them, *both downward*, in percentages of calcium carbonate, choosing such a scale unit that the percentages of calcium carbonate likely to be met in the clay or cement rock (left axis) and in the limestone (right axis) fall within the limits of the chart. It is necessary to use the same scale unit in graduating both axes, but neither scale needs to be carried upward to zero, nor is the relative position of the lower limits of the two scales a matter of any importance. If the final mixture is to be adjusted to 75 per cent $CaCO_3$, connect the points marked 75 per cent on the two scales, and divide the inclined axis thus gotten into twenty equal parts, each representing 100 lbs. of limestone *in one ton of final mixture*.

As an example of the use of this chart, suppose that we have a cement rock containing 58 per cent $CaCO_3$, and a limestone containing 97 per cent $CaCO_3$. Connect these two points, best by means of a straight line scratched on the lower surface of a sheet of transparent celluloid. Where the inclined scale is crossed is read 875 lbs., the weight of limestone to be contained in one ton of the mixture.

Not only may diagrams similar to that just described be used to calculate the proportions in which two raw materials of variable composition need to be mixed in order to give a mixture of constant composition, but the converse problem may be solved: if the ingredients of a mixture are of constant composition the proportions in which they are present in a given mixture may be readily determined. Thus, if a sample of red lead is assumed to consist of a mixture of litharge and lead dioxide (disregarding the possible presence of other oxides of lead) the percentage of each may be gotten from a determination of the percentage of lead in the mixture, points representing the percentages of lead in litharge and in lead dioxide, respectively, being located on separate axes and connected by a line, which is graduated from left to right in percentages of that oxide whose composition has been located on the right-hand axis. By connecting points on the two vertical axes representing the percentage of lead found in a given sample of red lead, the percentage of litharge and of lead dioxide may be read directly from the chart. The reader will have little difficulty in adapting this chart to other cases of indirect analysis.

Returning now to a consideration of the preparation of mixtures of limestone and clay for the manufacture of cement, if we wish to calculate the weight of limestone to be taken, not for a *ton of mixture* as before, but *for a ton of clay*, we have the diagram shown in Fig. 14. Notice that here the percentages of calcium carbonate are laid down along vertical axes, starting from a horizontal base-line, the graduations of one scale running downward, and those of the other upward. To use this chart pass a straight line through the point denoting the percentage of calcium carbonate in the limestone (*M*) and that denoting the percentage of calcium carbonate in the final mixture (*N*). This line intersects a horizontal line (of the cross-sectioning) passing through the percentage of calcium carbonate in the clay at some point *A*. From this point pass upward to the point *B*, where we read the number of pounds of limestone that will be needed for one ton of clay. Thus, if the clay contains 58 per cent $CaCO_3$ and the limestone 97 per cent $CaCO_3$, there will be needed 1535 lbs. of limestone for every ton of clay. If the percentage of calcium carbonate in the clay is so low that there will be needed more limestone than clay, the cross-sectioning of the chart may be carried further to the right; or the problem may be so changed as to calculate the number of pounds of clay to be used for one ton of limestone.

In Fig. 15 we have a chart for determining the number of pounds of water that must be added to a given weight of solution of definite specific gravity or percentage strength in order to produce a definite diluted solution; or the number of pounds of water that must be evaporated from a given solution in order to produce a more concentrated one.

The chart is constructed with three vertical axes, *A*, *B*, and *C*, the unit of scale *B* being twice that of scales *A* and *C*. The horizontal distance between the axes *A* and *C* is divided into 100 equal parts representing percentages of evaporation or dilution. Since dilution may amount to more than 100 per cent, the graduations are carried out to the right of scales *A* and *B*, say to 250 per cent.

As an example of the use of this chart, let us suppose that a sugar solution of 20° Brix is to be evaporated to a syrup of 55° Brix. Connect this point on scale *C* representing 55° Brix with the zero of scale *A* (representing water). At the point *M*, where the horizontal through 20° Brix is crossed, we read 64 per cent evaporation.

Conversely, if 64 per cent of water were to be evaporated from a solution of 20° Brix, locate the point *M* where the vertical through 64 per cent intersects the horizontal through 20° Brix (scales *A* and *C*). Connect the point *M* with the zero of scale *A*, and produce the line thus gotten until it cuts the *C*-scale at 55°, the required Brix of the syrup.

In a similar way we might calculate the amount of water that would need to be added to a syrup of 55° Brix to dilute it to 20° Brix. Note that in this case the result is the number of pounds of water to be added for every 100 pounds of *diluted* solution.

If it is desired to calculate the dilution for 100 parts of syrup as is generally the case, instead of for 100 parts of diluted solution, a somewhat different method is used. Thus, if we wish to determine the water that would have to be added to a solution of 55° Brix in order to produce one of 20° Brix, connect the points representing 20° Brix on scales *B* and *C*. Where this line cuts the horizontal through 55° Brix (scale *A*) we read 175, the number of parts of water to be added to one hundred parts of syrup (by weight).

Since scale *A* is used only in problems dealing with dilution, it may be omitted from the chart if only evaporation is to be considered. In any case it is better to letter scale *A* in red ink, since there is otherwise some danger of interchanging scales *A* and *B* in reading the chart. The reader will perceive that a chart of this sort may be used for diluting concentrated solutions of any kind from one percentage strength to another. If specific gravities or degrees Baumé are to be used the scales are graduated, first in percentages, the percentage graduations being erased after a scale of specific gravities or degrees Baumé has been laid down. It is only with sugar solutions and the Brix scale that the percentage strength of the solution will be directly given by the areometer reading. If volumes of solutions are to be brought into consideration in dilution problems, a modification of the diagram given in Fig. 3 will be found to offer the most convenient solution.

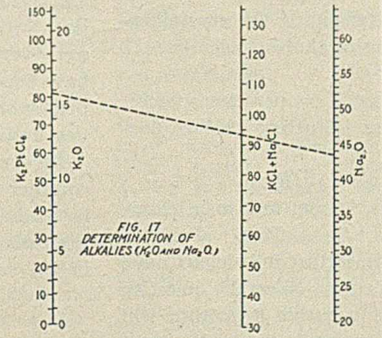


FIG. 17
DETERMINATION OF ALKALIES (K_2O AND Na_2O)

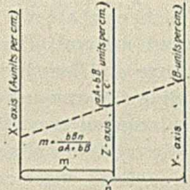


FIG. 16
ALINEMENT CHART

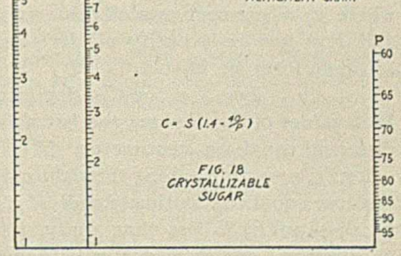


FIG. 18
CRYSTALLIZABLE SUGAR

ALINEMENT CHART

The next type of chart to be considered is that in which three variables are connected by the equation

$$ax + by = cz.$$

This chart consists of three parallel axes (Fig. 16), the left-hand one being for the values of x, the right-hand one for y, and the middle one for z. To construct this chart draw the left and right axes exactly parallel, at any convenient distance apart. Graduate the left axis in values of x at the rate of A units per centimeter, beginning the graduations at any convenient point on the axis, A being so chosen that the scale for x and the scale for z (to be graduated afterward) will not be inconveniently long or short. In a similar way graduate the right axis at the rate of B units per centimeter. Now it may be shown by geometry that if each value of z is to lie in the same straight line with corresponding values of x and y (on the other two axes), then the distance m from the left axis to the middle axis must be such that

$$m = \frac{bBn}{aA + bB},$$

where n is the distance between the two outside axes; and that the middle axis must be graduated with values of z at the rate of C units per centimeter, where

$$C = \frac{aA + bB}{c}.$$

The chart is used by lining up corresponding values of x, y and z by means of a straight edge, whence the name *alinement chart*.

In Fig. 17 we have a chart for determining the milligrams of sodium oxide and of potassium oxide, respectively, shown by an analysis in which the two metals are first weighed as chlorides, the potassium being afterward collected and weighed as potassium chloroplatinate. Since the factor for converting potassium chloroplatinate into potassium chloride is 0.3068, and that for converting sodium oxide into sodium chloride is 1.583, we have

$$0.3068\,x + 1.583\,y = z,$$

where x is the number of milligrams of potassium chloroplatinate obtained, y is the number of milligrams of sodium oxide in the sample, and z is the combined weight of sodium and potassium chloride.

Let the outside axes be taken 20 cm. apart. Graduate the left axis at the rate of 5 mg. of potassium chloroplatinate per centimeter. The right axis is to be graduated in milligrams of sodium oxide at the rate of 2 mg. per centimeter, beginning with 20 mg. (if that is the least weight of sodium oxide that is likely to be met in any of the analyses). The distance from the left axis to the middle axis is then

$$m = \frac{2 \times 1.583 \times 20}{5 \times 0.3068 + 2 \times 1.583} = 13.47 \text{ cm.}$$

Locate the middle axis at this distance to the right of the left axis. Now 40 mg. of sodium chloride are equivalent to 40 ÷ 1.583 = 25.25 mg. of sodium oxide. Therefore lay a straight edge to connect the zero of the potassium chloroplatinate scale with 25.25 of the sodium oxide scale. The point where the middle axis is crossed is marked 40. In the same way 100 mg. of sodium chloride correspond to 63.16 parts of sodium oxide; therefore connect the zero of the potassium chloroplatinate scale with 63.16 on the sodium oxide scale, and mark the point where the middle axis is crossed 100. The distance between the points 40 and 100 on the middle axis is then divided into sixty equal parts and the graduations continued upward and downward to the limits of the chart.

As an example of the use of the chart, let us suppose that a mixture of the chlorides of sodium and potassium weighs 94 mg. and that 81.8 mg. of potassium chloroplatinate are obtained. Connect these points on the middle and left axes, respectively, by a straight edge; where the latter intersects the right axis is read 43.5 mg. of sodium oxide, while just within the left margin of the chart we read 15.9 mg. of potassium oxide. The scale of potassium oxide here referred to is constructed by dividing the space between 0 and 100 of the potassium chloroplatinate scale into 19.38 equal parts, since the factor for converting potassium chloroplatinate into potassium oxide is 0.1938.

Of course the preceding chart might have been constructed with any other rate of graduation for the outside axes, the middle axis being placed accordingly, and either of the outside axes might have been begun at any convenient point. When one point of the middle axis has been located by calculation, the other graduations may be laid down by the method just described; or, if the calculated value of C in the equation above happens to be a round number all the divisions of the middle scale may be laid off directly with an engineer's rule. This type of chart may be used in a great many indirect analyses; for example, those in which the percentage of each of two metals in a mixture of their carbonates is determined from the volume of carbon dioxide that the mixture evolves on being treated with an acid; or those in which the amount of each of several gases in a mixture is determined from the decrease in volume observed and carbon dioxide formed when the mixture is burned. A modification of the chart in Fig. 13 will frequently serve the same ends. Other uses for the alinement chart are in calculating the formulas of isomorphous mixed minerals from analytical data, in calculating heat exchange and loss by radiation in evaporation problems, and in finding the amount of a given substance necessary to react with a mixture of two others.

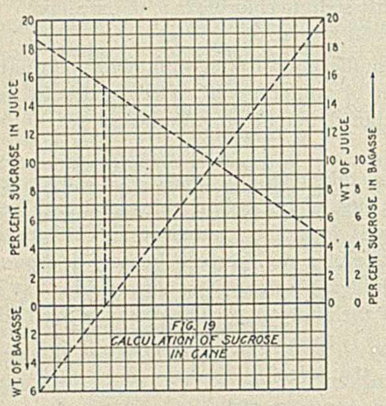


FIG. 19 CALCULATION OF SUCROSE IN CANE

Fig. 18 is an alinement chart for determining the crystallizable sugar in sugar-cane juice, according to the formula

$$C = S\,(1.4 - 40/P),$$

where C = per cent crystallizable sugar; S = per cent sucrose; and P = per cent purity of the juice. Putting this in logarithmic form we have

$$\operatorname{Log} S = \log C - \log\,(1.4 - 40/P).$$

Plot values of log C along the left axis, letting unit logarithmic distance equal 25 centimeters ($A = 1/25$). Plot values[1] of $-\log\,(1.4 - 40/P)$ along the right axis, letting unit logarithmic distance equal 100 centimeters ($B = 1/100$). Since the quantity $(1.4 - 40/P)$ is less than unity, its negative logarithm will be positive, and is hence measured upward along the right axis. If the total distance between the outside axes is 20 cm., the middle axis will need to be 4 cm. from the left axis. The middle axis is graduated at a rate which may be calculated to be 1/20 unit per centimeter (from the general equation for the value of C in the discussion above of the principle of the alinement chart).

This chart is given, not so much because of its practical importance, as because it illustrates as well the way in which a very complicated equation may often be solved by the alinement chart method. In practice it would be easier to calculate crystallizable sugar from another formula, in which the Brix of the solution is used instead of its purity, *e. g.*,

$$C + 0.4\,B = 1.4\,S.$$

This may be charted at once by the alinement method, without recourse to logarithms, or even as a figure-4 chart.

COMBINATION CHARTS

Other types of charts might be described, but it will be found that in practice the ones here given will serve for the solution of almost any problem that does not demand greater accuracy than that of which the graphical method is capable. The different types of charts are all interrelated, and there are so many intermediate types that the classification here adopted is but a very arbitrary one. A single chart may illustrate at once the principles of several different types, so that we have what might be termed combination charts, illustrated in Figs. 19 to 21.

Fig. 19 is a chart that is a combination of an *alinement chart* with a *mixture chart*, for calculating the percentage of sucrose in sugar cane, having given the weight and composition of the bagasse and expressed juice (dry grinding). It is worth noting that this chart may be used to solve the most general case of mixtures, namely, that in which two constituents of varying composition are mixed in any proportion to give a final mixture of varying weight whose composition is to be calculated.

In Fig. 20 is a combination of two alinement charts with a mixture chart for calculating the number of pounds of limestone to be added to one ton of cement rock to prepare a mixture for the manufacture of cement, according to the formula of Meade,[1] which demands 90 per cent of the calcium oxide that would be needed to form tricalcium silicate and tricalcium aluminate with the silica and alumina in the raw materials.

In Fig. 21 is a double logarithmic alinement chart for reducing the volumes of gases from one temperature and pressure to another. It might easily be constructed for problems in which the temperature is expressed in degrees Fahrenheit, and the pressure in inches of mercury. Since the reader who has been sufficiently interested to follow us thus far will be able to discover for himself the exact manner of construction of these last three charts, they are here presented without further comment.

CONCLUSION

In constructing graphical charts one should take care to use only drafting tools of tested accuracy, since triangles and T-squares not perfectly straight are often discovered. There are certain knacks in drafting that enable one to rule parallel lines with precision and subdivide the main graduations of the axes very rapidly. The drawings that illustrate this article have been so much reduced in photographing that none of them has been subdivided to the degree which would be advisable in practice, and only the larger divisions of the cross-sectioning appear.

In conclusion, it need hardly be remarked that one should consider carefully which one of the various charts that may be used in any given case is the simplest to construct, and which the easiest to read. It will often be found that a slight change in the conditions of a problem, or a simple transformation of the manner of its expression, will suggest methods of charting far more suitable than the one first brought to mind.

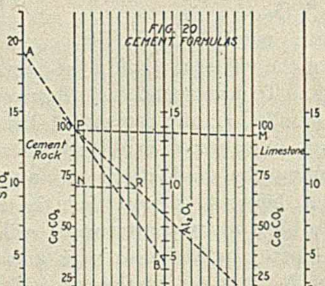


FIG. 20 CEMENT FORMULAS

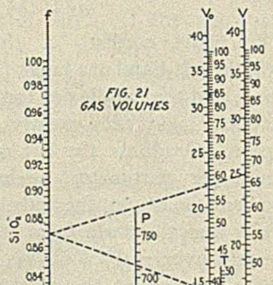


FIG. 21 GAS VOLUMES

Since the writer expects to publish in book-form a more detailed description of these charts and others than is possible in a periodical like this, he will be obliged to those who direct his attention to published or unpublished work on the subject.

In conclusion, he wishes to express his obligation to his assistant, Mr. Francisco Quisumbing, who drew many of the charts used to illustrate this article.

University of the Philippines
College of Agriculture
Los Baños, P. I.

---

[1] Tabulated by Geerligs, "Methods of Chemical Control in Cane Sugar Factories," Altrincham: Norman Rodger, 1905.

[1] Meade, "Portland Cement," Easton, Pa.: Chem. Pub. Co., 1907.

NECESSITY FOR AN AMERICAN DYESTUFFS INDUSTRY TO AID EXPORT TRADE IN TEXTILES[1]

By Henry Howard[2]

A year ago, at St Louis, I discussed the chemical industry under the general subject of "Problems Arising in War and Commerce." At that time importation had fallen off only $3^3/_4$ per cent from July to November inclusive, as compared with the same period in 1913. Importations of dyestuffs were coming in regularly from Germany and there was no actual shortage. As I pointed out, the greatest effect of the war upon the chemical industry was a national awakening to the absolute dependence of American upon foreign countries for products which are essential to our national welfare.

Germany was strictly limiting us to 75 per cent of the tonnage of dyestuffs that we bought from them during the twelve months preceding the war; that is, she allowed us to buy only one-twelfth of this quantity each month, so that, *if we attempted to increase the volume of our textile business and of other businesses using dyes beyond what it was the preceding year, we would be confronted with a shortage of dyes*, and I further pointed out that *this was likely to prove a serious obstacle in the development of any large foreign business in the goods affected.* How true this statement was is now apparent to every one.

GERMAN FIRMS RESPONSIBLE

Mr. I. F. Stone, President, National Aniline & Chemical Company, recently said:

> I say, therefore, that the German firms are responsible for the difficulty and the acute position of the American consumers. Their primary reason for this holding back of shipments was probably due to the fact that they did not want American consumers to get an oversupply of colors so that they could make up extra quantities of goods which they might use for export to customers in other countries who had formerly bought the same goods from Germany, but who could no longer obtain them.

Within three months after our St. Louis convention, the importation of all chemical products from Germany was stopped, and we have since been getting along with what had been accumulated outside of Germany plus the amount that our small dyestuffs industry could produce in this country.

There is no doubt that at present Germany has some dyes available for distribution, and the British Order in Council permits its shipment to this country. We must, therefore, draw our own inferences whether Germany does not want us to have these dyes unless we give cotton in exchange or whether she wishes to restrict our activity in foreign trade.

DYE SHORTAGE DISASTROUS

The result has been disastrous to what we all desire—namely: an increase in our foreign trade in textiles. Many textile mills have been obliged to curtail their output at a time when, if we had been independent of other countries, with a dye industry well established, these same mills could have been running night and day manufacturing goods for export and establishing foreign connections by aid of which a considerable percentage of this business might have been retained after the close of the war.

Let us go back for a moment now and see why there is no adequate coal-tar industry in this country. Investigation shows that the fault cannot be charged to the Democratic party but to the strenuous efforts of the foreign manufacturers and American importers, ably assisted by the short-sighted selfishness of these same textile manufacturers who are now the principal sufferers. I believe that, in many cases, these textile manufacturers did not act of their own initiative but were influenced by the clever arguments of American representatives of foreign color manufacturers.

In the winter of 1908–9 I took active part in Washington on behalf of the chemical manufacturers to try and maintain the small protection we had left, and to get suitable protection on basic coal-tar products so that the industry could be established here on a firm foundation from the ground up, because in no other way can it be independent of other nations. Yet our efforts failed, largely as the result of the opposition of the well-protected textile manufacturers.

COAL-TAR DUTY INCREASE PROTESTED

If you will look on Page 146 of the Tariff Hearings before the Committee on Ways and Means of 1908–9, you will find a memorial and protest in opposition to any advance in duties on coal-tar colors and dyes signed by the following companies:

Amoskeag Manufacturing Company, Manchester, N. H.
Hamilton Manufacturing Company, Lowell, Mass.
Pacific Mills, Lawrence, Mass.
Massachusetts Cotton Mills, Lowell, Mass.
Merrimac Manufacturing Company, Lowell, Mass.
Cocheco Manufacturing Company, Dover, N. H.
American Printing Company, Fall River, Mass.
The U. S. Finishing Company, New York.
The Apponaug Company, Apponaug, R. I.
Gardner & Company, Pleasant Valley, N. Y.
Passaic Print Works, Passaic, N. J.
Arnold Print Works, North Adams, Mass.
Windsor Print Works, North Adams, Mass.
Renfrew Manufacturing Company, Adams, Mass.
Queen Dyeing Company, Providence, R. I.
S. H. Greene & Sons Corporation, Riverpoint, R. I.
Aspinook Company, Jewett City, Conn.

The folly and unreasonableness of the textile manufacturers in lending their powerful influence to the foreign manufacturers of dyestuffs in their successful effort to crush out our coal-tar industry may be appreciated by a consideration of the following figures given by Mr. I. F. Stone in an address before the National Exposition of Chemical Industries, held in New York City last September:

> The lines of manufactures which are dependent on their supply of dyestuffs, to continue their regular production, the most important, perhaps, are the textile manufactures, comprising cotton, wool, carpets, knit goods, silk, cordage, shoddy dyeing and finishing. The following figures are taken from the Census of 1909:

	Establishments	Employees	Capital	Salaries and Wages	Value of Product
Cotton.........	1,324	387,771	$822,237,529	$147,270,903	$628,391,813
Wool..........	985	175,176	430,578,574	82,523,776	435,978,558
Carpets........	139	34,706	75,627,010	17,745,092	71,188,152
Knit Goods.....	1,374	136,130	163,641,171	52,431,680	200,143,527
Silk...........	852	105,238	152,158,002	46,097,364	196,911,667
Cordage.......	164	27,214	76,020,366	10,995,545	61,019,986
Shoddy........	88	2,320	6,886,825	1,196,376	7,446,364
Dyeing and Finishing.......	426	47,303	114,092,654	26,261,634	83,556,432
	5,352	915,858	$1,841,242,131	$384,522,370	$1,684,636,499

When you consider that the value of the coal-tar products annually imported is normally only $10,000,000, of which not more than 75 per cent or $7,500,000 is used for textiles, an increase of 10 per cent in the duty if the whole amount had been paid by the textile manufacturer would have been $750,000, or less than $4^1/_2$ cents

$$(\$750{,}000 \div \$1{,}684{,}636{,}000 = 0.00044)$$

for each $100 worth of textiles produced, a sum so insignificant that it could have had no appreciable influence on the ability of the textile interests to meet foreign competition, and would have been money well expended, not only as an insurance against the condition which now exists, but would in many cases have resulted in the ultimate lowering of the price of goods in which there is no competition at present.

FATAL TARIFF REDUCTION IN 1883

Few people remember that in 1882 we had quite a flourishing young coal-tar industry which, with consistent protection, would have long since been a large—if not a dominating—factor in our color supply. The fatal tariff reduction was made in 1883

---

[1] Address before the Third National Foreign Trade Convention New Orleans, January 27 to 29, 1916.

[2] Vice-President Merrimac Chemical Company; Chairman of Executive Committee of the Manufacturing Chemists' Association of the United States.

through the initiative of the importers, backed up by the coöperation of users of colors. Let me quote from a statement made by E. P. Wheeler, Vol. 1, page 230, of Report of the Tariff Commission, 1882:

> Would it be a wise policy for us to build up a manufactory of aniline dyes in this country when they can be made more cheaply abroad because the raw material is found in a cheaper condition in England? The English coal, as everybody knows, is richer in the hydrocarbons or inflammable matter than our American coal, and it is well known that we do import to some extent English coal to make gas, although the duty on it is a high one. The only objection that has been or could be made in regard to that would be that if we got into a war with some of the European countries we should be at a disadvantage in regard to these colors. I suggest that that is a very contingent and remote disadvantage; that the possibilities of such a war are insignificant.

AMERICAN DYESTUFFS INDUSTRY GAVE PROMISE IN 1882

In Vol. 1, page 207, there is a letter from H. K. Lansing, Treasurer of the Albany Aniline Works, dated Feb. 8, 1882, from which I will quote, and which shows the promising state of the industry at that time:

> We are now engaged in the manufacture of all the fine aniline blues, and expecting ere long to make all the finer colors made in Europe. As an illustration of the benefit the country has derived from our efforts, we can state that large crystals of red were sold in 1868 at $6.50 gold. We now supply the trade with an acknowledged better color at $2.50 per pound. Blues were sold one year ago at $4. Since we commenced making, the price has dropped to $2.50. We think we deserve the sympathy and encouragement of the powers that be.

In refreshing contrast to the textile manufacturers' action in 1908, allow me to quote from a statement of James Hendrick, President of the Albany Aniline & Chemical Works, page 256, Tariff Commission's Report, 1882:

> The Pacific Mills and other like manufactories in this country express the strongest hope that we shall receive from you the encouragement we are entitled to. In a letter addressed to me within a week by Mr. Saltonstall, the treasurer, he said there were some importers, or the agents of foreign color companies going through the mills in New England, expecting to get a petition signed in favor of the reduction of the duty on aniline colors, and he said they would have no sympathy from them and cautioned me against them.

EUROPEAN DYE MAKERS URGED TARIFF REDUCTION

Again, in a communication from V. G. Bloede, representing the American Aniline Works of Parkersburg, W. Va., dated Aug. 21, 1882, Vol. 1, pages 565–568, Tariff Commission Report, 1882, Mr. Bloede says:

> The actual disposition of the largest consumers of the anilines is fairly represented by the following sentence in a letter recently received by me from one of these consumers: "The representatives of a large European aniline works are making a great push to have the duties on anilines reduced. I enclose you their circular, which they are sending to all the manufacturers to obtain signatures. What do you as a manufacturer think of it, and what would you propose? We can stand it as it is, and, having all the protection we need on our manufactures, are willing to give all that is required to others."

The subsequent history of the aniline industry is lamentable. The Tariff Act of July 1, 1883, made a heavy reduction in the duty. No new factories were started, and within one year after the new tariff took effect, five of those already established were forced to succumb and go out of business, leaving only four to continue the work. These have since stayed in the business, but have not been able to develop to any extent.[1]

AMERICAN MANUFACTURERS READY TO COÖPERATE

In bringing to light past history I do not wish to be understood as bearing grievance against the textile manufacturers for any mistaken policy which they may have heretofore adopted. No one recognizes the error of this policy more keenly than these manufacturers themselves, and I am credibly informed that they now stand ready to coöperate in any way possible in order to establish a permanent coal-tar industry within the United States.

It is instructive to compare the present condition of textiles in this country with that of iron and steel. The latter industry, thanks to the consistent protection which for years was extended to every branch of the business, is now absolutely independent of the rest of the world in its ability to manufacture all standard grades of iron and steel products in this country, with the result that not only are all American users of iron and steel products getting their supplies as regularly as before the war began, but a large export business is being developed as the result of the paralysis of this industry abroad. In textiles the saving of a possible $4^1/_2$ cents on $100 worth of product has resulted in so throttling the textile industry that it is having hard work to supply our local markets, much less to gain a strong foothold in the foreign markets formerly supplied by the belligerent countries.

Now what lesson can we learn from these disquieting facts?

PERMANENT NON-PARTISAN TARIFF COMMISSION

It seems to me that first and foremost it points to the absolute necessity of a permanent non-partisan tariff commission of experts that will sift the facts, analyze the situation and recommend rates consistent with the tariff policy of the party in power, and thus enable Congress to accomplish what it wants to do.

Such a commission should be created at the earliest possible moment by Congress, and if our textile industry is to take any active part in foreign trade during the war the first business the Tariff Commission should tackle is the study of the Chemical Schedule with the object of enabling Congress to amend the tariff so as to develop a permanent coal-tar dye industry on a large scale in this country. At present, in spite of high prices, chemical manufacturers have been afraid to invest any large sums in permanent equipment, realizing as they do that as soon as the war is over the industry would quickly disappear under the present inadequate tariff.

DESTRUCTIVE SELLING POLICY OF FOREIGN DYE MAKERS

Unfair competition is another means by which the foreign syndicates have kept the coal-tar industry from getting a foothold here. For instance, aniline oil, one of the primary products, was selling at a high price a number of years ago, and an American company built a plant and started to market its product. Then the price was immediately cut on the imported article to a point about 10 per cent below the cost of production in this country, and kept there until the American firm gave up the business. When this result was accomplished, the price was advanced to about the original level.

Again, in 1913, a duty of 10 per cent was placed on aniline oil, and the manufacture was again started, with the result that the foreign producers not only absorbed the whole of the duty but actually lowered the price again to a point where the business showed a loss to the American manufacturer—and this condition was maintained until the war intervened.

Now such competition is manifestly unfair. It is not what might be called legitimate dumping to dispose of surplus product in some foreign country, but is a well-considered policy designed to destroy a new American industry. Such a practice ought not to be permitted, and I think I am right in saying that the present administration has under consideration legislation to prevent it.

GERMAN DYESTUFFS PLANTS AS MUNITION FACTORIES

There is one other reason—one of public policy—why a coal-tar dye industry is important to the future of this country. At present every one is thinking and talking of preparedness, and one of its most essential items is our ability to produce enormous quantities of high explosives when they are needed. Germany was able to do this over night in the plants used for coal-tar dyes in times of peace. England, France and Russia, substantially without this industry, were almost helpless in this respect, and it may be said justly that the existence of the highly developed

---

[1] See "Who Killed Cock Robin?" Hesse, THIS JOURNAL, 7 (1915), 694.

dye industry in Germany, coupled with its non-existence in Russia, France and England, has been a determining factor in their relative ability to obtain high explosives, and in the remarkable successes Germany has maintained in the war up to date.

Returning again to textiles. We already produce the cotton for the fabric and all the raw materials necessary for the dyes—how much better it would be for the cotton growers of the South and for manufacturers and laborers of the whole country if *more* finished goods and *less* raw cotton were exported, and the domestic consumption of raw cotton enormously increased.

In closing, I cannot do better than quote from the conclusions in my discussion of this subject a year ago as follows:

> Our dependence upon foreign countries for chemicals, whether they be in the nature of raw materials, intermediate products, or finished articles, is a matter of national concern, and I sincerely hope that the Government, the consumer and the chemical manufacturer may unite in friendly coöperation in working toward a common end, *viz.*, the establishment of a coal-tar dye and chemical industry in this country free and independent of all the world.

North Woburn, Massachusetts

MAGNESIUM[1]

By W. M. Grosvenor

The alkali earth division of the second group in the Periodic Table consists of more or less soft, white metals and all show great avidity for oxygen, decomposing water more or less readily. None except aluminum has found large commercial use but of the others magnesium leads the list by a long distance. Its chief uses are:

1—Scavenging alloys, *i. e.*, clearing up oxides of other metals and making far denser, cleaner, stronger and more homogeneous alloys. It is valuable in aluminum, nickel, copper, brass, bronze, etc., and special steels, because of its intense avidity for both oxygen and nitrogen.

2—Alloying itself, with aluminum or aluminum containing traces of one or more of the other metals Cu, Ni, Zn, Pb, Bi, Sb, Fe, etc. Magnesium greatly modifies crystallography and physical properties and alloys readily with most metals and melts at a convenient heat.

3—Illumination, as in military uses, for shrapnel trailers, star bombs, flare lights, etc. and in photography for flashlights. Its easy inflammability (about 800° C.), the high heat of combustion (134,000 cal.), the relatively low heat of vaporization (1100° C.), the intensely white oxide produced and the high temperature of volatilization of this oxide, are the essential factors.

MARKET AND PRICES

How much is used? Records of imports for the year prior to the war indicated 38,000 lbs. About 100 lbs. a day, therefore, seemed to be a safe production to undertake. Prices before the war had been very steady around $1.45 per lb. but it seemed reasonably certain the cost need not exceed $1.00 per pound, and after the war began the prices being paid for remnants of imported lots quickly rose to $2.50. Some of the first demands here were from wholly unexpected quarters, in surprising amounts and at amazing prices. The most urgent, almost pitiful demands, came from quarters that were not even suspected to be interested in the least. One consumer has contracted for 24,000 lbs. and another 15,000, these two alone taking for strictly domestic use more than was supposed to be the total importation. There are at least three other buyers of similar quantities but exact amounts are not yet established. Sales are largely made by yearly contract and even at present prices the consumption for strictly domestic use is about 50 tons. We found that a great deal of the material was being imported under other names and most carefully disguised—secrecy being preferred to economy. Prices as high as $10.00 per pound were gladly paid at first for domestic product. For some months then the prices jumped around from $5.00 to $7.50 but every effort was made to reduce conditions to some sort of order by dealing direct with the consumer. This was partly the result of a deliberate policy for better and more intelligent service of the consumer's precise demands as to quality and delivery, but partly also the result of meeting quite unexpectedly the competition of our own product at prices from 25 per cent below to 50 per cent above the prices we had made. Some of New York's clever War Goods brokers added 10 per cent each through a chain of four or five middle men. Others assumed direct quotations to have already been through this process and knocked off 20 per cent, trusting that "real cash business" would squeeze down the middle men they supposed to exist and still leave 5 per cent for the real seller. Now, however, for a number of months the price has been practically fixed at $5.50 per lb. of "Guaranteed 99%," actually about 99.5 per cent. Occasionally a lot that has been picked up in the antebellum market for speculation is let go at lower figures, or a lot of lower grade material comes on the market from abroad, but there is practically no volume of these sales.

In spite of the beautiful appearance of the German bars they rarely exceeded 98 and often fell as low as 96 per cent. The process of extrusion conceals impurities by drawing them out into minute threads. It is safe to say that the regular commercial grade of metal made here now is superior to anything ever imported.

REASONS FOR THESE PRICES

It may seem ridiculous to ask or pay such prices. Let us consider. The alloy market constitutes the bulk of the business, and governs prices. In aluminum castings, for instance, less than 2 per cent of magnesium cleans up the aluminum and leaves $^3/_4$ to $1^1/_2$ per cent in the casting, about doubling its tensile strength, and quadrupling its resistance to shock or jar. It reduces the cost of machining more than 50 per cent, halving the number of resets on the cutting tool, giving clean-cut machine surfaces, and permitting a polish to be secured with the last cut instead of a separate operation. With care, $1^1/_2$ per cent of magnesium at $5.50 per lb. is all that is needed, *i. e.*, $8^1/_4$ c. per lb. of casting actually required to do the same work. The increase in strength means, in some cases, a reduction in weight of casting of 50 per cent and generally not less than 25 per cent. The saving in machine work alone when the casting is to require much machine work more than pays for the use of magnesium.

So much for the consumer or user. Now the manufacturer of magnesium has at present certain considerations (of necessity rather than mere excuse) for the high prices. Cost of production abroad prior to the war approximated $1.00 per lb. Sales in England were about $1.30 and here about $1.45 per lb. At that time $MgCl_2.6H_2O$ was selling for about $18 per ton. Present prices here are now about $60. Other chemicals used in the manufacture have increased to ten times their normal price. One other factor, *i. e.*, insurance, must be considered in two forms: *First*, the insurance against cut prices and dumping that may come immediately upon the close of the war, making the plant and market-development work absolutely worthless. *Second*, the insurance against partisan interference. As a matter of fact in the case of two plants not a pound of material from either of which has gone for foreign military purposes so far as we know, there have been repeated efforts at molestation and some serious interruptions.

In considering prices it is well to mention separately export prices. Before the war nearly all the magnesium for England, as well as the U. S. and France came from Germany. Since the war both France and England are producing in considerable quantities of excellent purity. This fact and the failure abroad to realize the strenuous conditions here, account for the un-

---

[1] Address before the New York Section of the American Electrochemical Society, in joint session with the New York Section of the American Chemical Society, Chemists' Club, February 11, 1916.

willingness of buyers abroad to pay more than $3.50 for powdered metal (all the above-named prices were ingot or bar).

PRESENT PRODUCTION

At present there is being produced here at two points about all the present alloy market will absorb, and an increase of plant is being made of about 25 per cent the present capacity. One other producer makes only about his own requirements. Two others are soliciting business but have failed to fill orders—in one case the order is not over a year old and still stands unfilled. All told, we believe the present production is at the rate of something over $1,000,000 a year and will be slightly in excess of the present domestic needs.

POSSIBILITIES

The use of the metal for scavenging purposes depends on price of metal compared with price of material to be scavenged. For use with copper, brass, bronze, etc., the magnesium can be used at far higher prices than for steel. But the big consumption of the material can come only when it directly replaces aluminum as the predominant metal in the alloy, and arrives at a correspondingly low price. It makes beautiful castings, machines easily and well, is about a third lighter than aluminum and can be made about two to four times as strong. The coefficient of expansion reported is practically the same as for aluminum. When properly pure (over 99.5 per cent) it is apparently quite as resistant to corrosion as aluminum, equal if not superior in electrical conductivity (about half that of copper) and superior in heat conductivity to aluminum (also about half that of copper).

PROCESSES

I—REDUCTION OF FUSED $MgCl_2$ WITH SODIUM involves the production of metallic sodium; we have been using the Castner process for this purpose to satisfy ourselves just what the sodium would cost and what the possibilities in this direction were. Existing conditions, the demand for sodium and sodium peroxide, forbid its consideration with a minimum of about 2 lbs. of sodium consumed for every lb. of magnesium produced, and the necessity of producing dehydrated fused $MgCl_2$ to start with.

II—ELECTROLYSIS OF THE FUSED DOUBLE CHLORIDE (usually $MgCl_2.2KCl_2$) has been perfected and is very largely used abroad. We have commercially used and studied the process here and, with the cheapest water power and chloride, prices even under normal conditions by this process *must* rule above $1.00.

III—REDUCTION WITH CARBON (PATENTED) is absolutely fascinating in its possibilities. The product is a black or gray powder. Believing such a product would be valuable, the manufacture was carried out on a scale of about 25 lbs. per hr. As the difficulty of selling the product became apparent, much time and effort were devoted to attempts to recover the metal in fairly pure form. Owing to serious objection both on the side of cost and regularity of product this process was superseded.

The other processes—electrolysis of dissolved MgO,[1] reduction of fused $MgCl_2$ with aluminum,[1] reduction of oxide or carbonate to slag-forming residues,[1] etc.—will be discussed on some other occasion when the engineering problems they involve are believed to be finally solved in the best way and the patent office has finished considering them. The chemical side of each has been thoroughly worked out, however, so that some conclusions may be drawn from the large laboratory or small commercial operations. These may be of considerable interest.

At least one of the processes appears to be adapted to produce directly metal averaging 99.6 per cent purity in tons per day instead of pounds. Laboratory tests give a raw material cost of 4 c. per lb. of magnesium and indicate a fuel cost which approaches 3 c. as a theoretical limit, though the practical figure will probably be several times as high. The final selection of various possible engineering means and methods remains to be worked out, but it scarcely seems possible that either labor or repairs should exceed 2 c. per lb. Thus if commercial yields maintain the experimental level and three times the theoretical power is commercially required, we have prospects of a net factory operation cost (without interest, amortization, insurance, patent, administration or selling) of 17 c. per lb. If only 75 per cent yield is obtained this net factory cost would be about 22 c. or a total cost with all overhead expenses of 35 c. and a selling price of 40 c. to 50 c. according to tonnage.

It may be asked with perfect propriety, "Why talk about it now? Some fool will certainly want you to make a contract with him at lower prices, possibly at 50 c. He will not realize that it is only the present price of $5.50 that justifies or even makes possible the $1000 and $10,000 experiments that have been tried and must be tried again and perhaps again during the next three to five years before the tide turns. You will be pestered for years with this 17 c. talk." We have carefully considered this probability. The men who are doing this work do not cultivate talkativeness as a preference. Just at this time, however, certain consideration of public welfare should take precedence of preference. National self-preservation demands the subordination of personal interest. If we expect representatives at Washington to jettison the pork barrel, the army post, the high-tide navy yard, and political trading generally, and give us a fighting chance for our lives in the scrap that is certainly coming, we must set the example of considering national interest first. If we are to have the army and navy preparedness for which we have already wasted more money than Germany has paid for her wonderfully efficient fighting machine, if we are to have any preparedness instead of repairs or regrets, we must coöperate with all we have in service, information and suggestion.

Therefore, at the risk of criticism and possible financial sacrifice it seems to be a duty at this time to point out what may possibly be expected of magnesium. Few realize the extent to which it is valuable in military work. One of the great foreign explosive experts stated that he would be glad to pay $1.50 per lb. for 500 tons. A single contract for shrapnel being executed in this country would require about 50 tons. The illuminating bombs to make daylight over the enemies' works and trenches consume large quantities. The trailers attached to shells serve at night to show the effectiveness of the fire. For all these purposes magnesium produces a result that cannot be approached by antimony or aluminum. But consider what it means to aeroplane, dirigible, and motor construction, to high-speed engines of every type, to reduce weight one-third and double strength. This material has a density of 1.75 and may be hot-rolled to a tensile strength of 35,000 lbs. per sq. in. or cold-rolled very much higher. Although five or six men are being kept practically all their time on the development of these possibilities, the broad, quick development is a task for the energy of hundreds, even thousands. Feeling the responsibility which knowledge of the possibilities entails, it became the duty of those in charge of this work to let others know and be active in their side of preparation—the application of the material.

50 East 41st Street, New York

THE RÔLE OF THE CHEMIST IN THE CEMENT INDUSTRY[1]

By C. N. Wiley

Received January 3, 1916

Much mystery attended the processes employed in the early manufacture of Portland cement. When the brick layer of Leeds discovered that he could make an artificial water cement from a mixture of Thames chalk and Medway mud, he took every precaution to insure that none should discover the secret of his process. When engaged in making his raw mixture, it is said that he attired himself in flowing black gown and the pointed hat of the mystic and performed curious incantations over his

---

[1] Patent applied for.

[1] Address presented before the Alabama Section of the American Chemical Society, December, 1915.

operations. I. C. Johnson in 1845 wrote: "Thus he had a kind of tray with several compartments and in these he had powdered sulfate of copper, powdered limestone and several other matters. When a layer of washed and dried slurry and the coke had been put into the kiln, he would go in and scatter some handfuls of these powders from time to time as the loading proceeded, so the whole thing was surrounded by mystery."

One can imagine with what intense interest Mr. Johnson observed this remarkable procedure and it is small wonder that he was fired with a stronger determination to know of what the composition of this cement consisted. Procuring a sample, he had one of the most prominent chemists of England make an analysis and the chemist's report that the substance contained 90 per cent phosphate of lime mystified Johnson still further. But thinking that at last he had won the secret of this hydraulic compound, he made a large collection of bones from the butchers of the city and proceeded to calcine them. Needless to say, he was induced to discontinue his operations by the outraged citizens of the vicinity.

So up to this time, the chemist proved rather an obstruction than a help to the solution of the cement problem. But by the world-old method of trial and error, Johnson at last succeeded in making a cement which was equal in every respect to that of Aspdin and from this on the industry began to expand and thrive.

In the early days of the Portland cement industry, the correct adjustment of the proportion of carbonate of lime to clay was purely an empirical process. In the first place, mixtures were made in varying proportions from which samples of cement were prepared and the proportion giving the best cement was adopted. Any irregularity due to variations in the chemical composition of the materials, or carelessness on the part of the workmen, was ascertained by sampling the mixture frequently, the samples being burned in a trial kiln. From a close observation of the resulting cement, when tested for soundness, color etc., the "sampler" was, by long experience, enabled to judge whether the correct proportions were being maintained. This was a tedious and an unsatisfactory process, for while a sample was being prepared and tested, the bulk it represented had passed beyond the reach of alteration. If the slurry was run into backs, any error was corrected by altering the mixture and luting or stirring the contents of the back, from which a sample was occasionally prepared. With the Goreham process, no alteration of the previously prepared mixture was possible; it would probably be dry and ready for the kiln before the results of the sample were known. If the contents of any particular drying-flat or chamber proved to be over- or under-clayed, the burner could be instructed to burn it lightly or heavily as the case might be and this was really all that could be done.

When it is remembered that if the materials are in the first place suitable, success depended on the proper proportion of the carbonate of lime to clay and that for the same material this proportion was a constant one, it is evident that, if the carbonate of lime in a normal sample was known, the correctness of the mixture could be checked by the determination of this substance in the trial sample. And it was upon this determination that chemists depended largely for the proper composition of their mixtures.

An instrument known as Scheibler's calcimeter, originally devised by Dr. Scheibler for determining the amount of carbonate of lime present in animal charcoal used in sugar refining, was frequently employed for determining carbonate of lime in Portland cement mixtures. The principle of its action is well known to chemists and it was the principal instrument of mixture control in the cement industry up to ten years ago. The results obtained through it, although "near enough" for many technical purposes, were far from accurate. The carbonic oxide evolved is collected over water in which it is to some extent soluble and a correction has to be made dependent, of course, upon the volume of gas evolved. The Lunge nitrometer, in which the gas is collected over mercury, was also commonly used. Very little knowledge of chemistry or chemical manipulation was necessary for the use of the calcimeter or nitrometer.

Thus in the early days, the chemist was hardly known in the cement industry and it was unthought of for a cement manufacturer to employ the exclusive services of a professional chemist. The employee responsible for the maintenance of a correct and uniform mixture of raw materials was but a workman of more than the ordinary intelligence whose success depended on the rapidity with which he could make his test burnings and the degree of memory he possessed in profiting by past experiences.

Redgrave remarks in his book on calcareous cements that "the sample kiln should not be ignored when working with new and untried materials and much may be learned from the methods of the old-time sampler, his methods of work and the unconscious instinctive way in which he reasoned from the appearance of his samples. It should not be forgotten that Portland cement was discovered by a bricklayer and that its reputation was established long before the process of manufacture became a scientific question."

In this country, the early manufacture of Portland cement was chiefly confined to the Lehigh Valley region through which ran a belt of argillaceous limestone, the composition of which was almost in the exact proportions for making a high-grade cement equal in every respect to the more complicated mixtures of European manufacturers. The process of trial and error was largely responsible for the early success of men like D. O. Saylor and it was not until somewhat later that the chemist was first called into consultation and his advice was asked more for the purpose of locating new deposits of suitable rock and in the working out of problems which arose in the operation of the manufacturing process.

John W. Eckert may be called the father of cement chemists in this country. At the time Saylor and his associates were perfecting their processes above Allentown, Eckert was working as an assistant to Professor W. H. Chandler at Lehigh College, now University, South Bethlehem, Pa. He was asked to make analyses of rock from the different beds in the quarries of the Coplay Cement Works, of which D. O. Saylor was president. Cement was then made from each of these distinctive rocks and these cements were analyzed. In this way it was determined which beds were suitable for Portland cement and the other beds could be used in the manufacture of their Anchor brand natural cement. In his report of 1875–6, the State Geologist commenting on this says that "much technical and scientific supervision is necessary to determine which stone to use and which to reject in order to make a cement capable of undergoing the tests now applied by engineers and architects." So it might be said that the activity of the chemist in the cement industry depended greatly on the increasing severity of the specifications laid down by engineers and architects.

Eckert was finally engaged by the Coplay Cement Works to devote his entire time and knowledge to the process of manufacture and he thus became the first cement chemist in this country. His efforts resulted in more certainty and less chance in the preparation of proper mixtures and a more uniform product naturally resulted.

Somewhat later, Robert W. Lesley, of the pioneer manufacturers, was experimenting with the bricks into which the slurry was pressed preparatory to burning and he solicited the coöperation of George W. deSmedt, then a Government chemist engaged in the study of asphalts and kindred materials. Together these two men worked out various problems and were the first to mix the slurry with hydrocarbons before casting into bricks. The incorporation of this hydrocarbon not only made an excellent binder but in the kiln the burning out of this binder rendered the brick more or less porous so that the mass could be more evenly burned.

Lesley and deSmedt also discovered the difference between crystalline and gelatinous silica and Lesley took out a patent for the manufacture of gelatinous silica which they thought was of great importance.

All cements in those days were quick-setting and many efforts were made to retard this setting for obvious reasons. When P. I. Giron, affectionately called "Pig Iron" by his men, a French chemist in the employ of the Atlas Cement Co., was in France he had noticed the workmen adding a white substance to cement before they applied same in building sidewalks. As gypsum was in common use in France in building operations, he suspected that this was the white material and he found that by adding a small amount of this substance to the cement, the setting time would be materially lengthened. Dyckerhoff in Germany was also making use of plaster to season his cement and he obtained a slower setting cement. Lesley took out a patent for seasoning cement, the principle of which was to sprinkle the clinker with sulfuric acid.

The question as to what Portland cement really is early received much attention from investigators. Chemical investigations, so far, have failed more or less completely to throw light on the complex structure of this substance, although mineralogical examinations have been more successful. Although chemical methods have failed to reveal the actual structure of Portland cement, much has been learned by the study of synthetic compounds. Probably Vicat was the pioneer in this line of research, followed by Rivot, Chatoney and Fremy.

In Germany, Heldt, Fuchs, Schott, Michaelis, Erdmenger, Dyckerhoff, Meyer and others were attacking the problem along this line. Up to 1885 the various theories advanced defined more or less definitely the chemical composition of the cement, but all believed that upon addition of water the cement broke down into simpler compounds and free calcium hydrate. Believing that if this free lime could be removed from the anhydrous cement much more could be learned of the actual composition, investigators sought reagents by which this extraction could be accomplished. Rebuffat was the first to make use of an aqueous sugar solution, but Michaelis and Feret objected that results obtained in this way must be incorrect.

Probably the most satisfactory test which we have for free lime is that devised by Professor A. D. White. The method is based on the formation on the slide of a microscope of a characteristic crystalline calcium phenolate readily recognizable in polarized light. The reagent is prepared by dissolving crystallized phenol in an immiscible and rather non-volatile solvent, such as nitrobenzol, and adding a trace of water. Thus it is possible, by this test, to determine whether the chemical balance between the calcium and the other constituents in a good cement has been attained.

As mentioned above, much has been learned of the constitution of cement through mineralogical investigations. As these investigations were conducted in many cases by chemists, it is only proper to grant the chemist credit for his part in solving the problem. LeChatelier was one of the first to attack the problem along these lines and he was followed by many investigators. In this country, the work was being carried on by such chemists as Richardson, the Newberrys, Campbell and others and much was learned from their experiments. Several years ago, Day and Sheperd and scientists of the Geophysical Laboratory have, from extensive investigations, come to a conclusion as to the true constitution of Portland cement and they are now engaged on studies of hydration.

The technical chemist has not had the time to devote nor the opportunity to pursue investigations like the above but he has contributed to the knowledge of the subject in no small degree by working out technical processes whereby a high-grade product may be made and maintained. He has found that the cement rocks of the Lehigh Valley are not necessary for the production of a high-grade product but has gone into almost every State of our Union and has found there materials which when properly combined would produce a Portland cement of high quality. On account of the variation in composition of these raw materials, he has developed methods for their proper control. The increasing severity of cement specifications has caused a greater watchfulness throughout the process of manufacture until at the present day the chemist has in control every step of the process from the time the rock is won from the deposit until the finished cement is placed in the hands of the ultimate user. And he has gone yet further, for he has shown the user how this cement may be used to best advantage and has pointed out the necessity for closer inspection of the materials with which it is combined.

The chemist has shown that a true Portland cement can be made from blast furnace slag, heretofore a waste product. The utilization of this waste product has resulted in a great industry producing over 10 per cent of the total production in this country.

So in these years of progress and expansion, the cement industry has seen the humble "sampler" develop into the present highly trained scientist whose word is law concerning the process of manufacture. The chemist alone is responsible for the quality of the product, and the fact that American-made Portland cement is recognized as superior to that made in other countries is a tribute to the untiring efforts and ability of our chemists.

BIRMINGHAM, ALABAMA

CURRENT INDUSTRIAL NEWS

SELENIFEROUS PYRITES IN THE MANUFACTURE OF SULFITE CELLULOSE

Some selenium, says the *Paper Maker*, is contained in all pyrites. The percentage of selenium is ascertained by the hydrosulfide method and the ratio between sulfur and selenium fluctuates between 1 : 10,000 and 1 : 100,000. The quantitative determination is best carried out as follows: a mud rich in selenium is deposited in the colder parts of the gas pipes of chemical pulp mills; the mud is lixiviated until the reaction is neutral and treated in the water bath with concentrated potassium cyanide solution until its reddish color disappears; the solution is then filtered and the selenium is precipitated as cherry-red flakes by hydrochloric acid. When pyrites is roasted, the selenium escapes as selenium dioxide and enters into the roasting gases and the cooking liquor. As a rule, however, small quantities of selenium do not matter. Sulfurous acid is oxidized in the air but selenious acid is reduced, red selenium being deposited. This reduction forms an excellent contact surface. Both the flying dust and also the selenium formed can be only partially removed from the roasting gases even with very good scrubbing apparatus. Some selenium will always be contained in the liquor.

The flying dust acts catalytically on the sulfur dioxide and the lime, which are converted respectively into sulfuric acid and plaster of Paris and are thus lost to the cooking process. In the cooking stage, when the percentage of sulfur dioxide and lime suddenly falls, the sulfuric acid, which is formed, colors the pulp dark, makes it brittle, difficult to bleach and thus renders it of inferior quality. This defect is met with especially when making readily bleachable chemical pulp because a longer time and a higher temperature must be employed. Systematic investigations have shown that the percentage of selenium in pyrites is primarily not an injurious constituent but the percentage of dust, in the same pyrites, containing dust, yielded a bad liquor while one free from dust but with the same percentage of selenium yielded a perfect liquor.—McMillan

SPANISH PLATINUM DEPOSITS

Careful inquiries, says the *Mining Journal*, have been made regarding the recent platinum discoveries in Spain. The locality may be indicated by following the direction of the Sierra Nevada as it enters the province of Malaga. The end of the chain is called the Sierra de Ronda and contains several ranges of igneous rocks of the peridotite family, the most extensive covering a space of 45 mi. by $12^{1}/_{2}$. The rock-system shows a striking analogy to that of the Urals. The peridotites of the Spanish rocks vary considerably according to the proportion of basic and acid elements they contain. The central mass is formed of the most basic rock, dunite, which consists of a combination of olivine and chromite, the platinum being always associated with the latter; further the metal is not concentrated but scattered through the mass. The rocks have been submitted to a careful examination, both chemical and spectroscopic, and their composition minutely studied. The platinum zone was determined to be 40 ft. deep with an average thickness of 5 feet and, from this, an estimation of the profitable tonnage has been made. Of the samples taken, one-third were rejected as too high, owing to pure grains of metal having been picked up; of the remainder, a third gave from 2 to 3 grams per ton of wash, another third gave 0.25 to 2 grams, and the remaining third was considered too poor for treatment. Little alumina is found to be present so that the treatment of these alluvials would be cheap and easy, and it is generally taken that the working of platinum sands can be economically undertaken from the level of 0.25 gram per ton.

Further investigations are being made to embrace the whole fields and the Spanish Government, recognizing the importance of the discovery, is supplying the necessary funds for carrying out the work.—M.

SULFURIC ACID FROM NITRE CAKE

Investigations have been made by a committee of sulfuric acid users in Yorkshire, England, with a view to combating the scarcity of this acid; nitre cake, a by-product of the manufacture of sulfuric and nitric acids, has been found a suitable substitute.

The cake contains the equivalent of 30 per cent pure sulfuric acid and has hitherto been looked upon as a waste product. Experiments made with the cake indicate that its use presents certain difficulties, but it is hoped that these will be overcome. Since it has only 30 per cent available sulfuric acid, it must be used in larger quantities and on account of the liquid which drains from it, its storage and transport give rise to difficulties. It is also pointed out that the general use of the cake for the above purposes will probably entail a sudden disorganization in the textile and other trades.—M.

CULTIVATION OF MEDICINAL HERBS

In consequence of the shortage of drugs due to the war, steps are being taken, according to the *Pharmaceutical Journal*, to experiment on the home cultivation of these in Queensland, under the control of the Board of Agriculture. Ample funds are to be provided.

It is proposed to work in conjunction with a hospital and, thus, to make the experiments of practical value. As a first step, seeds and plants will be imported and distributed to the various high schools to be tested in the school gardens, and the plants will be sent to districts where the soil appears to be most suitable to give successful results. The products will be tested in the laboratories of the hospital and the Board of Agriculture. The results will be published and will give an idea of the districts best suited for the cultivation of certain plants. When this stage is reached, persons desiring to take up drug growing will be invited to communicate with the Board and will get the necessary instructions. Growers will be guaranteed a certain market and a definite price for their produce.—M.

MINING IN THE GREEK ISLANDS

Recent official reports show that previous to the war, the mining industry in the Greek Islands was suffering from depression. In 1914 the iron mines at Syra were not worked at all, and the production from Syphnos, Seriphos, and Kythnos amounted to only 133,825 tons compared with 206,416 tons of the previous year. The Naxmis emery industry, which suffered severely from strikes in 1913, showed a production of 6,876 tons, the greatest part of which was exported to the United States.—M.

BRITISH RUBBER TRADE FOR 1915

According to figures published in the *India Rubber Journal*, the import of raw rubber during the past year reached the record figure of 182,565,900 lbs. The value was \$97,080,288, which works out at a little over \$0.50 per lb. The greatest bulk of the import is now of British growth. Forest production seemed to have been somewhat ousted by plantation production and the import of forest-grown rubber now ranks at but little over one-quarter of the total.

Thus, in a very few years, a trade has been built up which renders every manufacturing country dependent on Britain for its raw material. From the figures it would seem that more material has been re-exported than one should have expected under present conditions. It cannot, however, be said that neutrals have been much inconvenienced by the hoarding up of supplies at home.—M.

SHELLS

Dr. J. E. Stead in a paper to the Cleveland Institute of Engineers reports on analyses made by him of a large number of fragments of German shells. According to his opinion, which is that of an expert, a shell should not be rejected on the result of its chemical analyses provided the mechanical tests are satisfactory. The shell used by the Germans, he found to be, generally, of relatively high tenacity and is much more liable to break up by shock than the material found in British shells. It seemed probable that some of the German shells were made by the basic Bessemer process judging from the relatively high percentage of nitrogen found present in one of the toughest and best fragments examined. This specimen also contained 0.07 per cent sulfur and phosphorus. Shells with between 0.07 and 0.1 per cent phosphorus did not burst in the gun, hence it does not seem to be absolutely necessary that great freedom from that element is required.—M.

SULFUR CEMENT

It is often necessary, according to the *Engineer*, to seal up holes in transformer or oil-switch cases where wires pass through. For this purpose, the most commonly used material seems to be a mixture of sulfur and plaster of Paris. Either material used by itself may answer the purpose in some cases but, if the two are mixed half and half, it gives a very hard substance when it has set and one which is impervious to transformer oil. The sulfur may be melted in a ladle or pot and then an equal quantity of plaster of Paris mixed thoroughly into it. The mixture should be poured into place while hot. Trouble is often experienced from oil being siphoned out of transformer cases on account of the braided insulation on the lead wires. When this occurs it is usually found that the insulation on the wires dips down into the oil. If the oil level is lowered below the terminal board inside the case and the insulation on the leads scraped off so that where the wire enters the surface of the oil its metallic surface only is exposed to possible contact with the oil and the leads are properly sealed, there will be little trouble due to siphon action.—M.

MINING IN KOREA

Korea is reported to be rich in minerals. The districts of Pingyang and Kangtong, Province of Pyong-an produce large quantities of anthracite coal, the mines in the former place being under Government control. The naval briquette factory at Tokuyama (Japan) uses up annually over 84,000 metric tons of Pingyang anthracite valued at about $165,000. A new coal mine, opened at Anzu in the Province of South Pyong-an, in 1911, is being developed.

Japanese capitalists are beginning to pay more attention to the gold mines in Korea, and several new claims, *viz.*, Chik-san, Kungsong, Syonchon and Syn-an in the district of Pingyang show promise. The principal placer gold deposits are found in Syn-an district.—M.

BRITISH FOREIGN TRADE IN 1915

Official figures for British Foreign Trade in the year 1915 have now been published. In the chemical industry, imports of nitrate of soda were 132,158 tons as compared with 171,910 tons for 1914 and 140,926 tons for 1913. Nitrate of potash was imported to the extent of 276,580 cwts. as against 209,439 cwts. and 237,880 cwts. for the two preceding years. The imports of calcium carbide were 521,523 cwts. against 575,443 cwts. in 1914 and 513,797 cwts. in 1913 and of sulfur 711,102 cwts. against 435,979 cwts. in 1914 and 364,283 cwts. in 1913, while the exports of pyrites amounted to 903,401 tons against 803,249 tons and 781,711 tons for the preceding two years. The value of acids imported for last year was £4,231,216 against £1,575,836 for 1914 and £1,718,922 for 1913, the increase, of course, being due to the war. The coal-tar products were much the same as for the previous year; benzol and toluol amounted to 7,334,436 gallons; tar oil and creosote to 35,687,286 gallons. The exports of China clay show a decrease: the amount exported last year was 333,206 tons as against 628,620 in 1914 and 629,703 tons in 1913. Petroleum imports also show a slight decrease, the total being for last year 595,158,694 gallons against 646,712,631 gallons for 1914 and 488,106,963 in 1913. Exports of mining machinery were valued at £571,000 against £819,486 for 1914 and £1,018,150 for 1913.—M.

EFFECT OF BOMBARDMENT ON CONCRETE AND BRICKWORK

A feature of the pictures of the Belgian forts bombarded by 42 cm. guns, is, says a contemporary, that the walls and roofs struck by projectiles are not pierced by shots but completely shattered even where the explosive force of shells plays no part. These fortifications were built chiefly of concrete and armored concrete.

Professor P. Rohland states that the same phenomenon has been observed in experimental practice with targets of reinforced concrete. Shots did not break holes as in steel targets but caused the whole target to crumble to small fragments. The reason for this, he further holds, lies in the fact that there is a condition of high tension in sheets or walls, roofs, etc., of concrete due to the colloidal chemical nature of cement where separate particles are pressed extraordinarily close together. When this tension is relieved at any point by a bursting shell, the complete crumbling of the entire sheet of concrete is the inevitable result. Hence, he advises a return to the use of brick for fortifications. When a brick wall is struck by shot, the result is merely the tearing of a big hole, since, owing to the looseness of structure, only the parts in immediate contact with the spot hit are affected.—M.

MANUFACTURE OF DRUGS AND CHEMICALS IN JAPAN

Further particulars have been published regarding the scheme, devised by the Japanese Government, for subsidizing the manufacture of dyestuffs, drugs and chemicals. The products provided for under the new law, according to the official organ of the Board of Trade, are the following: acetanilide, benzoic acid, carbolic acid, salicylic acid, antipyrin, chloral hydrate, chloroform, cresol, formalins, glycerine, guaiacol, caustic soda, potassium carbonate, creosote, alkaloids; also, the by-products from coal tar by dry distillation, *viz.*, light oil, neutral oil, crude and refined benzol, toluol, xylol, naphthalene and anthracene. Three companies have been formed, one to specialize in glycerine, the second in formaline and the third in drugs.—M.

THIOPHENE IN BENZENE

The following method for estimating the amount of thiophene in benzene is said to give good results. A little more than the calculated quantity of mercuric oxide is dissolved in glacial acetic acid and the liquid cooled, mercuric acetate being deposited. The benzene to be tested is added and the mixture heated on a boiling water bath for about 15 minutes. The precipitate formed, which consists of thiophene tetra-mercuriacetate, is separated from the cold liquid, washed several times with ether, dried at 100° and weighed.—M.

POTASH FROM THE ASH OF THE PRICKLY PEAR

The *Chemical News* states that spraying with arsenic trichloride solution is being used to exterminate the prickly pear pest in the Cactus Estates of Dulacca in Queensland.

The ash of the pear contains 15 per cent potash and a yield of 7 tons of ash per acre has been obtained. Half a ton of 80 per cent potassium carbonate was collected from the ash of 5 acres of the burnt cactus. The ash is gathered up by means of a suction plant.—M.

AUSTRALIAN METALS

According to a recent statement made by the Commonwealth Premier, the outlook for the Australian metal market at the beginning of 1915 was very gloomy, due mainly to German domination. The whole metal industry seemed to be on the point of collapse. Now, however, things have changed somewhat; the industry is in a flourishing condition and prospects are bright. Copper ores can now be treated locally without the need for exportation and arrangements are being made for the establishment of zinc and lead refineries.—M.

BRITISH SULFATE OF AMMONIA

In view of the uncertainty in Great Britain as to the sufficiency of supplies of sulfate of ammonia to meet home demands during the next few months, it has been decided on the recommendation of the Fertilizers' committee, with the government's approval, to suspend for the present the issue of licenses for the export of sulfate of ammonia. Under normal conditions, the production of this substance considerably exceeds home requirements, but it is hoped that farmers will this year greatly increase their demands for fertilizers so as to stimulate as far as practical the production of the land and so reduce the importation of foodstuffs into British Isles.—M.

METHOD FOR DETERMINATION OF HARDNESS

Mr. M. F. Turpin, in the *Revue de Metallurgie* for February, 1915, describes a simple device adapted to determine hardness in many manufacturing processes. It entails the use of a steel ball protruding from the end of a hollow mandrel backed by a cylindrical slug of known hardness according to the Brinell scale. The slug is surmounted by a plunger which protrudes from the opposite end. When a test is to be made the ball is brought into contact with the sample and the free end of the plunger is struck with the hammer. The indentation made is then compared with the standard slug. The device is 30 mm. in diameter and 90 mm. long.—M.

BRITISH BOARD OF TRADE

During the month of January the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.

Aluminum powder
Asbestos, crude
Automatic gas lighters
Bangles, imitation ivory
Bottles for poison
Boxes, small tin, printed in colors
Burners, paraffin oil lamp
Calcined bone ash
Casein, liquid or powder
Celluloid, suitable for accumulator cells
Chalk flint boulders
Chains, small unsilvered
CHEMICALS
  Acetone
  Potassium carbonate
  Magnesium chloride
  Calcium sulfide (luminous)
  Saltpetre (at least 99% sodium nitrate)
  Sodium peroxide
  Uranium oxide
  Cream of tartar substitute
Cotton wool, absorbent for surgical purposes
Electric pocket lamps
Frames, photograph
Glass tubes
Gold leaf
Hoop iron
Incandescent lamps
Incandescent mantles, upright and inverted
Jars, stone
Lampwick
Margarine
Machinery for making lead pencils
Metallic vessels for resisting corrosion by acids
Orpiment, red
Oil, crude for use in Semi-Diesel engines
Pearls, imitation
Porcelain articles for wreaths
Presses, copying
Paper for artificial flowers
Rings, steel for leather purses
Sewing machines
Stockings, knitted ramie, for incandescent mantles
Talc sheets
Vacuum flasks

—M.

MINERAL PRODUCT OF UNITED KINGDOM FOR 1913 AND 1914

The following table showing quantity and value of minerals produced in the United Kingdom is taken from the general report on Mines and Quarries.

	1913		1914	
MINERAL	Tons	Value (£)	Tons	Value (£)
Alum Shale	8,741	874	6,078	607
Arsenical Pyrites	35	29	....	.....
Arsenic	1,695	16,616	1,988	19,052
Barium compounds	50,045	42,136	48,930	43,506
Bauxite	6,055	1,563	8,286	2,159
Bog Ore	3,835	959	2,342	585
Chalk	4,858,126	213,479	4,291,170	197,154
Chert Flint	74,858	12,781	76,213	13,304
Chromite	....	.....	100	50
Clay and Shale	13,892,807	1,790,805	13,124,361	1,731,779
Coal	287,430,473	145,535,669	265,664,393	132,596,853
Copper ore	2,569	21,138	2,373	16,985
Copper precipitate	163	5,891	185	5,529
Diatomite	154	308	....	.....
Fluorspar	53,663	14,955	33,816	11,005
Gold Ore	4	434	47	318
Gravel and Sand	2,409,152	184,818	2,498,872	215,351
Gypsum	285,338	90,450	265,365	83,868
Igneous Rocks	7,098,473	1,386,022	7,135,243	1,369,242
Iron Ore	15,997,328	4,543,558	14,867,582	3,921,683
Iron Pyrites	11,427	5,988	11,654	4,759
Lead Ore	24,282	293,525	26,013	309,813
Lignite	81	40	300	150
Limestone (other than chalk)	12,740,664	1,369,168	12,158,441	1,295,512
Ochre	15,135	14,460	11,069	10,635
Oil Shale	3,280,143	822,394	3,268,666	837,249
Salt	2,247,758	608,869	2,069,989	560,893
Sandstone	3,977,303	1,143,431	3,464,528	1,057,096
Slate	370,756	926,739	318,912	806,196
Soapstone	40	30	180	90
Sulfate of Strontium	18,425	14,287	13,157	10,439
Tin Ore (dressed)	8,355	960,134	8,085	661,865
Uranium Ore	95	.....	344	Not stated
Wolfram Ore	182	17,483	205	19,722
Zinc Ore	17,294	69,502	15,419	56,652
Total £		160,112,607		145,863,032

—M.

BLEACHING OF FATS AND OILS

According to *Nature*, palm-oil, which is used in very large quantities in the soap industry, may be bleached (1) by exposure in thin layers to air and sunlight, (2) by blowing air through the hot oil, (3) by action of bleaching powder or chromic acid.

The great development in scientific methods of catalytic reduction as a means of hardening fats and oils appears to have suggested the idea that similar methods might be applied to the oxidation and bleaching of oils. Experiments reported in the *Transactions of the Chemical Society, London* (**107,** 1828) shows that a large number of metallic compounds can be used to stimulate the oxidation, the most effective being those containing manganese and cobalt, although nickel, iron and lead were also active. Of the compounds employed, the borates were found to be more effective than the oxalates, palmitates, sulfates or oxides, and the most effective of a dozen catalysts was cobalt borate. Using only 0.01 per cent of this salt a reddish sample of oil was bleached white in the course of $3^1/_2$ hours by passing air through it at 80 to 90° C. The bleaching was found to be permanent during 15 months and did not destroy the faint odor of violets which is characteristic of the oil; the bleached oil also gives a colorless soap and its soap-making qualities were in no way interfered with.—M.

THE CRUCIBLE SITUATION IN THE UNITED STATES

The crucible manufacturers have been put to sore straits for the past eighteen months in the securing of their raw materials. The embargo on Ceylon plumbago (lifted after a few months) left the market in a depleted condition: the natural result was a tremendous advance in price.

Next came the exhaustion of the foreign clay, which is used in crucible making as a binder. The clay used, as far back as crucible history in this country goes, has come from the little principality of Klingenburg in the Black Forest in Bavaria, where, it is said, the entire government expenses are paid out of the export duties collected from the clays shipped out. This Klingenburg clay has, for years past, been the only clay the crucible makers seemed to think they could satisfactorily use. No shipments of this clay have been made since the beginning of 1915. Some makers have husbanded the enormous supplies of the foreign clay which they had on hand when hostilities started. This husbanding the stock of the now almost priceless raw material, has been done by partially substituting clays from various parts of the United States, and mixing with the Klingenburg clay.

The tests and trials made by the crucible makers during the past 12 months have been almost endless. The fact that it takes from 6 to 10 weeks to prepare a graphite crucible for service in the foundry gives some slight idea of what the crucible maker has to contend with. Added to this delay, and before he can even start in on these goods that will not be marketable for two months to come, the chemists' laboratory tests and trials must be made: these run into the thousands. Then must come the practical tests in a small way in the foundry, for the crucible maker would stare bankruptcy in the face, if he were to continue making up hundreds of thousands of dollars worth of goods out of Ceylon plumbago, costing from $17^1/_2$ to 25 cents per lb., only to find at the end of two or three months that the product was useless.

However, in many cases the crucibles made with American clays have gone a surprisingly long time in the fires. In one instance there is a report on a No. 300, which ran 40 heats on manganese bronze, and dozens of others as high as 38 and 40 heats on No. 100's melting car box-metal. The annoyances now seem to be the non-uniformity of the products secured. crucibles made by the same potter, out of similar materials, at the same time, and burnt in the same kiln, when run by one melter on same grade of metals, rise and fall to a variation that is a shock to both user and maker. But all this will in time be rectified. As soon as the manufacturers have become more familiar with the mixing and blending of our native clays, they will no doubt be able to produce in time a crucible as satisfactory, or superior to those manufactured heretofore.

The user, however, must exercise more care in handling the American clay crucibles. It is imperative that these crucibles be thoroughly dry and warm before going into the fire and that they be heated up *very slowly* on the initial heat. Some users make a little fire with charcoal inside the crucible, and others put hot ashes in before placing the pot in the fire, so that the crucible is hot when it goes into the fire for the first heat. There are certain advantages in heating the crucible from the inside first rather than the outside.

The matter of wedging must also be guarded against, as American clays have not the same tensile strength when hot, as foreign clay.

The advance in prices of crucibles is due to the unusually high price of Ceylon plumbago just at present, just as with zinc, copper, aluminum, lead, etc., but as soon as the war insurances are a thing of the past, plumbago will be at a normal figure once more, and crucibles will again be marketed at as low or lower prices than they have been for many years past.

CENSUS BUREAU'S SUMMARY FOR THE PETROLEUM REFINING INDUSTRY FOR 1914

A preliminary statement of the general results of the 1914 census of manufactures for the petroleum-refining industry issued by the Bureau of the Census, Department of Commerce, reports the quantity of crude petroleum used by the refineries and the value of the various products manufactured. It also gives the production of casing-head gasoline in 1914 and includes the following summary of the production of crude petroleum by fields in that year as reported by the United States Geological Survey.

CRUDE PETROLEUM PRODUCTION

	1909	1914	% Increase
California	55,471,601	99,775,327	79.9
Mid-Continent (Kansas, Oklahoma, etc.)	50,833,740	97,995,400	92.8
Pennsylvania grade (Appalachian)	26,535,844	24,101,048	—9.2
Illinois	30,898,339	21,919,749	—29.1
Gulf	10,883,240	13,117,528	20.5
Lima-Indiana	8,211,443	5,062,543	—38.3
Colorado, Wyoming, and other fields	336,667	3,790,940	....
Total production (barrels—42 gallons)	183,170,874	265,762,535	45.1

The value of the annual production has increased by $159,363,746, or 67.2 per cent over those of 1909.

The gasoline product of the petroleum refineries does not include casing-head gasoline condensed from natural gas at the gas wells. The total gasoline production, including casing-head gasoline, was 24,711,565 barrels of 50 gallons, or 1,235,578,250 gallons.

The production of lubricating oils here reported does not include that of establishments engaged in the compounding or blending of petroleum oils, but only the output of petroleum refineries.

Of the 176 refineries in 1914, 48 were in Pennsylvania, 38 in California, 23 in Oklahoma, 13 in Kansas, 9 in Texas, 9 in Illinois, 8 in New Jersey, 7 in Ohio, 6 in New York, 4 in Colorado, 3 in Maryland, 3 in West Virginia, 2 in Wyoming, and one each in Indiana, Louisiana and Missouri.

The comparative statistics for 1914 and 1909 are summarized in the accompanying table.

	1909		1914		Per cent Increase	
PETROLEUM REFINING IN THE U. S.	Barrels	Value	Barrels	Value	Bbls.	Value
No. of Establishments	147		176		19.7	
Total Production Crude Petroleum	183,170,874		265,762,535		45.1	
Crude Petroleum Used	120,775,439	$152,307,040	191,262,724	$249,727,856	58.4	64.0
PRODUCTS						
Naphthas and Lighter Products:						
Gasoline (from Crude Petroleum)	10,806,550	39,771,959	23,908,242	106,140,170	170.2	206.5
All others			5,292,522	15,779,137		
Illuminating Oils	33,495,798	94,547,010	38,705,496	96,806,452	15.6	2.4
Fuel Oils	34,034,577	36,462,883	74,669,821	84,017,916	119.4	130.4
Lubricating Oils	10,745,885	38,884,236	10,348,521	55,812,120	—3.7	43.5
Residuum or Tar, including Liquid Asphaltic Road Oils	1,787,008	2,215,623	2,696,887	4,017,858	50.9	81.3
Greases	138,302	1,567,647	280,128	3,536,491	102.5	125.6
Paraffin Wax	946,830	9,388,812	1,150,776	8,897,106	21.5	—5.2
Asphalt, other than Liquid Asphalt—Tons (2000 lbs.)	233,328	2,724,752	465,157	4,867,213	99.4	78.6
All other products		11,434,737		16,486,942		44.2
Total Value of Products		$236,997,659		$396,361,405		67.2

Gasoline from Natural Gas (casing-head gasoline, not included in refinery products) barrels (50 gallons) (United States Geological Survey) .. 853,053
Total Gasoline Production, excluding duplication as far as possible, barrels (50 gallons) 24,711,565

NOTES AND CORRESPONDENCE

FOREIGN APPRECIATION OF THE AMERICAN CHEMICAL SOCIETY

Editor of the Journal of Industrial and Engineering Chemistry:

All members of the American Chemical Society, which for some time has had the largest membership of any chemical society in the world, should be interested in the following, translated from p. 3 of the *Chemiker Zeitung* for 1916:

> "The technical chemical literature of America is very important but it has hitherto been altogether too little appreciated in Germany. The most distinguished of the American publications is the *Journal of Industrial & Engineering Chemistry*, published by the American Chemical Society; this journal furthermore publishes comprehensive articles on the economic phases of chemistry."

Further, they should be interested in the following, translated from p. 35 of England's "Handelskrieg und die Chemische Industrie," by A. Hesse and H. Grossmann:

> "It should here be pointed out that the Americans have most skillfully avoided that division into scientific and technical societies which has so unfortunately occurred with us, and that they have succeeded in very rapidly building up a large and, therefore, very efficient organization which provides for and embraces *all* interests."

This first and very much belated foreign recognition of our having one of the most efficient chemical organizations in the world, of publishing the best technical chemical journal in this country, and that heretofore American chemical work has been insufficiently appreciated abroad, ought to be a great satisfaction to every American; it ought to make each American chemist not now a member of the A. C. S. most anxious to become one of us. Above all it should make all of us ready and willing to leave nothing undone to maintain the proud position we have now reached after forty years of continued effort and during which long time recognition both at home and abroad has been largely withheld from us and from those of our members who have labored unostentatiously but effectively.

All of us who are now reaping the benefits of this self-sacrificing and arduous labor cannot escape and must not shirk the great duty of doing everything that may be needful to prevent any retrogression in the good work of those who have preceded us, and further, to enhance and to advance this proud achievement which is now placed in our keeping.

BERNHARD C. HESSE

25 BROAD STREET, NEW YORK
February 14, 1916

SOME OVERLOOKED INVESTIGATIONS ON WHEAT

Editor of the Journal of Industrial and Engineering Chemistry:

The Chemical Section of the Colorado Experiment Station has been engaged for several years in a study of Colorado wheat, to find out, if possible: (1) whether Colorado wheat has any distinctive quality which may be considered characteristic of it; (2) to determine the factor or factors in our conditions which are accountable for the same.

The result of our first two years' work was the publication of *Bulletin* 205 of this Station, entitled "Yellow-berry in Wheat; Its Cause and Prevention." Further reports on this work are contained in *Bulletin* 208 already issued, and 217 which will appear soon.

I endeavored to give credit in these publications to everyone to whom I am in any way indebted. I hold this to be the imperative duty of every author, even if his production should be of insignificant importance. Since the manuscript of *Bulletin* 217 was turned over to the Director of the Station, I have found that H. Ritthausen and Dr. R. Potts carried out a series of experiments in 1872, an account of which may be found in *Die landwirtschaftlichen Versuchs-Station,* Band XVI, 1873, pp. 384–399, which, in the main, is parallel to mine to such an extent, and the conclusions are so similar, that it might be thought that I had copied their plan of experimentation and adopted their conclusions. This applies to the bulletin on Yellow-berry to such an extent that some of my conclusions look like paraphrases of theirs. It does not apply to *Bulletins* 208 and 217 to the same extent. Still, it applies in some measure, and a portion of the work still to be reported will again be parallel.

Ritthausen and Dr. Potts used spring or summer wheat. They used nitrates and phosphorus on some of their plots alone and in excessive quantities. I, also, did these things, and for the same reasons, but I used potash on some other plots and they did not.

They hold that climatic conditions as a cause for the quality of wheat is so general, indefinite and unsatisfactory that one must seek some more evident one—a view that I have repeatedly expressed, and which I, in a general way, maintain in *Bulletin* 205, in which I show that it is insufficient as an explanation.

They state that their check plots produced light-colored, half-mealy or transitional kernels. The plots to which phosphoric acid or superphosphates were applied, produced the same kind of seed.

I record that my check plots produced grain affected with yellow-berry, mealy or half-mealy kernels, and that this condition was not affected by the application of phosphorus as superphosphate.

They record the effects of nitrate to be the production of small, well-formed kernels which were hard, flinty and dark-colored.

My statement is that the application of nitrate depresses or entirely prevents yellow-berry and produces small, flinty, and often shrunken berries.

They observed that nitrates used in conjunction with other fertilizers produced effects similar to those produced by nitrates alone. I have made the same observation.

I used potash on three series of plots and they did not. I observed that potash greatly increased the amount of yellow-berry. They did not.

The examination of the kernels and flour also will run in their larger features parallel, which, of course, is to be expected. The two studies are not identical, but the general features are so similar that one might readily be considered a copy of the other, *which is not the case.*

My work was planned and three seasons' work done on my general project before I learned of the existence of this article, giving the record of this work done by these authors at Poppelsdorf. I shall in no wise change the plan of my work, as I hoped from the beginning to carry my investigation far beyond its present stage. The work so far done seemed necessary, before it would be justifiable for me, or anyone else, to assign any cause or causes for the characteristics of our wheat. Indeed, it is not even yet certain that one can properly speak of Colorado wheats as having any predominant and fixed characteristic.

It is a matter of surprise to me that this work of Ritthausen's has received apparently no attention. I found an abstract of the article in the *Journal of the Chemical Society,* London. This abstract did not give a very adequate idea of the facts presented in the article. I have also found it mentioned in the literature given by Schindler, in his "Der Getreidebau" at the end of the section "Der Weizen."

Colorada Experiment Station W. P. Headden
Fort Collins, Colorado, January 21, 1916

TEMPERATURE CONTROL IN WOOD DISTILLATION

Editor of the Journal of Industrial and Engineering Chemistry:

The note by Mr. R. B. Goetschius in This Journal 8 (1916), 196, on "Temperature Control in Wood Distillation Plants" has been read with much interest. Since much of the agitation on this subject referred to by him has been largely the result of experiments made by the United States Forest Products Laboratory the discussion is timely and of especial interest, as it affords an opportunity to clear up several points which are apparently misunderstood.

It is probably correct that the present design of wood distillation plants is not adapted to the greatest possible increases in products resulting from scientific temperature control but experiments in the laboratory, and also in commercial plants, subject to all the variables of factory operation have shown much greater possibilities along this line than is generally supposed by plant operators. The results of preliminary experiments which form the basis for this statement were given in This Journal 7 (1915), 663.

Fortunately, it is not possible to control the distillation irrespective of any variation in size of pieces in a commercial size retort, so that all the water is distilled out of the charge before destructive decomposition takes place. Any control embodying such a conception would certainly result in a very great absence of control during the latter stages of the distillation as the decomposition of a large volume of very dry wood is likely to be extremely violent.

Experiments by the Forest Products Laboratory have shown that apparently certain well defined relations exist between the rate of rise of the temperature in the retort, the flow of distillate, and the yield of products. The interaction between the various products in the retort in the presence of the hot charcoal undoubtedly plays an important part in the yields. Temperature control in the distillation of wood, as interpreted by these experiments, is then to make the greatest possible proportion of the distillations follow the proper combination of these factors which will give the best yields. A technical operation involving the rate of rise of the temperature as an important factor is obviously best conducted by employing pyrometers.

In a continuation of these studies in longer tests in commercial plants, results of which have not yet been published, it was found, strangely enough, that about equal mixtures of large pieces of split wood and smaller pieces of sawed wood more readily gave the desired rate of rise of temperature than either of the two kinds alone. Therefore, instead of requiring evenly sized wood in order to secure good results with pyrometers, possibly by proper control the variability of the size of wood may even prove an advantage.

Aside from this more scientific basis for the application of control there are other reasons which it would seem were alone sufficient for employing pyrometers in wood distillation plants. The great variability of raw material in size, moisture content, etc., has been well pointed out. Would not any method which would tend to overcome some of these difficulties be an advantage? Also, operators who have, unfortunately, had to rely on untrained firemen have found pyrometers to be of great assistance in preventing excessive firing and other injurious practices.

It is undoubtedly true that the proper combination of the various factors, such as flow of distillate and temperature rise, will vary somewhat with different plants because of differences of size and condition of wood and the best adaptation of these principles will have to be worked out for the individual plant. The great value of knowing as accurately as possible these conditions in applying scientific control has been well demonstrated, and it is believed that a general adoption of pyrometer temperature control in the primary distillation will help to bring the wood distillation industry out of the somewhat empirical condition which has marked it up to within the last few years.

Forest Products Laboratory
Madison, Wisconsin, February 11, 1916
R. C. Palmer

REMARKS ON THE PRODUCTION OF RADIUM BY THE BUREAU OF MINES

Editor of the Journal of Industrial and Engineering Chemistry:

The work of the Bureau of Mines in coöperation with the National Radium Institute Company in the production of radium has been given an unusual amount of newspaper publicity. The statements supplied by Dr. Parsons and others interested in the work have often been considerably altered or abbreviated in publication and a great deal of misconception in regard to the work prevails in the public mind. However, we read in the memorandum for the press, issued several months ago by the Secretary of the Interior, that the Bureau of Mines has "devised methods for the production of radium from carnotite ore of Colorado and Utah at an average cost of $36,500 a gram, two-thirds cheaper than the market price of $120,000 asked by foreign producers, the new cheaper methods making it more certain that medical institutions will be able to procure a sufficient quantity of radium for the treatment of cancer and malignant growths," etc.

The writer has been interested in the commercial production of radium from carnotite since 1912 and naturally has followed with interest the work of Dr. Parsons and his associates along this line. The problem to be solved was clearly appreciated[1] before any work was carried out by the Bureau of Mines and it was somewhat of a shock to the writer to see how little has been accomplished in the attack on the real problem as testified by the data given in a recent bulletin.[2] Briefly, the problem consists in devising means for economically working up the low-grade carnotite ore, which forms by far the greater proportion of the radium ore occurring in Colorado and Utah. This would involve an economical process for concentrating the ore, as well as an efficient chemical method for extracting the radium, uranium and vanadium from the concentrates, and the refining of these products.

The carnotite ore from the Colorado field will average about 1 per cent, or less, of uranium oxide and by hand-picking from 5 tons of mine ore, it is usually possible to sort out a ton of material averaging between 1.5 and 2.0 per cent of uranium oxide. The remaining ore has in the past been considered too poor to ship and so has accumulated on the ore dump, where through weathering, etc., losses of the values result. Up to date the company with which the writer is associated has shipped about 5,000 tons of carnotite ore from its mines to the reduction plant at Canonsburg, Pa. Naturally, the endeavor has been to ship as high a grade of ore as possible, consistent with the quantity requirements, since the ore must be packed to the foot of the trails by burro, then hauled 40 to 60 miles by wagon to the nearest railroad, making transportation charges very high. Rich claims have been stripped bare in this effort, and still the average on all of the shipped ore was 1.6 per cent of uranium oxide. Approximately 20,000 tons of low-grade ore were either not mined or not shipped owing to the poor quality of the ore.[1]

The results so far attained by the Bureau of Mines may be summarized briefly. About 1000 tons of high-grade carnotite ore (2.5 to 2.6 per cent U_3O_8) have been treated (without concentration) by a method (extraction with concentrated nitric acid) which is not directly applicable to concentrates, and a fairly high extraction of radium has been attained (85 to 90 per cent). The uranium in the ore has been extracted as crude sodium uranate with an efficiency of about 85 per cent, and the vanadium as iron vanadate with an efficiency of 21.4 per cent. Nearly 5 grams of radium (element) have been extracted from the ore in the form of raw radium barium sulfates containing about 1 mg. of radium per kg. of salt, and of this material about half has been worked up to yield radium salts of sufficient purity for the designed therapeutic uses. Nothing essentially practical has been contributed to the art of radium production, and the cost data, as given, are of no great significance for actual large scale production of radium, since the conditions under which the Bureau of Mines produced the radium were abnormal and cannot be duplicated in present practice on account of the lack of high-grade ore.[2] In *Bulletin* **104**, there is no summary which would show the total amounts of each chemical required per ton of ore, and there is no cost price stated for the acids and alkalies. The result is that there is no simple way for an outsider to figure costs on the Bureau of Mines process. Furthermore, in figuring the cost of any article it is necessary to add

---

[1] Bureau of Mines, *Bull.* **70** (1913), 8.

[2] Bureau of Mines, *Bull.* **104**. "Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite," by C. L. Parsons, R. B. Moore, S. C. Lind and O. C. Schaefer.

[1] Since the beginning of 1911, the carnotite ore shipped in Colorado and Utah had a uranium oxide content of approximately 200 metric tons. Of this ore, about 55 per cent has been treated in the United States and the balance has been shipped abroad. In the earlier years a large proportion of the carnotite ore was shipped abroad by the General Vanadium Company for the recovery of vanadium. The radium is the residue after the extraction of the vanadium was not refined; however, these residues have since been offered for sale—so that the radium will probably be extracted. The total amount of radium in the carnotite ore so far mined and shipped amounts to about 66 grams and assuming an efficiency of extraction of 70 per cent the recovered radium would be about 46 grams, of which 25 grams should have been extracted in the United States and about 21 grams (including General Vanadium Co. residues) abroad. This represents the bulk of the world's present supply of radium, since none of the other deposits of radium compare with the Colorado and Utah deposits.

[2] Considering that these investigations were made in part (*Bull.* **104**, p. 13) "to enable the miner and prospector to obtain a just return for the ores" it is hard to reconcile this statement with the pitifully inadequate prices paid to the miners by the National Radium Institute for high-grade ore—after the war had cut off the European ore market. Before the war carnotite containing 2 per cent U_3O_8 was sold to French buyers at $3.30 per lb. of U_3O_8, and offers went as high as $4.00 for this ore. These prices figure $132 and $160 per ton of 2 per cent ore, and at the same rate, would give $178.20 and $216 per ton of ore containing 2.6 per cent U_3O_8, such as was worked by the Bureau of Mines, and shown in *Bull.* **104** in the costs at $96.36 per ton. In addition to the ore mined from the Crucible Steel Mining and Milling Co.'s claims, ore was purchased directly from miners and for this ore the National Radium Institute paid in one known instance $1.70 per lb. of U_3O_8 in about 25 tons of ore, f. o. b. Placerville, Colo., that averaged 3.19 per cent U_3O_8 or at the rate of $108.46 per ton of ore. For ore containing from 2 per cent to 5 per cent U_3O_8 they offered, f. o. b. Denver, $2 per lb. of U_3O_8, or $80 per ton of 2 per cent ore. (Freight rate Placerville to Denver $6 per ton, Placerville to New York $11.57 per ton, Placerville to Hamburg or Liverpool, *via* Galveston, $14.50 per ton.) When it was evident that the National Radium Institute was in the field to buy ore, the State Commissioner of Mines in Colorado made public announcement advising miners to hold their ore for at least $2.50 per lb. of U_3O_8 in 2 per cent ore and proportionally higher prices for higher grade ore. Yet it is on the basis of the rich ore obtained "for a song" that the Bureau bases its production figures for cheap radium. Consistency seems lacking in the argument that the miner will profit by cheaper radium. It is possible that the various arguments are to apply independently, one to the miners, others for the physicians and hospitals, etc.

the cost of marketing (which has not been done in the $37,599 per gram of radium—*Bull.* 104, p. 117) and a sum for the safe and certain profits on the investment. These charges are indispensable and very considerable items for an article like radium. Indeed, with an uncertain market such as radium has, the allowances for these items must be far higher in proportion to the cost of production than on such staples as gasoline, copper, etc., and for these articles the selling price is by no means the cost of production of the most favored producer.

Average mining costs cannot be estimated by stripping out 800 tons of high-grade ore from one rich claim, nor will the mining of several hundred tons of ore on adjacent claims give an average for the whole Colorado field. In actual practice a great deal of preliminary work must be done before the ore is uncovered and only in rare cases are considerable bodies of high-grade ore found which would compare with the *Maggie C* claim, from which the Bureau of Mines secured most of the ore. With rich claims advantageously located, so that little if any packing by burro was necessary and with the good roads already constructed, it is not surprising if ore costs were low.

Dissolving carnotite in strong nitric acid was the analytical method used more than ten years ago in the quantitative determination of radium in this material. This is the basis of the Bureau of Mines method and when applied to rich ore ground to 20 mesh gives an efficient extraction. The same method, however, will not apply to the 200 mesh concentrates, since the finely powdered silica in the concentrates makes it almost impossible to filter the mixture (see also *Bull.* 104, p. 111). Low-grade ore containing 0.8 to 1 per cent U_3O_8 must be concentrated. A 2.5 per cent U_3O_8 concentrate from such ore is much higher in Mg, Al, Fe and Ca salts than a straight 2.5 per cent ore and would require more nitric acid than the unconcentrated ore. It is not yet shown that the presence of considerable amounts of gypsum (which frequently occurs with the carnotite and would be found in the concentrates) would not introduce difficulties in the way of a poor extraction, should mechanical or other means be found to overcome the filtration difficulty. These are the problems of the practical radium producer which the Bureau of Mines has barely touched, problems of the highest importance for the real conservation of our radium deposits.

Under the agreement made, the Crucible Steel Company, which owns the claims that were worked (*Bull.* 104, p. 8) "agreed that if the National Radium Institute should be formed these claims would be leased to the Institute on a 15 per cent royalty basis under an agreement providing for the return of the uranium and vanadium content of the ore to the company." Vanadium in the form of ferro-vanadium has a high value in the steel industry, and yet the Bureau was satisfied with an extraction process for radium where the vanadium recovery is shamefully low. This is admitted for we read (p. 107): "The process described in this bulletin could not be recommended were the recovery of the vanadium in the ore the main object." However, in spite of the contract to deliver to the Crucible Steel Co. the uranium and vanadium, we find that little effort was made to extract this vanadium for (p. 109) "lately, on an average 55.5 per cent of the vanadium in the ore remains in the residue, and 13.6 per cent remains in the iron-calcium precipitate, while 8.1 per cent appears in the sodium uranate and 21.4 per cent in the iron vanadate. The total average recovery in vanadium, including that from the sodium uranate, is, therefore, a little less than 30 per cent." No statement is made as to the amount of this material delivered nor as to the opinion of the Crucible Steel Co., with regard to the results of the process for uranium and vanadium. Doubtless such a method of extraction could hardly appeal to that company as satisfactory.

As regards the mining and concentration of lower grade ore, *Bulletin* 104, p. 11, says: "A separate report on the mining and concentration of radium ores is being prepared and will shortly be published by the Bureau." Dr. Parsons in a lecture at the Chemists' Club in New York, before the New York Section of the Society of Chemical Industry, on December 17, 1915, stated that the concentration experiments were being made using the air separator, the Raymond mill being used. He was not prepared to state results. However, the writer can say, as a result of the experiments of one company, that this mill will not give an economical treatment of low-grade ores, and it can hardly be said that this result is due to lack of experience, since the Raymond separator has been in use by the Standard Chemical Company since the beginning of 1912. In trying this particular apparatus the Bureau of Mines was only borrowing a method already in use.

The National Radium Institute has profited largely by the coöperative agreement with the Bureau of Mines, since the conditions under which the agreement was made were such as to insure either the delivery of the radium or the termination of the work if the radium could not be produced. However, it does not require the production of 5 grams of radium from high-grade ore by a "skimming the cream" method to determine whether or not radium could be produced by the Bureau of Mines, and it is significant that costs were figured on this method rather than on a method involving the use of the average ore. Costs, using the Bureau process and based on normal conditions, would show nearly double the stated cost of production and would, of course, not verify the earlier assertions of the officials of the Bureau with regard to their process. Having demonstrated the ability to prepare radium, it is rather odd that the purposes of the Bureau and the National Radium Institute, namely, the study of the mining and concentration of ores and the working up of the concentrates, has been delayed while radium was being extracted for a private corporation for use—in one instance at least—in a private hospital for private gain. According to *Bull.* 104 (pp. 8 and 9), such a coöperative agreement is legal and justified in view of similar coöperative work betwen the Department of Agriculture and farmers, and the Assistant Secretary of the Interior approved of the arrangement. This explanation, however, really does not seem to justify the actual arrangements made, for in the case of the Department of Agriculture the results obtained benefit many others since the results are general in nature, whereas here a corporation has, through some considerable expense to the Government, profited in securing much valuable material under special arrangements, and under conditions which do not offer equal opportunity to all. Ostensibly the purpose of this work by the National Radium Institute is to further the cause of radium therapy—and the production of radium. The results so far have been the exact reverse. The market for radium for therapeutic purposes in America has been killed, since the physician who reads in the newspaper that the Government has produced radium for one-third the present selling price hesitates to buy radium, and as a result of the statements widely spread both by the Bureau of Mines and by the president of the National Radium Institute to the effect that it is useless to try to cure cancer without the application of comparatively enormous amounts of radium,[1] we find the surgeons and physicians hesi-

---

[1] In connection with the matter of high dosage it is of interest to note that the London Radium Institute, a charitable foundation not for gain, which has over 2 grams of radium for application, in the last report of work shows the following amounts of radium element as the highest used in the treatment of those malignant conditions which require heavy dosage: Cancer esophagus, 61 mg.; cancer uterus, 107; cancer bladder, 64.2; cancer breast, 187; cancer thyroid, 225; cancer rectum, 134; cancer prostate, 97; periosteal sarcoma, 86; lymphosarcoma, 225; lymphadenoma, 268; splenic leukemia, 145; fibroid disease of the uterus, 107; mediastinal tumor (patient died suddenly less than 2 months after treatment), 480. The quantities given are maximum and more frequently smaller amounts suffice.

To the certain knowledge of the writer, there are in the United States, besides the hospitals benefited by the radium produced by the Bureau of Mines, 3 institutions and medical men possessing 200 or more mg. of radium tating to venture into the field of radium therapy. The result, practically, is to confirm the National Radium Institute in a monopoly of radium for therapeutic purposes. Legislation in regard to the Government radium lands is again pending and it seems more than a coincidence that *Bulletin* 104 should appear with its glitter of cheap radium—at this moment.

STANDARD CHEMICAL COMPANY CHARLES H. VIOL
PITTSBURGH, February 16, 1916

COMMENTS ON "GAUGING OF STORAGE TANKS"[1]

Editor of the Journal of Industrial and Engineering Chemistry:

We have studied the above-mentioned article by Mr. Ogden with a great deal of interest. There is certainly a very real need of a simple and accurate method of gauging the volume of material contained in these storage tanks. Such a method should take account of the material contained in the bumped heads, should be reasonably accurate and should be simple and easy to apply. The writer is inclined to be of the opinion, however, that Mr. Ogden's method scarcely meets this need satisfactorily, basing this opinion upon the following features of Mr. Ogden's method: (1) *lack of accuracy,* (2) *lack of simplicity or general applicability.*

DESCRIPTION OF METHOD

Mr. Ogden treats the contents of the tank as consisting of two component parts, (1) the content of material in the cylindrical portion of the tank, *i. e.,* the tank exclusive of the bumped heads, and (2) the content of material held by the bumped heads. By determining the values of these component volumes for each vertical inch of height and adding them together, Mr. Ogden obtains the total content of material for each vertical inch of height. This amounts to a virtual calibration of the tank for each inch of height.

In discussing this article, we shall endeavor to follow this method of Mr. Ogden in treating the two-component volumes separately and we shall designate them as Vol. *A* (*volume of cylindrical tank*) and Vol. *B* (*volume of a single bumped head*). Then *Total Vol.* = Vol. *A* + 2 Vol. *B*

Volume *A* is equal to the product of the length of the tank and the cross-sectional area of the liquid formed in a plane perpendicular to the axes of the tank. This cross-sectional area is the segment of a circle. Mr. Ogden correctly states that its value can be obtained by integral calculus but that a simpler method consists in the use of trigonometry and geometry. Mr. Ogden seems to feel, however, that the latter method is still too complex for his purposes and he, therefore, adopts an approximation consisting substantially as follows: Vol. *A* is considered as consisting of a number of flat slabs 1 in. thick, of trapezoidal cross-section, and piled one upon the other. Mr. Ogden obtains by geometry the value of the medial line of each trapezoid. Multiplying this value in inches by the length of the tank in inches, he obtains the volume of each slab. Adding the volumes of these slabs, he obtains the varying values for Vol. *A.* Clearly this is quite cumbersome and only an approximation with its degree of accuracy dependent upon the ratio of the "unit of calibration" (in this case 1 in.) to the total diameter of the tank. If the value of this ratio is small, the inaccuracy introduced is not very considerable. On the other hand, if this ratio is large, the method becomes very inaccurate. Regardless, however, of the degree of accuracy attained, there scarcely seems to be a very real need of a method of approximation since we have very accurate Engineering Tables which give accurately the area of the circular segment from a knowledge of the ratio of its height to the diameter of the circle.[1]

In determining Volume *B* there is more warrant for an approximation since no method has apparently up to the present time been published which gives this volume content accurately. Vol. *B* consists of a portion of the segment of a sphere. Mr. Ogden treats the radius of this sphere as equal to the diameter of the tank which assumption, in view of the practice of tank design, is essentially correct. Mr. Ogden's method of determining Vol. *B* is substantially as follows: Volume *B* is considered as consisting of a number of 1 in. slabs piled one upon the other. Through the center of each of these slabs, Mr. Ogden passes a horizontal plane. The area of the plane section is, strictly speaking, a circular segment, but is regarded by Mr. Ogden as parabolic. The base and altitude of this parabolic section are determined geometrically by Mr. Ogden and the area of the section taken as $^{2}/_{3}$ of their product. The volume of each slab is then determined as the product of this area and the thickness 1 in. and Vol. *B* is determined for varying heights as the sum of the volumes of these slabs. This method of calculation is not only inaccurate by reason of the assumption of the section being parabolic, but it is also inaccurate in assuming the volume of each slab to consist of the product of the area of the medial section and the thickness of the slab. As in the case of Vol. *A*, the magnitude of the latter error is dependent upon the ratio of the "unit of calibration" to the diameter of the tank.

ACCURACY—As stated previously, Mr. Ogden's method introduces a number of inaccuracies, the magnitude of which is chiefly dependent upon the ratio of the "unit of calibration" to the diameter of the tank. For a given tank of 7 ft. diameter, the error introduced is not very large if the tank is calibrated for each 1 in. of height. The calculation, however, involved in making this calculation for each 1 in. of height is very large and consumes a great deal of labor. On the other hand, if the calibration is made for 3 or 4 in. intervals, the labor of calculating is decreased, but errors of considerable magnitude are introduced. It, therefore, becomes a method which requires the sacrifice of accuracy or of simplicity of calculation.

At the conclusion of Mr. Ogden's article, he gives an example attempting to compare the true volume of a cylindrical tank and the volume obtained by using his method. This comparison is somewhat misleading. In the first place, it is made between the total volumes of the tank and not between volumes of material partially filling the tank. The errors introduced by Mr. Ogden's method are by no means at their maximum percentage value in the case of the calculation of the total volume of the tank. A true index of the accuracy of Mr. Ogden's method can be obtained only by making the comparison at the point at which the errors of Mr. Ogden's method are at their maximum percentage value.

SIMPLICITY OF CALCULATION AND GENERAL APPLICABILITY—The main criticism of Mr. Ogden's method does not rest, however, with its inaccuracy, but rather with its lack of simplicity and difficulty of application. As seen from the foregoing description of Mr. Ogden's method, the determination of the volume content of material in any tank requires a long and laborious calculation of the volume content of each inch of material in the tank, which amounts to a virtual calibration of the tank. Clearly the labor involved in such a calculation which must be made in the case of each tank containing material to be measured, is a feature which argues strongly against this method. In the past, it has been the custom of engineers to treat these storage tanks as though they were true cylinders. The vertical "innage" of material in the tank is measured and is expressed as a decimal fraction of the diameter. Reference is then made to the engineering tables for "Area of Circular Segments" and a factor is found which corresponds to the above

---

element, and, besides these there are 10 institutions and physicians that possess 100 or more mg., and 16 that have 50 or more mg. available. The results in radium therapy reported by these institutions and physicians show that the quality of their work compares favorably with the work in institutions where over a gram of radium is available, the number of patients treated, of course, being smaller.

[1] R. I. Ogden, THIS JOURNAL, 8 (1916), 58.

[1] See Kent, "Mech. Eng. Handbook," 8th Ed., pp. 121–122.

mentioned decimal fraction. This factor multiplied by the product of the square of the diameter of the tank and the length represents the volume content of material in the tank regarding the same as a true cylinder. Thus, from a knowledge of the height of material in the tank and the tank dimensions, the volume content of the material can be obtained with fair accuracy and by means of a very simple calculation. While this method is inaccurate in so far as it fails to take account of the bumped heads of the tank, yet it does not require a long or laborious calculation of the volume contents of each inch of the tank.

In conclusion, the writer feels that there remains a very real and present need for a method of gauging these storage tanks which will be more accurate and less laborious than Mr. Ogden's method and which will, at the same time, take account of the material contained in the bumped heads.

THE BARRETT CO., 17 BATTERY PLACE
NEW YORK, January 19, 1916

K. B. HOWELL

U. S. DYESTUFF SITUATION AT CLOSE OF 1915—CORRECTION

In my article under the above title, THIS JOURNAL 8 (1915), 166, the following corrections should be made:

Page 167, Col. 2: monthly output of naphthalene should read "1,000;" phenol, "830 tons."

Page 168, the following additions should be made:

MANUFACTURERS OF COAL-TAR CRUDES

"The United Gas Improvement Co., Philadelphia.
"The Semet-Solvay Co., Pittsburgh.

"A number of firms engaged in the manufacture of high explosives, or organized for the special purpose, are engaged in the production of synthetic phenol."

MANUFACTURERS OF COAL-TAR INTERMEDIATES

"In addition to the above, mention may well be made of the following companies, which have put up large plants for the manufacture of aniline, but which consume the bulk of the output in their own works:

Millville Manufacturing Co., Millville, N.
B. F. Goodrich Co., Akron, Ohio.
Goodyear Chemical Co., Akron, Ohio.
Lyman G. Bourne, Inc., Auburn, Ind.
Naugatuck Rubber Goods Manufacturing Co., Naugatuck, Ct.
Merck & Co., Rahway, N. J.
The du Pont de Nemours Co., Wilmington, Del.
The Aetna Explosives Co., Pittsburgh, Pa."

MANUFACTURERS OF ARTIFICIAL DYESTUFFS

"The United States Coal-Tar Products Co., New York City.
"The Sherwin-Williams Co., New York City."

WASHINGTON, February 9, 1916

THOMAS H. NORTON

ALUMINA IN ALUMINUM SALTS—CORRECTION

The factor weight to be taken in the analysis of aluminum salts by my rapid method should be "3.4067" and not 3.4038 as given in my paper printed in THIS JOURNAL 7 (1915), 1059.

This factor is based on titration with $N/2$ acid. When acids are prepared without reference to normality strengths, this factor weight is derived as follows: the value of 100 cc. of the acid, in terms of H_2SO_4, is multiplied by four times the factor that gives the equivalent Al_2O_3; *i. e.*, if the standard acid used has a strength of 0.02 g. H_2SO_4 per cc. the factor would be: $2 \times 0.3473 \times 4 = 2.7784$.

LAUREL HILL, LONG ISLAND
NEW YORK, January 3, 1916

WILFRED W. SCOTT

RADIUM, ETC., FROM CARNOTITE—CORRECTION

In my article in THIS JOURNAL, 8 (1916), 51 will be found the statement: "Three or four crystallizations only are necessary to bring the major part of the radium to a concentration of 60 to 80 per cent radium bromide." This should read: "Twelve to twenty crystallizations only are necessary."

January 22, 1916

C. L. PARSONS

SCIENTIFIC SOCIETIES

FIFTY-SECOND MEETING OF THE AMERICAN CHEMICAL SOCIETY—UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN—APRIL 18 TO 21, 1916

The Fifty-Second meeting of the American Chemical Society will be held at the University of Illinois, Urbana-Champaign, from Tuesday, April 18th, to Friday, April 21st, inclusive. The Beardsley Hotel, Champaign, has been chosen as headquarters. Additional accommodations can be obtained at the Hotel Inman, located on University Avenue, one block from the Illinois Central station and on the car line to the University. All meetings will be held at the University of Illinois which can be reached by car from the corner of Main and Neil Streets, one block south of the Beardsley Hotel.

CHAIRMEN LOCAL SECTION COMMITTEES

EDWARD BARTOW, *General Committee.*
W. A. NOYES, *Finance.*
C. W. BALKE, *Reception and Registration.*
C. G. DERICK, *Entertainment and Program.*
D. M. MCFARLAND, *Transportation and Excursions.*
E. W. WASHBURN, *Smoker.*
S. W. PARR, *Banquet.*
G. D. BEAL, *Press and Publicity.*
H. L. OLIN, *Exhibits.*
MISS ISABEL BEVIER, *Entertainment of Ladies.*

PROVISIONAL PROGRAM

MONDAY, April 17th, *Evening*, Council Dinner followed by Business Meeting.
TUESDAY, April 18th, *Morning*, General session.
Afternoon, Excursions to University buildings and grounds, including exhibition of live stock, floral display, and a visit to the plant-breeding laboratories. Review of University brigade.
Evening, Concert by the University Military Band. Smoker.
WEDNESDAY, April 19th, *Morning*, Sectional meetings.
Afternoon, Dedication of the new Chemistry Building. Governor Edward J. Dunne, of Illinois, will preside. Addresses will be given by President Edmund J. James, W. R. Whitney, of the General Electric Company, and member of the U. S. Naval Board, and Professor Alexander Smith, of Columbia University. Reception and inspection of Chemistry Building.
Evening, Subscription dinner.
THURSDAY, April 20th, *Morning*, Sectional meetings.
Afternoon, Excursions on University campus, including laboratories of mechanical, mining, hydraulic, electrical and railway engineering. Sectional meetings.
Evening, PUBLIC LECTURES: "Production of Radium," by C. L. Parsons, Bureau of Mines, Washington.
"Use of Radium in the Cure of Cancer," by C. F. Burnham, M.D. Baltimore.
FRIDAY, April 21st, Excursion to Danville, Illinois, for the purpose of visiting:
Hegeler Brothers' Zinc Smelter and Sulfuric Acid Plant;
Western Brick Company's Kilns;
Three Rivers Coal Company's Strip Coal Mine.

Especial attention is called to the excursion by special train to Danville on Friday, April 21st. The smelter of the Hegeler Zinc Company was built in 1908, and is one of the most modern and best arranged in the country; the capacity has recently been trebled; the smelter utilizes the fumes from roasting the zinc ore. The brick and tile plant of the Western Brick Company is one of the largest in the country. Of unusual interest are the open-pit shale and coal mines furnishing material and fuel; the strip-pit coal mine gives a splendid illustration of the location of coal; usually a bed of coal a quarter to a half-mile long and fifty to one hundred feet wide is exposed. Arrangements are being made for optional visits to other plants.

All titles of papers should be in the Secretary's hands on or before April 7th or in the hands of the secretaries of divisions by April 5th in order to be placed on the final program. By vote of the Council no papers can be presented at the meeting the titles of which are not printed on the final program.

ADDRESSES OF DIVISIONAL SECRETARIES

Agricultural and Food Chemistry, G. F. Mason, H. J. Heinz Company, Pittsburgh, Pa.
Biological Chemistry, I. J. Phelps, Bureau of Chemistry, Washington.
Fertilizer Chemistry, F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Va.
Industrial Chemists and Chemical Engineers, S. H. Salisbury, Jr., Lehigh University, So. Bethlehem, Pa.
Organic Chemistry, H. L. Fisher, Columbia University, New York City.
Pharmaceutical Chemistry, Dr. Beorge D. Beal, University of Illinois, Urbana, Ill.
Physical and Inorganic Chemistry, James Kendall, Columbia University, New York City.
Water, Sewage and Sanitation, Dr. H. P. Corson, U. S. Public Health Service, Grove City, Pa.

C. L. PARSONS, *Secretary*

NEW YORK SECTION OF AMERICAN ELECTROCHEMICAL SOCIETY

ELECTROCHEMICAL WAR SUPPLIES SYMPOSIUM

The New York Section of the American Electrochemical Society met jointly with the New York Sections of the American Chemical Society and the Society of Chemical Industry at Rumford Hall, Chemists' Club, February 11, 1916.

The introductory address, by W. L. Saunders, of the Naval Board, emphasized the lack of relation existing between our industries among themselves, as well as the lack of information possessed by the United States Government concerning the capacities of the industries of the country. Mr. Saunders feels that the training of the men of the United States in the industries is far more important than training them as soldiers. He called special attention to the fact that industrial efficiency of a nation may be measured by its coal consumption, and gave the per capita consumption of coal by countries as follows: United States, 5 tons per annum; England, 4 tons per annum; Germany, 4 tons; Russia, $^1/_4$ ton; and France, 1.6 tons. Special emphasis was put on the fundamental importance of the chemical industries of the United States, since chemistry is the basis of all industrial projects. It is Mr. Saunders' opinion that our industries could scarcely be organized along lines of preparedness for war in a period of ten years.

Electrochemical War Supplies. By LAWRENCE ADDICKS. On account of illness, Mr. Addicks was unable to be present, but the chairman, Mr. Colin G. Fink, read a brief letter from Mr. Addicks, in which he emphasized the basic importance of the electrochemical industry in its relation to war supplies and preparedness for war.

Air Saltpeter. By W. S. LANDIS. Mr. Landis called attention to the fact that, at the outbreak of the war, Germany had no plants for the making of nitric acid from air, but it possessed in its various well organized and highly developed chemical industries plants and trained employees that were easily made available for the manufacture of ammunition and various war products. For instance, at the beginning of the war, Germany possessed only three Cyanamid factories with combined capacities of a little over 50,000 tons per year; at that time it was importing nitrogenous products that approximated 850,000 tons of nitrate of soda, 40,000 tons of nitrate of lime and at least 20,000 tons Norwegian cyanamid per annum. Eighteen months after the beginning of the war, Germany was producing nitrates for war purposes and for agricultural purposes on an annual basis of 600,000 tons Cyanamid, and 10,000 tons arc process nitric acid. The present German investment in the air-fixation processes is over $100,000,000.

It was pointed out that in order to accomplish this result the strain on the staffs of the chemical works must have been enormous and the importance of the United States having within its boundaries plants that could be thus diverted from their original purpose was especially emphasized. The manufacture of Cyanamid on this side of the Atlantic is now conducted on Canadian soil under American direction.

Mr. Landis reports that the manufacture of Cyanamid at Niagara Falls is carried on at a considerably higher efficiency than that existing in Germany at the time of his visit to the works there, which was just at the beginning of the present war. Furthermore, the product being made is of higher grade and the transformation into ammonia is at an efficiency equal to that of the German process, while the operation is actually conducted with fewer men and a simpler form of apparatus. Furthermore, the American manufacturers possess intimate knowledge of the design of such plants and very shortly a fair-sized plant will be producing nitric acid from Cyanamid by oxidation of the ammonia which can be obtained directly from Cyanamid. [For further reference to the making of ammonia from Cyanamid and reference to the apparatus now in use at Niagara Falls see THIS JOURNAL, 8 (1916), 156.] Mr. Landis concluded with the statement that this country is now in as good, if not a better position to supply nitric acid in case of war than Germany was in the fall of 1914.

[Dr. Baekeland asked concerning the cost of obtaining nitrogen from air for use in making Cyanamid and other air-nitrate products. Dr. Landis replied that this process was very simple and the cost so slight as to make it an exceedingly minor feature in the process.]

Hydrogen for Military Purposes. By E. D. ARDREY (U. S. Army). The speaker discussed the preparation of hydrogen and various methods by which it can be produced. He also went into considerable detail concerning the methods used by the different nations in recent war times for the production of hydrogen for use in military balloons.

New War Products. By ALBERT H. HOOKER. Mr. Hooker called attention to the wonderful development of electrochemical industries at Niagara Falls since the Niagara Falls power plant started, about 1891. The list of products without which it may be safely said the industries of the United States would be practically paralyzed includes the following: chloroform; crystallized graphite and carborundum used in preparation of parts for autos, shells, machines of all kinds; ferrotungsten and ferromolybdenum—75 per cent of the steel products of the United States to-day depend on the supply from Niagara; caustic soda—for refining of oils and general use in all chemical industries; metallic sodium; hypochlorites, for which the Niagara plants are the main source; liquid chlorine; cyanamide—used as fertilizer and as an intermediate product in the manufacture of ammonia from air nitrogen. Mr. Hooker deprecated any attempt to injure the spectacular beauty of Niagara Falls, but stated that many times the power now taken from the Niagara River could be developed without changing the appearance of the falls any more than ordinary changes caused by the winds and regular variations in the level of Lake Erie. He also emphasized the wisdom of having available the maximum possible power that might be developed from the Niagara Falls in case of war, since under war conditions it would be absolutely necessary to make air nitrates by electrical methods as our supply of ammunition would be entirely dependent upon our supply of saltpeter in case the natural resources of Chile were made unavailable.

Magnesium. By W. M. GROSVENOR. This paper is printed in full in this issue of THIS JOURNAL, page 275.

Liquid Chlorine. By G. ORNSTEIN. The author discussed the various chemical processes for producing chlorine and showed slides of the various types of cells now in use for this purpose. He took up the history of liquid chlorine and showed the machinery used in handling it. He discussed its use for making bleaching solutions and its various advantages over ordinary hydrochlorite. He also described in considerable detail the use of liquid chlorine in water sterilization. The last part of the paper was given up to a brief discussion of the market price of liquid chlorine and the possible injuries caused by the inhalation of chlorine. It is the author's opinion that the newspaper accounts of these effects have been exaggerated. The use of liquid chlorine in the manufacture of picric acid was mentioned but it was the speaker's opinion that liquid chlorine is more valuable for peaceful purposes than those of war.

Electric Steel. By G. W. SARGENT. Mr. Sargent reported that he had understood that the meeting was to discuss informally the subject of electrochemical supplies and that he had not prepared a formal paper, but would do so and present the same at the regular meeting of the Society at Atlantic City.

Electrolytic Zinc. By W. R. INGALLS. In the absence of Mr. Ingalls his paper was briefly abstracted by Dr. J. W. Richards.

PERSONAL NOTES

The nineteenth annual meeting of the American Society for Testing Materials will be held at Atlantic City, N. J., June 27 to July 1, 1916.

The United States Civil Service Commission announces the following open competitive examinations: *Analyst*, for men only, at a salary of $800 to $1,020, on March 8, 1916. *Junior chemist*, qualified in fuels, for men only, at a salary of $1,020 to $1,200 per annum, on March 22 and 23, 1916. Further information may be had from the United States Civil Service Commission, Washington, D. C.

John A. Hill, president of the Hill Publishing Co., died suddenly from heart failure on January 24th, at the age of fifty-seven years. Mr. Hill was the organizer and largest stockholder of the Hill Publishing Co., which prints the following technical journals: The *American Machinist*, foreign editions of which are issued in London and Berlin, *Power*, the *Engineering and Mining Journal*, *Engineering News*, and *Coal Age*. He was also president of the McGraw-Hill Co., Inc. Mr. Hill was vice-president of the Machinery Club and a member of the Engineers' Club of New York, the Railroad Club, the Campfire Club and the American Society of Mechanical Engineers.

Prof. H. V. Tartar, head of the Oregon Experiment Station Department of Chemistry, has been granted a two-year leave of absence to pursue research work at some of the leading eastern universities.

News has been received from Sweden that the actual delivery of the Nobel prize in Chemistry for 1914, awarded to Prof. Theodore W. Richards, of Harvard University, together with the other Nobel prizes for 1914 and 1915, will be postponed until June 1st of this year. The prize winners are invited to go then to Sweden in person to receive their prizes, and to give their Nobel lectures.

Charles V. Mapes, an industrial agricultural chemist of New York City, died January 23rd, in his eightieth year.

The Oklahoma Chemical Co., Sand Springs, Okla., contemplate the erection of a sulfuric acid plant at Lake Station. Other chemicals, including silica and caustic soda, will be manufactured.

It is reported that work has been actively commenced and new machinery is being erected to produce potash from Searles Lake, Cal. A reduction plant will be established at San Pedro, Cal., by the company, which is an English corporation.

Mr. James H. Payne, a consulting chemical and metallurgical engineer of Baltimore, died January 26th, at the age of thirty-four. He was educated at the Massachusetts Institute of Technology and had been successively employed by the Eastman Kodak Co., Texas Portland Cement Co., Security Cement and Lime Co., Virginia Portland Cement Co., Jamestown Portland Cement Co., with Richard K. Meade and with the Braden Copper Co., in Chile. For the past year he had been occupied with independent consulting work. He was a specialist in the use of rotary furnaces and had designed plants for reburning lime waste, nodulizing pyrites cinder, etc. At the time of his death he was interested in the manufacture of barytes compounds.

At a meeting of the Council of the Royal Society of Arts, London, January 24th, the Society Albert Medal was awarded to Sir J. J. Thomson for his researches in chemistry and physics and their application to the advancement of arts, manufacture and commerce.

Prof. W. H. Perkin, F. R. S. of Oxford University, has been appointed head of the research department of the British Dyes Limited, and chairman of the Advisory Committee to succeed the late Prof. Raphael Meldola.

The Institute of Arts and Sciences of Columbia University, New York City, gave the following series of lectures during the month of February on Highway Engineering:

"The Regulation of Different Classes of Traffic on Public Highways," by Edwin Duffey, Commissioner of Highways of the State of New York.

"Limitations of Tests which Define the Essential Properties of Stone Block, Paving Brick, Wood Block and Cement-Concrete when Used in Pavements," by W. W. Crosby, Chief Engineer, Maryland Geological and Economic Survey.

"The Manufacture of Paving Brick," by W. P. Blair, Secretary, National Paving Brick Manufacturers' Association, Cleveland.

"Essential Details of the Construction and Maintenance of Brick Pavements," by W. A. Howell, Engineer of Streets and Highways, Newark, N. J.

"Aggregates, Mixing Plants and Expansion Joints for Cement-Concrete Pavements," by L. R. Ferguson, Assistant Secretary Association of American Portland Cement Manufacturers, Philadelphia.

"Bond Issues as a Source of Revenue for Highway Improvements," by E. P. Goodrich, Consulting Engineer to the President of the Borough of Manhattan, New York City.

"The Legal Status of Highway Boundaries and Disposal of Surface Waters," by J. C. Wait, Attorney-at-Law, New York City.

The Chattanooga Chemical Co., of Chattanooga, Tenn., has started work on its new plant to cost $150,000, to manufacture phenol, toluol, etc. The machinery and other equipment have been purchased and the plant will shortly be ready to start operations. Lewis T. Wolle, president of the Chattanooga Gas and Coal Products Co., is president and general manager of the new concern.

Mr. William H. Bowker, of Boston, died on January 4th, at the age of sixty-five years. Mr. Bowker was for forty-three years actively at work in the fertilizer trade and was one of the best informed men connected in any way with the fertilizer industry.

The regular monthly meeting of the Detroit Section of the A. C. S. was held on February 17th. Mr. Matthew H. Bishop, president of the "Lawyers' Club," addressed the meeting on "The Law for the Business Man." The March meeting will be held on March 16th, at which Mr. Joseph M. Bourg, of the Park Chemical Co., will lecture on "The Chemical Composition of Steel in Its Relation to Its Industrial Uses."

The thirty-eighth regular meeting of the Connecticut Valley Section of the A. C. S. was held on February 12th. The program consisted of the following papers: "The Chemistry of Synthetic Caoutchouc," by Prof. Joseph S. Chamberlain, and "The Color Problem in the Paper Industry," by Mr. R. F. Hatch.

Morse Hall, home of the chemistry department at Cornell University, was destroyed by fire on February 13th with a loss of $300,000; the insurance amounts to $200,000. The blaze started in the photography rooms of J. P. Troy on the third floor. Records of research, and valuable apparatus and chemicals, which owing to the war cannot be duplicated at present, were lost in the flames. Five thousand books from the chemical library on the first floor were saved by students. The university department of chemistry announces that it purposes to continue its work.

Waldemar R. Kremer was appointed general sales manager of the Vilter Manufacturing Co., at the recent meeting of the board of directors succeeding the late Mr. Fred Ulrich. Mr. Kremer has been connected with the company for nearly ten years as consulting electrical and mechanical engineer in the sales department. He is a graduate of the electrical and mechanical engineering courses of the Royal Polytechnical Institute, Munich, Germany, and the Massachusetts Institute of Technology, Boston. In his new capacity he will have general charge of sales and supervision of branch offices and agencies in this and foreign countries.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is $2.50 per year, payable in advance, to the Superintendent of Documents.

BUREAU OF THE MINT

Annual Report and Report on the Production of the Precious Metals in the Calendar Year 1914. Director of the Mint. 304 pp. Cloth, 60 cents. "The gold production of the United States, including its insular dependencies, for the calendar year 1914 is estimated to have been $94,531,800, and the production of silver is estimated at 72,455,100 fine ounces.

"The output of gold in the United States, including its outlying territories in 1914, exceeded that of 1913 by $5,647,400. Of this excess $1,300,000 was from Alaska, nearly $1,800,000 from Colorado, and $1,000,000 from California. Gains and losses in other sections were unimportant.

"The construction of a Government railway into Alaska is looked forward to as a step likely to have great influence upon future developments in that territory. Otherwise there is nothing in sight upon which to base a prediction as to an expansion or falling off of mining operations except that the effect of the European war in controlling copper and lead production will have the incidental effect of reducing the yield of gold and silver from copper and lead ores.

"The amount of gold consumed in the industrial arts during the calendar year 1914 was $42,728,893, of which $34,621,619 was new material. Silver consumed amounted to 29,233,117 fine ounces, of which 22,474,787 fine ounces were new material. The net exports of United States gold coin for the fiscal year 1915 were $23,445,028."

Full data are given for the production of gold and silver in each state and in other countries of the world and the movement of gold and silver together with a number of other interesting statistics are discussed.

The charge for ore assays made by the mint and assay offices of this Bureau has been reduced from $3.00 to $1.00 for gold and silver and $1.00 for each of the following metals: Copper, tin, zinc, iron, lead, and tungsten. In this connection it is interesting to note that the average cost per assay at the Philadelphia mint was $0.686 for approximately 53,000 assays made, including apparently all overhead expenses. At some of the other mints the cost of assay is reported as low as $0.30 for gold or silver, apparently not including overhead expenses, however.

The purchases of silver for coinage amounted to 3,400,000 fine ounces at an average price of $0.51 per ounce. These purchases "so stimulated the market, whose unsteadiness had threatened a partial paralysis of the silver-mining industry all over the world, that production of silver has continued practically without abatement. It also had the effect of aiding the production of gold, inasmuch as all silver bullion carries a certain amount of gold."

The sale of electrolytic slimes containing platinum has been partially discontinued in order to permit the melting and spinning of the platinum for the use of Government laboratories. During the past months, platinum melting equipment has been installed in the New York office and the Philadelphia mint has perfected machinery for spinning the metal and manufacturing it into utensils for use in Government laboratories. In this connection it is interesting to note the quantity of these by-products obtained, which are reported as follows:

	Ounces	Value
Platinum..........	2,507.08	$92,677.82
Palladium..........	320.24	12,540.88
Iridium	102.00	5,100.00
Osmiridium	4.79	167.65
Copper.............	14,880.97	2,738.55

BUREAU OF MINES

Gasoline Mine Locomotives in Relation to Safety and Health. O. P. Hood and R. H. Kudlich; with a chapter on **Methods of Analyzing Exhaust Gases,** by G. A. Burrell. Bulletin 74. 83 pp. Paper, 15 cents. This article discusses the volume and character of exhaust gases under different conditions of operation and describes results of tests on locomotives to determine the extent to which they vitiate mine air, and results in the production of carbon monoxide. The methods of gas analysis described are the same as those in Bureau of Mines Bulletin 42.

Sampling and Analyzing Flue Gases. Henry Kreisinger and F. K. Ovitz. Bulletin 97. 64 pp. Paper, 15 cents. "This bulletin is intended to be a companion to Technical Paper 80,[1] and is written in non-technical language, as far as possible, so that it may be readily understood by persons who have not had the advantage of a technical education. Whenever possible, illustrations of apparatus and methods of handling have been used rather than elaborate descriptions."

Practically none of the material describes new work and the descriptions are extremely elementary, including illustrations and descriptions of equipment with which every person who has ever done any chemical work would be thoroughly familiar.

Manufacture and Uses of Alloy Steel. Henry D. Hibbard. Bulletin 100. 77 pp. Paper, 10 cents. "The object of this report is to give briefly information of present value relating to the manufacture and uses of the various commercial alloy steels, with the hope of stimulating the demand for such steels and extending their practical use. The report is issued by the Bureau of Mines as a contribution to the increase of efficiency in the preparation and utilization of the mineral resources of the United States."

For each of the steels discussed, methods of manufacture and working, properties and uses, composition and general information of interest are given, including in several instances a brief bibliography and a discussion of the theory involved. Alloy-treated steels and structural alloy steels are discussed, including the following: (1) Simple tungsten steels; (2) simple chromium steels; (3) manganese steel; (4) simple nickel steels; (5) nickel-chromium steels; (6) silicon steels; (7) high-speed tool steels; (8) chromium-vanadium steels.

The Limits of Inflammability of Mixtures of Methane and Air. G. A. Burrell and G. G. Oberfell. Technical Paper 119. 30 pp. Paper, 5 cents. The conditions influencing the explosibility of methane and air mixtures are discussed and experiments to determine the limits are described in detail. The smallest proportion of methane that was found to permit self-propagation of flame was 4.9 per cent; this result was obtained by ignition at the bottom of a box containing this mixture with an electric flash produced by pulling apart two copper wires through which a current of 7 amperes and 220 volts was flowing. The maximum percentage which permitted self-propagation of flame was between 15 and 15.4 per cent methane.

---

[1] Henry Kreisinger, "Hand Firing Soft Coal under Power-Plant Boilers," *Tech. Paper* 80, Bureau of Mines, 1915, 83 pp.

PUBLIC HEALTH SERVICE

Standards for Milk; Their Necessity to the Welfare of the Dairy Industry. John F. Anderson. *Public Health Reports*, 31 (Jan. 7, 1916), pp. 2–8. This is an address before the International Association of Dairy and Milk Inspectors, delivered in Washington, October 27, 1915. The contrast between the standards of different communities is pointed out and the importance of greater uniformity emphasized.

SANITARY LEGISLATION

Production, Care and Sale of Milk and Milk Products. The following ordinances establishing standards for milk and milk products and prescribing regulations as to the production, care and sale of these articles are printed in *Public Health Reports*, 31 (1916). In each case certain requirements as to fat, water, total solids, or bacterial count are included. Great diversity of standards is to be noted. The page reference and date in parenthesis is in each case the page and date of the report in *Public Health Reports*. The last regulation gives a modified standard for grade "B" milk and specifies new regulations as to pasteurization.

Kansas City, Missouri, Ord. 23314, July 17, 1915. (P. 34, Jan. 7th.)
Phoenix, Arizona, Ord. 64, August 14, 1915. (P. 96, Jan. 14th.)
California State Act, June 11, 1915, Chap. 742. (P. 147, Jan. 21st.)
Wichita, Kansas, Ord. 5261, November 18, 1915. (P. 292, Feb. 4th.)
Bay City, Michigan, Ord. December 6, 1915. (P. 280, Feb. 4th.)
Richmond, Virginia, Reg. Board of Health, December 13, 1915. (P. 346, Feb. 11th.)
N. Y. State, Reg. Public Health Council, October 5, 1915. Chap. 3. (P. 344, Feb. 11th.)

Use of Boric Acid as a Preservative. United States Supreme Court Decision in the Case of Price *v.* State of Illinois, 35 Sup. Ct. Rep. 892. Decided June 21, 1915. This decision upholds the Illinois Pure Food Law which prohibits the use of boric acid in a preservative for foodstuffs. It is concluded that "the law to prohibit the use of boric acid in a preservative, although such preservative was not a food in itself and was not shown to be injurious or unwholesome," was proper and valid.

Analysis of Ice. Kansas Board of Health Regulation, October 4, 1915. (Pp. 275–6, Feb. 4th.) These regulations require the analyses of ice in the State Board of Health laboratory at intervals, and set a limit of 100 bacteria per cubic centimeter and a requirement that no organisms of *B. coli* group be found by test of 1 cubic centimeter. Ice which does not meet these requirements must be sold for refrigeration purposes only and not for domestic consumption.

BUREAU OF STANDARDS

United States Standard Tables for Petroleum Oils. Anonymous. Circular 57, issued January 29, 1916. 64 pp. and 2 insert cards. This circular contains the following 5 tables:

1—Specific gravity at 60°/60° F. of oils having, at the designated temperatures, the apparent specific gravities indicated.

2—Degrees Baumé at 60° F. of oils having, at the designated temperatures, the apparent degrees Baumé indicated.

3—Volume that would be occupied at 60° F. by a quantity of oil, of various specific gravities, occupying unit volume at the designated temperatures.

4—Degrees Baumé, pounds per gallon, and gallons per pound corresponding to the designated specific gravities.

5—Specific gravities, pounds per gallon, and gallons per pound corresponding to the designated degrees Baumé.

"The expansion tables contained in this circular are based upon the results of experiments carried out at this Bureau between July, 1912, and December, 1914. During that time about 100 samples of crude and refined petroleum oils from various parts of the United States were examined and their densities determined at various temperatures.

"This investigation has shown that within the limits of ordinary measurements the rate of change of specific gravity with change of temperature is the same for all oils of the same specific gravity. In the calculation of the expansion tables (Tables 1, 2 and 3) the average rate of expansion found for all oils of each designated specific gravity has been used."

The tables contained in this circular apply to all petroleum oils, both crude and refined, produced in the United States. Each grade of oil, gasoline, illuminating oil, lubricating and fuel oil, etc., falls into its proper place in the tables by reason of its specific gravity. In the case of oils containing paraffin or other materials that become solid at low temperatures the expansion shown by the tables is somewhat too small at temperatures below the point of solidification.

Microstructural Changes Accompanying the Annealing of Cast Bronze. Henry S. Rawdon. Technologic Paper 60, issued January 25, 1916. 17 pp. [For extended abstract see This Journal, 8 (1916), 109.]

The Determination of Barium Carbonate and Barium Sulfate in Vulcanized Rubber Goods. John B. Tuttle. Technologic Paper 64, issued January 21, 1916. 5 pp. [To appear in full in the next issue of This Journal.]

Detection of Resin in Drier. E. W. Boughton. Technologic Paper 66, issued January 15, 1916. 9 pp. "A method has been developed for the detection of resin in driers which is reliable except when the resin content is very small, *e. g.*, less than 6 per cent of the ash-free non-volatile portion."

Three separate procedures are described. The first is comparatively simple but less sensitive. If this does not detect the resin, the second, more complicated but more sensitive procedure, may be followed; and if this in turn gives negative results, the third practically conclusive test, but one which requires greater time for its performance, can be applied.

Some Qualitative Tests for Gum Arabic and Its Quantitative Determination. C. E. Waters and J. B. Tuttle. Technologic Paper 67, issued January 31, 1916. 15 pp. "An incorrect report to the effect that a certain sample of mucilage contained no gum arabic led to a study of many of the published tests for this gum, as well as to a search for others than the few that proved to be reliable.

"The object of this paper is to bring together all the more important qualitative and quantitative methods that have been published and to present a new procedure for the determination of gum arabic.

"It was found that basic lead acetate gives the most characteristic reaction, while mixtures of copper sulfate and sodium hydroxide, and of neutral ferric chloride and alcohol are of value as confirmatory tests.

"A summary of the more important methods that have been proposed for the quantitative estimation of gum arabic is next given, followed by a description of the steps that led the authors to the use of alcoholic copper acetate-ammonia solution for this determination."

Turpentine Tables. Anonymous. Supplement to Technologic Paper 9. 2 Cards. These tables include the following four sheets of conversion data:

1—For reducing observed specific gravities of turpentine at various temperatures to true specific gravity at 60°/60° F.

2—For reducing observed degrees Baumé of turpentine at various temperatures to true degrees Baumé at 60° F.

3—Showing the degrees Baumé, pounds per gallon, and gallons per pound corresponding to various specific gravities.

4—Showing the specific gravity, pounds per gallon, and gallons per pound corresponding to various degrees Baumé.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Tests Used in Cotton Industry. W. A. Graham Clark. Special Agents' Series 105. 22 pp. Paper, 5 cents. This bulletin explains briefly the correct use of common terms including the various systems of cotton-yarn numbering, designation of various kinds of cloth, and the translation of foreign terms; 25 conversion tables applicable to the industry are included.

Cotton Goods in China. Ralph M. Odell. Special Agents' Series 107. 242 pp. Paper, 25 cents. In addition to a detailed study of the cotton-goods trade of China and a description of cotton growing and manufacturing in that country, there are included descriptions of about 200 samples of cotton goods of interest in this connection.

Dyestuff Situation in the United States, November, 1915. THOMAS H. NORTON. Special Agents' Series 111, 19 pp. Paper, 5 cents.

GEOLOGICAL SURVEY

Origin of the Zinc and Lead Deposits of the Joplin Region, Missouri, Kansas, and Oklahoma. C. E. SIEBENTHAL. Bulletin 606. 283 pp. "A valuable contribution to the study of the lead and zinc deposits of the Mississippi Valley, which are not only of great economic importance but have long been intensely interesting to students of ore deposits because they constitute a conspicuous example of the occurrence of sulfide ores in a region where plutonic or volcanic activities can have had no part in their genesis. The author holds that the Joplin ores were segregated from disseminated zinc and lead minerals in the Cambrian and Ordovician rocks of the Ozark uplift, by circulating artesian alkaline-saline sulfureted waters, and his careful observations and cogent reasoning have gone far to establish the general conclusion that ordinary cold artesian water may under some circumstances be a very efficient agent in the solution, transportation, and deposition of the constituents of certain sulfide ores. The illustrations include topographic and geologic maps and cross-sections of the Ozark uplift, diagrams showing early and late stages in Ozark artesian circulation, and halftone plates showing the manner of occurrence of the ores in certain of the mines."

Recent Alunite Developments near Marysvale and Beaver, Utah. G. F. LOUGHLIN. Bulletin 620-K, from Contributions to Economic Geology, 1915, Part I, pp. 237-70. Published December 3, 1915.

Notes on the Fine Gold of Snake River, Idaho. J. M. HILL. Bulletin 620-L, from Contributions to Economic Geology, 1915, Part I, pp. 271-94. Published December 21, 1915. "Under the present conditions of distribution, character of the gold, and methods of its recovery, it seems very doubtful if any ventures of a size large enough to expect success can be commercially profitable."

The Aztec Gold Mine, Baldy, New Mexico. WILLIS T. LEE. Bulletin 620-N, from Contributions to Economic Geology, 1915, Part I, pp. 325-30. Published January 15, 1916.

Cassiterite in San Diego County, California. WALDEMAR T. SCHALLER. Bulletin 620-P, from Contributions to Economic Geology, 1915, Part I, pp. 351-4. Published January 15, 1916. Further prospecting in this district has not revealed any general deposits nor the source of the cassiterite which has recently been found in small quantity. Further prospecting is contemplated.

Geology and Coal Resources of Northern Teton County, Montana. EUGENE STEBINGER. Bulletin 621-K, from Contributions to Economic Geology, 1915, Part II, pp. 117-56. Published January 5, 1916. The scope of this paper is limited to the geologic and economic features of this district which have a bearing on the value and quantity of coal resources.

Natural Gas Resources of Parts of North Texas. Bulletin 629. 126 pp. This bulletin includes the following three articles which have been prepared by representatives of the Geologic Survey in coöperation with the cities of Dallas and Ft. Worth, Texas: (1) **Gas in the Area North and West of Fort Worth.** EUGENE W. SHAW. (2) **Gas Prospects South and Southeast of Dallas.** GEORGE C. MATSON. (3) **Notes on the Gas Fields of Central and Southern Oklahoma.** CARROLL H. WEGEMANN.

Gold, Silver, Copper, Lead, and Zinc in Arizona in 1914. V. C. HEIKES. Separate 15, from Mineral Resources of the United States, 1914, Part I, pp. 427-75. Published December 14, 1915. In 1914 Arizona mines produced these metals valued at $60,000,000 which represented a decrease of $11,000,000 in value from the previous year. The decrease was principally in copper but slight decreases were noted also in lead and zinc. Gold and silver showed slight increase. The output of zinc increased in quantity but declined in value.

Gold, Silver, Copper, Lead and Zinc in Idaho and Washington in 1914. C. N. GERRY. (Mines Report.) Separate 18, from Mineral Resources of the United States, 1914, Part I, pp. 597-654. Published December 17, 1915. "The value of the mine production of gold, silver, copper, lead and zinc in Idaho in 1914 was $24,645,848, an increase of $496,799 over the value in 1913. This was not a large increase, as the metal market was dull during half the year, but the total value was greater than in any previous year. Marked increase, and, in fact, a record production, was made in silver, lead and zinc, but there was a decrease in gold, in copper, and in the quantity of ore marketed or treated."

Gold, Silver, Copper, Lead and Zinc in Nevada in 1914. V. C. HEIKES. (Mines Report.) Separate 19, from Mineral Resources of the United States, 1914, Part I, pp. 655-716. Published December 21, 1915. The mine production from 4,500,000 tons of ore, including the placer output, was valued at $29,300,000, representing a decrease of nearly $8,000,000 in value as compared with 1913. The number of producers was about the same as the previous year. The production of copper was nearly 28 per cent of the total value but represented a decrease of $6,000,000 in the previous year. Each of the other metals also decreased slightly in value.

Gold, Silver, Copper, Lead and Zinc in Utah in 1914. V. C. HEIKES. (Mines Report.) Separate 20, from Mineral Resources of the United States, 1914, Part I, pp. 717-56. Published December 23, 1915. The mine production in 1914 was valued at $37,000,000 or $7,700,000 below the previous year. Fifty-four per cent of the production was copper, but this was valued at $5,000,000 less than the previous year. Gold, silver and zinc showed decreases, but lead increased in quantity though decreased slightly in value.

Gold, Silver, Copper, Lead and Zinc in Montana in 1914. V. C. HEIKES. (Mines Report.) Separate 21, from Mineral Resources of the United States, 1914, Part I, pp. 757-97. Published December 24, 1915. The mine production of this state amounted to approximately $48,000,000 but showed a decrease of $14,000,000 in value compared with the previous year, due principally to the reduced output of copper, although silver and lead also decreased slightly.

The Production of Iron Ore, Pig Iron and Steel in 1914. ERNEST F. BURCHARD. Separate 16, from Mineral Resources of the United States, 1914, Part I, pp. 477-539. Published December 9, 1915. "The quantity of crude iron ore mined in the United States in 1914 amounted to 41,439,761 long tons, as compared with 61,980,437 long tons mined in 1913, a decrease of 20,540,676 long tons, or 33.14 per cent......The average price of ore per ton for the whole country in 1914 was $1.81, as compared with $2.19 in 1913. These quantities of ore, both mined and marketed, include the iron ore used for fluxing other metallic ores at smelters in the Western States, but the marketed ore does not include the iron ore sold for the manufacture of paint. The quantity of iron ore for paint marketed in 1914, which is reported in detail in another chapter of Mineral Resources, amounted to 18,452 long tons, valued at $46,995. The ore reported as sold for fluxing purposes other than in the manufacture of pig iron amounted to 42,677 long tons, valued at $114,985, in 1914."

The statistics also include data of imports, exports, the Cuban iron industry, and the production of iron ore in the principal countries of the world. There is also included a new section on beneficiated iron ores which include those iron ores which are improved in quality by some physical or chemical treating such as hand-picking, drying, roasting, washing, jigging, magnetic separation or agglomeration.

"The production in 1914 of all kinds of pig iron, including such ferro-alloys as spiegeleisen, ferromanganese, ferrosilicon, and ferrophosphorus, produced in blast furnaces as well as some that were electrically produced, was 23,332,244 long tons, compared with 30,966,152 tons produced in 1913, a decrease of 7,633,908 tons, or 24.65 per cent.

"The marketed production of pig iron in 1914 amounted to 22,263,263 long tons, valued f. o. b. at the furnaces at $298,777,429, a decrease in quantity of 26.74 per cent, and in value of 34.81 per cent. The average price per ton in 1914 was $13.42, a decrease in 1914 of $1.66 a ton. These values represent the approximate price per ton f. o. b. at the furnaces; this approximate price eliminates freight costs, selling commissions, and other items, which are included in the market prices of certain grades of pig iron as published in the trade journals."

PRODUCTION OF PIG IRON IN 1914, BY GRADES (LONG TONS)

Bessemer and low phosphorus	7,859,127
Basic (mineral fuel)(*a*)	9,670,687
Forge pig iron	361,651
Foundry and ferrosilicon	4,533,254
Malleable	671,771
Spiegeleisen	79,935
Ferromanganese	106,083
White, mottled, direct castings, etc	49,736
Total	23,332,244

(*a*) Includes a small quantity of basic iron made with charcoal.

MARKETED PRODUCTION OF FERRO-ALLOYS IN 1914 (LONG TONS)

	Quantity	Value
Ferromanganese	100,731	$4,440,253
Spiegeleisen	76,625	1,586,139
Ferrosilicon and ferrophosphorus	77,182	1,621,830
Ferromolybdenum, ferrovanadium and ferrotungsten	986	1,702,023
Total	255,524	$9,350,245

Copper in 1914. B. S. BUTLER. (General Report.) Separate 17, from Mineral Resources of the United States, 1914, Part I, pp. 541–96. Published December 8, 1915.

"The following statistical statement summarizes the copper industry in the United States in 1914:

Production of copper	
Smelter output	1,150,137,192 lbs.
Mine production	1,148,431,437 lbs.
Refinery production of new copper:	
Electrolytic	991,573,073 lbs.
Lake	158,009,748 lbs.
Casting and pig	60,840,368 lbs.
Total domestic	1,210,423,189 lbs.
Total domestic and foreign	1,533,781,394 lbs.
Total new and old copper	1,790,000,000 lbs.
Total ore produced	35,187,118 short tons
Copper ore produced	35,175,541 short tons
Average yield of copper	1.60 per cent
Imports	306,350,827 lbs.
Exports	840,080,922 lbs.
Consumption:	
Total new copper	711,624,158 lbs.
Total new and old copper	968,000,000 lbs.
Value of production in the United States	$ 152,968,246

"The smelter production of copper in 1914 showed a considerable decrease from that of 1913. The refinery production, like that of the smelters, showed a reduction from that of 1913, due to the same causes.

"Regardless of the unfavorable conditions, the average cost of producing copper in 1914 was doubtless considerably less than in 1913. The average cost per pound in 1914 of producing electrolytic and casting copper, as compiled from the annual reports of companies giving this item, was 8.62 cents, as compared with 9.49 cents in 1913 and with 8.74 cents in 1912. This cost for electrolytic and casting copper is probably somewhat below the average cost of the entire output, but doubtless represents the general trend of costs for the three years. The average cost per pound for Lake copper, as compiled from the reports of companies giving this item, was 10.94 cents in 1914, as compared with 13.44 cents in 1913 and with 10.28 cents in 1912. The cost figures for the year are somewhat surprising, in view of the marked curtailment of output for a part of the year, which might be supposed to raise the cost.

"The demonstration of this elasticity and ability to meet varying conditions should be a source of satisfaction to all interested in the copper industry.

"The average selling price of electrolytic copper, as compiled from the reports of companies giving that item, was 13.4 cents in 1914, and that of Lake copper was also 13.4 cents. This was not quite 2 cents a pound lower than the selling price for 1913, and it is evident that the profits of the industry were considerably less in 1914 than in 1913, regardless of the lowering of the cost price."

Lead in 1914. C. E. SIEBENTHAL. (General Report.) Separate 22, from Mineral Resources of the United States, 1914, Part I, pp. 799–827. Published January 14, 1916. "The output of refined lead produced in the United States from domestic ores in 1914 was 512,794 short tons, valued at $39,997,932, based on the average New York price of refined lead."

The Production of Natural Gas in 1914. JOHN D. NORTHROP. Separate 32, from Mineral Resources of the United States, 1914, Part II, pp. 747–818. Published December 15, 1915. "The quantity of natural gas commercially utilized in the United States in 1914 exceeded that so utilized in any previous year in the history of the natural-gas industry. The quantity produced and used, which amounted to approximately 591,866,733,000 cu. ft., constitutes a new record, exceeding by nearly 10,000,000,000 cu. ft., or 1.7 per cent, the former record established in 1913.

"Of the record-breaking production of natural gas credited to 1914, it is estimated that a total of 203,104,358,000 cu. ft., or about 34 per cent, was supplied to domestic consumers at an average price of 28.04 cents per 1,000 cu. ft., and that 388,762,375,000 cu. ft., comprising the remaining 66 per cent, was supplied to industrial consumers at an average price of 9.56 cents per 1,000 cu. ft. During the last four years the ratio of domestic to industrial consumption has varied but slightly. Formerly, a relatively greater proportion of the annual yield was supplied to industrial consumers."

The Stone Industry in 1914. G. F. LOUGHLIN. Separate 33, from Mineral Resources of the United States, 1914, Part II, pp. 819–91. Published December 31, 1915.

Petroleum in 1914. JOHN D. NORTHROP. Separate 34, from Mineral Resources of the United States, Part II, pp. 893–1098. Published January 12, 1916. "The combination of the figures for marketed production and of the estimated quantity of oil placed in producers' storage gives more than 290,000,000 bbls. as the total yield of the oil wells of the United States in 1914."

The Public Interest in Mineral Resources. GEORGE OTIS SMITH. Separate from Part I, Mineral Resources of the United States. 9 pp. Published December 31, 1915.

DEPARTMENT OF AGRICULTURE

Methods for the Examination of Bituminous Road Materials. PREVOST HUBBARD AND CHARLES S. REEVE. Department Bulletin 314. 48 pp. "Its object is to present a description of methods now in use by the Office of Public Roads and Rural Engineering for the examination of bituminous road materials in such form that, with a little practice and proper equipment, such examinations may be made by an intelligent person. The various tests have, therefore, been described rather more in detail than would be necessary if they were intended for the use of chemists only, and illustrations of practically all of the apparatus required have also been included."

The tests included are the following: Specific gravity, specific viscosity, float test, penetration test, melting point, flash and burning points, volatilization test, distillation test, dimethylsulfate test, bitumen soluble in carbon disulfide, bitumen insoluble in paraffin naphtha, bitumen insoluble in carbon tetrachloride, fixed carbon, paraffin scale, extraction of bituminous aggregates, grading the mineral aggregate, voids in the mineral aggregate and bituminous emulsions.

BOOK REVIEWS

Engineering as a Career. A series of papers edited by PROFESSOR F. H. NEWALL, University of Illinois, and C. E. DRAYER, Railroad Engineer, Cleveland, O.: D. Van Nostrand Co. 214 pages. Price, $1.00, net.

The enormous strides made by engineers and engineering in recent years, at rates that are themselves increasing year by year, and in fields often not even suspected by the general public, have made engineering probably the most promising of all careers for the young man of proper calibre. This being the case, it would seem as if a book devoted to an exposition of engineering as a career would be a valuable contribution not only to engineering literature as a statement of the status of engineering at the present time, but to every prospective student and his family.

One would expect to find in a true story of this sort an irresistible lure, attracting any boy with a spark of ambition in him, for what boy has not dreamed of doing great things? With such a possibility in view this book is a most disappointing product. In the first place, it fails utterly in giving a representation of engineering activities as they are, and it is just about attractive enough to drive any prospective students of engineering into the ministry where, if report is to be believed, there is plenty of room. Twenty-two different authors, in 214 pages, have contributed essays averaging 10 pages each, and yet, to use the language of the stage, they have utterly failed to "put it over," collectively speaking.

C. E. LUCKE

The Rare Earth Industry. By SIDNEY J. JOHNSTONE, B.Sc. D. Appleton & Co., 1915. Royal 8vo., vii + 136 pp. Price, 7s 6d, net.

This book is the second of a series of Manuals of Chemical Technology edited by Geoffrey Martin. In its text content of 126 pages, 33 are devoted to the Thorium and Cerium Industry, while the remainder of the book consists of a technological description of Titanium, Zirconium, Tantalum and Niobium, Tungsten, the Incandescent Electric Glow Lamp Industry, Uranium, and Vanadium, with a final chapter of 16 pages on the Industry of Radioactive Substances, which has been written by Alexander S. Russell, M.A., D.Sc.

The book is designed to be essentially of a practical character, and limits itself to the commercial aspects of the elements and subjects enumerated in the nine chapters.

The salient points of each element and its uses are brought into prominence, though in many cases in only the most general way. The impression of a compilation is brought to the attention of the reader rather than that of first-hand knowledge on the part of the author.

On the whole, the most important methods for extraction of the earths and the rare metal compounds are outlined, and the preparation of the elements and their uses are noted. Attention is drawn throughout the book to the manufacture and uses of the various rare elements in whatever form they are adaptable to the problems of modern artificial illumination.

The final chapter on the Industry of Radioactive Substances is a brief résumé of these bodies, their sources, separations, methods of testing their strength, and their medicinal and general uses.

The work is a general description of the technological uses of the more commercially important rarer elements, together with brief descriptions of certain phases of the industries to which these elements are allied.

VICTOR LENHER

Guide to the Reports, Evidence and Appendices of the Royal Commission of Sewage Disposal. By G. B. KERSHAW. New York: D. Van Nostrand Co. 8vo. 178 pp. Price, $2.00.

As is stated in the preface, the object of preparing this synopsis has been to provide a handy reference book or guide to the subject matter of the various reports and appendices presented by the Royal Commission on Sewage Disposal.

These documents terminated with the issue of the tenth report: their total number (published under separate covers) amounts to some thirty volumes, and it is no easy matter for the reader interested in a special subject to find the particular volume he requires, and even when the volume has been found, to isolate the special section required.

In this synopsis, the Commission's reports have been dealt with seriatim, the plan followed being to extract from each report, appendix, etc., all the headings and sub-headings, thus giving in condensed form the subject matter contained in them.

Opposite to each heading or sub-heading will be found the page or pages of the Report in which they occur, while the number of the Report is given at the top of each page.

The index is in three divisions, covering "Names," "Places" and "Subjects," respectively. Each one of the several Reports is treated separately and headings are given which permit ready reference to the ground covered by the Report, so that a miminum of time is required to find data dealing with such subjects as "Sewage Pollution of Tidal Waters," "Contamination of Shell Fish," "Land Treatment of Sewage," "Septic Tanks," "Sewage Filters," "Contact Beds," "Sewage Sludges," "Nuisances," "Standards for Sewage Effluents," "Disposal of Distillery Refuse," "Excessive Growth of Green Sea Weeds," "Disposal of Manufacturing Wastes" and the like.

The bulky volumes of The Reports of the Royal Commission are exceedingly difficult to properly use without assistance such as is offered by this valuable guide.

W. P. MASON

Farben und Farbstoffe. By A. ZART. Illustrated with 31 figures. B. G. TEUBNER, Leipzig, 1915. 100 pp. Price, 1.25 M.

This is a small volume forming part of a series of monographs in popular science, being a collection "aus Natur und Geisteswelt," a form of technical literature which is both common and popular in Germany. The present little handbook deals with the theory of color and the history of dyestuffs. It then briefly discusses the nature of inorganic pigments together with the general methods of their preparation and manufacture. Chapters on the natural dyestuffs and the coal-tar dyes are also given, together with considerable matter relative to the commercial preparation of synthetic dyes. The uses of the various dyes in dyeing and printing is also described, and the general methods of testing the nature and fastness of dyestuffs.

The book is remarkably up-to-date, and while the descriptions are necessarily brief and rather sketchy, yet the examples are well chosen and exhibit a good grasp of the subject. The matter is presented in a simple and clear manner in keeping with the popular scientific character of the book. The volume is especially apropos just now in view of the wide-spread and popular interest in dyestuffs, and is even well worthy of being read by any chemist who is at all interested in this subject and who has a fair reading knowledge of German.

J. MERRITT MATTHEWS

NEW PUBLICATIONS

By Irene DeMatty, Librarian, Mellon Institute of Industrial Research, Pittsburgh

CORRECTION: Painting by Immersion and by Compressed Air. A. S. Jennings. The price of $2.75 quoted in This Journal, 7 (1915), page 1094, should read $3.50.

Alternating Currents, Laboratory Manual. L. C. Eddy. 12mo. 21 pp. Price, $0.50. D. Van Nostrand Co., New York.

Analytical Chemistry. Vol. 2. Quantitative Analysis. F. P. Treadwell. 4th Ed. 8vo. Price, $3.75. Chapman & Hall, London.

Analytic Mechanics. J. A. Miller and L. B. Lilly. 8vo. 297 pp. Price, $2.00. D. C. Heath & Co., New York.

Analytical Mechanics. H. M. Doudourian. 2nd Ed. 8vo. 431 pp. Price, $3.00. D. Van Nostrand Co., New York.

Catalysis and Its Industrial Applications. E. Jobling. 8vo. Price, $0.65. J. & A. Churchill, London.

Cellulose: Die Hydrolyse der Zellulose und des Holzes. Erik Haegglund. 8vo. 52 pp. Price, $0.35. F. Enke, Stuttgart.

Chemistry: Handwoerterbuch der Chemie. 122 Lfg. Price, $0.65. F. Vieweg & Sohn, Braunschweig.

Colloid-Chemistry. Wolfgang Ostwald. 8vo. Price, $3.00. P. Blakiston's Son & Co., Philadelphia.

Colloids: An Introduction to the Physics and Chemistry of Colloids. Emil Hatschek. 2nd Ed. 8vo. 118 pp. Price, $0.75. J. & A. Churchill, London.

Color and Its Applications. M. Luckiesh. 8vo. 357 pp. Price, $3.00. D. Van Nostrand Co., New York.

Dams and Weirs: an Analytical and Practical Treatise. W. G. Bligh. 8vo. 206 pp. Price, $1.50. American Technical Society, Chicago.

Electrical Measurements and Testing. C. L. Dawes. 4to. 39 pp. Price, $0.75. J. Wiley & Sons, New York.

Electroplaters' Handbook. J. H. Weston. 16mo. 178 pp. Price, $1.00. F. J. Drake & Co., Chicago.

General Laboratory Apparatus and Supplies. Catalogue (1916). Lenz & Naumann, Inc., 17 Madison Ave., New York.

Heat Power Engineering, Elements of. C. F. Hirschfield and W. N. Barnard. 2nd Ed. 8vo. Chapman & Hall, London.

Inorganic Chemistry: Gmelin and Kraut's anorganische Chemie. 190–194 Lfg. Friedheim and Peters. 7th Ed. Price, $0.40. Karl Winter, Heidelberg.

Irrigation Practice and Engineering. Vol. 3. Irrigation Structures. B. A. Etcheverry. 8vo. 438 pp. Price, $4.00. McGraw-Hill Book Co., New York.

Marine Steam Engines. R. Sennett and H. J. Oram. 8vo. 502 pp. Price, $6.00. Longmans, Green & Co., New York.

Materials, Strength of: Tabellen ueber die Tragfachigkeit von Stuetzen aus Flussstahl, Flusseisen, Gusseisen und Holz. Ed. Gubler. 8vo. Price, $0.75. Wepf, Schwabe & Co., Basel.

Mechanics: Hancock's Applied Mechanics for Engineers. N. C. Riggs. Rev. Ed. 8vo. Price, $2.50. Macmillan Co., New York.

Mining: An Introductory Course in Mining Science. Joseph Parker. 2nd Ed. 8vo. 192 pp. Price, $0.50. Oliver & Boyd, London.

Patents: Handbook of Patent Law. (All Countries.) W. P. Thompson. 16th Ed. 8vo. 240 pp. Price, $0.75. Stevens & Sons, London.

Petroleum: Chemische Technologie des Erdoels. Richard Kissling. 8vo. 805 pp. Price, $7.50. F. Vieweg & Sohn, Braunschweig.

Potassium Salt-Beds: Die Entstehung der deutschen Kalisalzlager. Ernst Jaenecke. 8vo. 109 pp. Price, $1.00. F. Vieweg & Sohn, Braunschweig.

Reinforced Concrete Construction. Vol. 3. G. A. Hool. 8vo. 688 pp. Price, $5.00. McGraw-Hill Book Co., New York.

Rubber: Technologie der Kautschukwaren. Kurt Gottlob. 8vo. 256 pp. Price, $2.35. F. Vieweg & Sohn, Braunschweig.

Sugar: A Handbook for Cane Sugar Manufacturers and Their Chemists. G. L. Spencer. 16mo. 529 pp. Price, $3.50. J. Wiley & Sons, New York.

Tables: Chemiker-Kalendar for 1916. R. Biedermann. 2 Vols. Price, $0.98. J. Springer, Berlin.

Temperature Measurement: Die Grundlägen, Methoden und Ergebnisse der Temperaturmessung. F. Henning. 8vo. 297 pp. Price, $2.50. F. Vieweg & Sohn, Braunschweig.

RECENT JOURNAL ARTICLES

Chemistry: Some Scientific Advances during 1915. H. R. Hosmer. *General Electric Review*, Vol. 19 (1916), No. 2, pp. 92–95.

Chrome-Iron Ore as Lining for Reverberatory Furnaces. Edgar Hill. *Engineering and Mining Journal*, Vol. 101 (1916), No. 6, pp. 267–268.

Coal and Coke Efficiency in Blast Furnace Operation. B. F. Burman. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 3, pp. 137–140.

Colloids and Colloidal Slimes. E. E. Free. *Engineering and Mining Journal*, Vol. 101 (1916), No. 6, pp. 249–254.

Crystal Twinning by Direct Strain. C. A. Edwards. *Iron Trade Review*, Vol. 58 (1916), No. 6, pp. 341–346.

Electrically Heated Bomb Furnace. D. F. Calhane and H. A. Lavene. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 3, pp. 140–143.

Electrolysis: Effects of Electrolysis on Underground Piping Systems. A. F. Ganz. *Natural Gas Journal*, Vol. 10 (1916), No. 1, pp. 23–25.

Fertilizer: The Present Fertilizer Situation. Harry Hodgson. *The American Fertilizer*, Vol. 44 (1916), No. 3, pp. 27–29.

Formic Acid as a Reagent in Essential Oil Analysis. W. H. Simmons. *The Analyst*, Vol. 40 (1915), No. 477, pp. 491–494.

Gasoline Vapor: Action of Gasoline Vapor in Air. G. A. Burrell. *Compressed Air Magazine*, Vol. 21 (1916), No. 2, pp. 7895–7896.

Gas Welding and Cutting. C. K Bryce. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 31 (1915), No. 8, pp. 696–707.

Glass: Das Jenaer Glas und der Krieg. E. Zschimmer. *Chemiker-Zeitung*, Vol. 40 (1916), No. 1/2, pp. 7–8.

Grading Industries. E. S. Wiard. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 2, pp. 91–96.

Heat Transfer, A Study of. T. G. Thurston. *Refrigerating World*, Vol. 50 (1916), No. 1, pp. 25–26.

High Temperature Insulation and Control. P. A. Boeck. *Steel and Iron*, Vol. 50 (1916), No. 2, pp. 61–66.

Hoists: Handling Materials in Manufacturing Plants. R. L. Streeter. *Engineering Magazine*, Vol. 50 (1916), No. 5, pp. 682–707.

Hydrogenation: Die katalytische Fetthaertung mittels Nickeloxyden. W. Meigen. *Journal fuer praktische Chemie*, Vol. 92 (1915), No. 22, pp. 390–411.

Iron: Das Gluehen von Eisenoxyd bei der gravimetrischen Eisenbestimmung. E. Selch. *Zeitschrift fuer analytische Chemie*, Vol. 54 (1915), No. 9, pp. 457–463.

Iron: Versuche ueber das Verhalten von Eisen gegenueber von Wasser und waesserigen Loesungen im Dampfkessel. E. Bosshard and R. Pfenninger. *Chemiker-Zeitung*, Vol. 40 (1916), No. 1/2, pp. 5–6.

Iron and Steel Plant: New Plant of the Youngstown Iron and Steel Co. C. C. Lynde. *Blast Furnace and Steel Plant*, Vol. 50 (1916), No. 2, pp. 68–75.

Iron Ore: Conservation of Iron Ore. C. K. Leith. *Bulletin of the American Institute of Mining Engineers* (1916), No. 110, pp. 227–231.

Milk: The Persistence of Hydrogen Peroxide in Milk. E. Hinks. *The Analyst*, Vol. 40 (1915), No. 477, pp. 482–491.

Natural Gas: Necessary Use and Effect of Gas Compressors on Natural Gas Field Operating Conditions. S. S. Wyer. *Bulletin of the American Institute of Mining Engineers* (1916), No. 110, pp. 281–297

Nitrogen: The Fixation of Atmospheric Nitrogen. R. G. Skerrett. *The Iron Age*, Vol. 97 (1916), No. 6, pp. 359–362.

Oils and Fats: Recent Advances Relating to the Composition and Analysis of Edible Oils and Fats. E. R. Bolton and Cecil Revis. *The Analyst*, Vol. 40 (1915), No. 477, pp. 494–503.

Oils and Other Reagents in Flotation. R. J. Anderson. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 3, pp. 135–137.

Ore: Dropping Ore through a 1135-Foot Raise. C. M. Carter. *Engineering and Mining Journal*, Vol. 101 (1916), No. 6, p. 262.

Packing for Ammonia-Compressor Stuffing Boxes. F. L. Fairbanks. *Power*, Vol. 43 (1916), No. 6, pp. 179–181.

Paper: The Volumetric Estimation of Paper. E. H. Hiaerne. *Paper*, Vol. 17 (1916), No. 20, pp. 14–15.

Platinum: Ueber den Einfluss von katalysatorgiften auf die Lichtelektrische Empfindlichkeit des Platins. F. Krueger. *Zeitschrift fuer Elektrochemie*, Vol. 21 (1915), No. 23, pp. 562–569.

Plumb-Bob Illuminator. R. K. Warner. *Engineering and Mining Journal*, Vol. 101 (1916), No. 5, p. 223.

Pulverized Coal: Its Preparation and Use in Industrial Furnaces. S. H. Harrison. *Engineering Magazine*, Vol. 50 (1916), No. 5, pp. 742–753.

Research Problems. W. H. Coghill. *Mining and Scientific Press*, Vol. 112 (1916), No. 5, pp. 159–160.

Steel: Science Testing of Malleable and Cast Steel. A. Harley. *The Foundry*, Vol. 44 (1916), No. 2, pp. 61–67.

Temperatures: Judging Non-Ferrous Metal Pouring Temperatures. R. R. Clarke. *The Foundry*, Vol. 44 (1916), No. 2, pp. 71–75.

Tool Making: Johansson Gauges in Tool Making. L. Ruthenberg. *American Machinist*, Vol. 44 (1916), No. 6, pp. 242–245.

Valves, Their Uses and Abuses. G. A. Camblin. *Ice and Refrigeration*, Vol. 50 (1916), No. 2, pp. 113–114.

Water Power Laws and Their Relation to Industry and Progress. F. Darlington. *Engineering Magazine*, Vol. 50 (1916), No. 5, pp. 722–733.

MARKET REPORT—FEBRUARY, 1916

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON FEBRUARY 19TH.

INORGANIC CHEMICALS

Acetate of Lime, gray	100 Lbs.	7.00	@	7.25
Alum, lump	100 Lbs.	4.25	@	4.75
Aluminum Sulfate, high-grade	100 Lbs.	5.00	@	5.25
Ammonium Carbonate, domestic	Lb.	9	@	9½
Ammonium Chloride, gray	Lb.	8½	@	9
Ammonium Phosphate, commercial, 98–100%	Lb.	11	@	11¼
Aqua Ammonium, 16°, drums	Lb	2½		
Arsenic, white	Lb.	5¼	@	5½
Barium Chloride	Ton	110.00	@	120.00
Barium Nitrate	Lb.	15	@	16
Barytes, prime white, foreign	Ton	19.00	@	23.00
Bleaching Powder, 35 per cent	100 Lbs.	13.50	@	14.50
Blue Vitriol	Lb.	20½	@	21
Borax, crystals, in bags	Lb.	7	@	7¼
Boric Acid, powdered crystals	Lb.	12¾	@	14
Brimstone, crude, domestic	Long Ton	22.00	@	22.50
Bromine, technical, bulk	Lb.	5.00	@	6.50
Calcium Chloride, lump	Ton	—	@	11.78
Calcium Chloride, granulated	Ton	—	@	14.78
Caustic Soda, 74 per cent	Lb.	6¼	@	6½
Caustic Soda, 76 per cent	Lb.	6¼	@	6½
Chalk, light precipitated	Lb.	4¾	@	5½
China Clay, imported	Ton	11.00	@	16.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered	100 Lbs.	80	@	1.05
Glauber's Salt, in bbls.	100 Lbs.	60	@	75
Green Vitriol, bulk	100 Lbs.	75	@	80
Hydrochloric Acid, commercial, 18°	100 Lbs.	2.50	@	3.00
Hydrochloric Acid, C. P., conc., 22°	100 Lbs.	3.00	@	3.50
Iodine, resublimed	Lb.	4.25	@	4.30
Lead Acetate, white crystals	Lb.	13⅝	@	14
Lead Nitrate	Lb.	16½	@	16¾
Litharge, American	Lb.	6¾		
Lithium Carbonate	Lb.	90	@	1.00
Magnesium Carbonate	Lb.	10	@	12
Magnesite, "Calcined"	Ton	37.50	@	40.00
Mercuric Chloride, commercial	Lb.	1.85	@	2.15
Nitric Acid, 36°	Lb.	7½	@	8
Nitric Acid 42°	Lb.	9	@	9½
Phosphoric Acid, sp. gr. 1.750	Lb.	30	@	32
Phosphorus	Lb.	35	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, casks	Lb.	65	@	—
Potassium Bromide	Lb.	5.50	@	—
Potassium Carbonate, calcined, 80 @ 85%	Lb.	1.00	@	1.15
Potassium Chlorate, crystals, spot	Lb.	65	@	—
Potassium Cyanide, bulk, 98–99 per cent	Lb.	30	@	35
Potassium Hydroxide	Lb.	55	@	60
Potassium Iodide, bulk	Lb.	3.70	@	3.75
Potassium Nitrate	Lb.	—	@	—
Potassium Permanganate, bulk	Lb.	2.00	@	—
Quicksilver, flask, 75 lbs.		325.00	@	—
Red Lead, American, dry	Lb.	7¼	@	—
Salt Cake, glass makers'	100 Lbs.	55	@	65
Silver Nitrate	Oz.	36	@	38
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash, 48 per cent	100 Lbs.	—	@	—
Sodium Acetate	Lb.	10¾	@	11
Sodium Bicarbonate, domestic	100 Lbs.	1.60	@	1.70
Sodium Bicarbonate, English	Lb.	3½	@	3⅝
Sodium Bichromate	Lb.	45	@	50
Sodium Carbonate, dry	100 Lbs.	3.75	@	4.00
Sodium Chlorate	Lb.	40	@	50
Sodium Fluoride, commercial	Lb.	15	@	—
Sodium Hyposulfite	100 Lbs.	3.00	@	3.25
Sodium Nitrate, 95 per cent, spot	100 Lbs.	3.10	@	—
Sodium Silicate, liquid	100 Lbs.	85	@	1.10
Sodium Sulfide, 30%, crystals, in bbls	Lb.	2	@	2½
Sodium Sulfite, crystals	Lb.	7	@	8
Strontium Nitrate	Lb.	38		
Sulfur, flowers, sublimed	100 Lbs.	2.30	@	2.70
Sulfur, roll	100 Lbs.	1.90	@	2.20
Sulfuric Acid, chamber, 60°	100 Lbs.	2.00	@	2.50
Sulfuric Acid, conc., sp. gr. 1.842	100 Lbs.	2.50	@	3.00
Sulfuric Acid, oleum (fuming)	100 Lbs.	2.50	@	3.00
Talc, American	Ton	9.00	@	13.00
Terra Alba, American, No. 1	100 Lbs.	75	@	80
Tin Bichloride, 50°	Lb.	14	@	—
Tin Oxide	Lb.	47	@	49
White Lead, American, dry	Lb.	6½	@	—
Zinc Carbonate	Lb.	24	@	25
Zinc Chloride, commercial	Lb.	12	@	18
Zinc Oxide, American process	Lb.	9	@	18
Zinc Sulfate	Lb.	7¼	@	7½

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.	Lb.	1.15	@	1.20
Acetic Acid, 28 per cent, in bbls	Lb.	7½	@	8
Acetic Acid, glacial, 99½%, in carboys	Lb.	32	@	36
Acetone, drums	Lb.	35	@	40
Alcohol, denatured, 180 proof	Gal.	50	@	52
Alcohol, grain, 188 proof	Gal.	2.62	@	2.64
Alcohol, wood, 95 per cent, refined	Gal.	55	@	57
Amyl Acetate	Gal.	4.50	@	5.50
Aniline Oil	Lb.	90	@	1.00
Benzoic Acid, ex-toluol	Lb.	4.00	@	4.60
Benzol, 90 per cent	Gal.	80	@	90
Camphor, refined in bulk, bbls.	Lb.	44	@	—
Carbolic Acid, U. S. P., crystals, drums	Lb.	1.25	@	1.30
Carbon Bisulfide	Lb.	6	@	15
Carbon Tetrachloride, drums, 100 gals.	Lb.	16	@	17
Chloroform	Lb.	70	@	75
Citric Acid, domestic, crystals	Lb.	65	@	70
Cresol, U. S. P.	Gal.	1.15	@	1.25
Dextrine, corn (carloads, bags)	100 Lbs.	3.10	@	3.20
Dextrine, imported potato	Lb.	12	@	13
Ether, U. S. P., 1900	Lb.	18	@	20
Formaldehyde, 40 per cent	Lb.	9½	@	10
Glycerine, dynamite, drums included	Lb.	45	@	—
Oxalic Acid, in casks	Lb.	58	@	60
Pyrogallic Acid, resublimed bulk	Lb.	1.25	@	1.45
Salicylic Acid	Lb.	4.00	@	4.15
Starch, cassava	Lb.	3¾	@	4½
Starch, corn (carloads, bags)	100 Lbs.	2.25	@	2.36
Starch, potato	Lb.	6	@	6½
Starch, rice	Lb.	8	@	10
Starch, sago	Lb.	3¼	@	3¾
Starch, wheat	Lb.	5	@	6
Tannic Acid, commercial	Lb.	75	@	76
Tartaric Acid, crystals	Lb.	55	@	57

OILS, WAXES, ETC.

Beeswax, pure, white	Lb.	47	@	55
Black Mineral Oil, 29 gravity	Gal.	13	@	14
Castor Oil, No. 3	Lb.	17¾	@	18¼
Ceresin, yellow	Lb.	10	@	14
Corn Oil, crude	100 Lbs.	9.25	@	—
Cottonseed Oil, crude, f. o. b. mill	Gal.	63	@	64
Cottonseed Oil, p. s. y.	Lb.	9¾	@	10
Creosote, beechwood	Lb.	8.50	@	9.00
Cylinder Oil, light, filtered	Gal.	20	@	25
Fusel Oil, crude	Lb.	4.00	@	4.50
Japan Wax	Lb.	13	@	—
Lard Oil, prime winter	Gal.	92	@	96
Linseed Oil, raw (car lots)	Gal.	72	@	—
Menhaden Oil, crude (southern)	Gal.	—	@	—
Naphtha, 68 @ 72°	Gal.	30	@	35
Neat's-foot Oil, 20°	Gal.	95	@	97
Paraffine, crude, 117 & 119 m. p.	Lb.	3½	@	4
Paraffine Oil, high viscosity	Gal.	24½	@	25
Rosin, "F" Grade, 280 lbs.	Bbl.	5.80		
Rosin Oil, first run	Gal.	—	@	32
Shellac, T. N.	Lb.	22	@	23
Spermaceti, cake	Lb.	25	@	26
Sperm Oil, bleached winter, 38°	Gal.	74	@	75
Spindle Oil, No. 200	Gal.	19½	@	20
Stearic Acid, double-pressed	Lb.	14¼	@	15
Tallow, acidless	Gal.	78	@	80
Tar Oil, distilled	Gal.	30	@	31
Turpentine, spirits of	Gal.	55	@	56

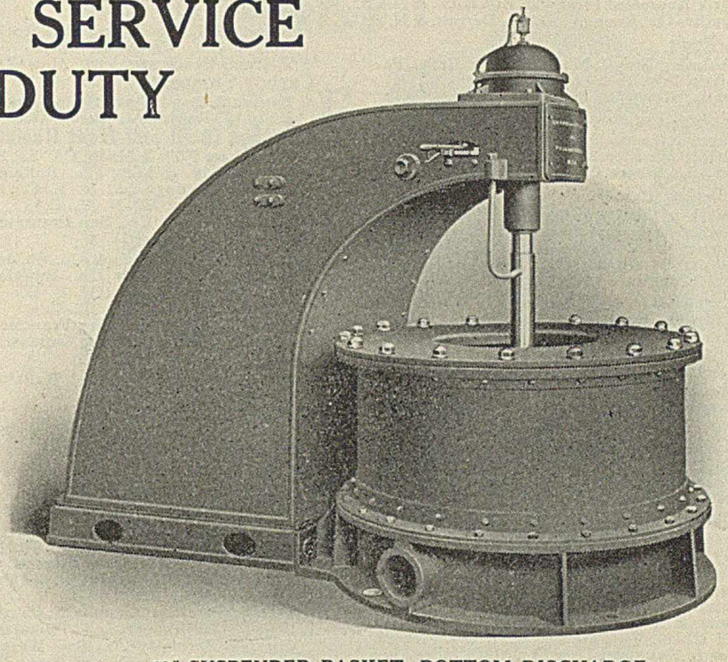
METALS

Aluminum, No. 1, ingots	Lb.	53	@	55
Antimony, ordinary	Lb.	44		
Bismuth, New York	Lb.	—		
Copper, electrolytic	Lb.	28½		
Copper, lake	Lb.	28½		
Lead, N. Y.	100 Lbs.	6.30		
Nickel, electrolytic	Lb.	50	@	—
Nickel, shot and ingots	Lb.	45	@	—
Platinum, refined	Oz.	87.50	@	90.00
Silver	Oz.	56⅝		
Tin	100 Lbs.	42.12½		
Zinc, N. Y.	Lb.	21½		

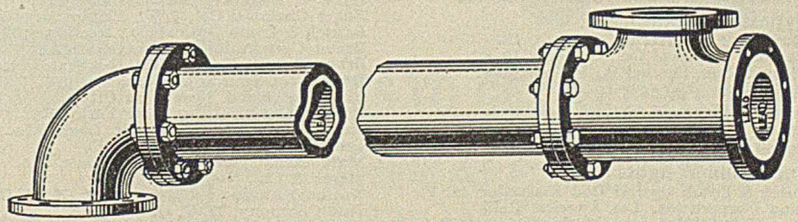
FERTILIZER MATERIALS

Ammonium Sulfate	100 Lbs.	4.25		
Blood, dried	Unit	3.35		
Bone, 4½ and 50, ground, raw	Ton	37.50		
Calcium Cyanamid	Unit of Ammonia	2.45		
Calcium Nitrate, Norwegian	100 Lbs.	—		
Castor Meal	Unit	—		
Fish Scrap, domestic, dried, f. o. b. works	Unit	3.85	&	10
Phosphate, acid	Unit	80	@	85
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.75	@	3.00
Tennessee, 70–80 per cent	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent	Ton	490.00	@	—
Pyrites, furnace size, imported	Unit	14¼	@	14¾
Tankage, high-grade; f. o. b. Chicago	Unit	3.15	&	10

Index to Advertisers



40″ SUSPENDED BASKET, BOTTOM DISCHARGE



CLASSIFIED INDEX TO ADVERTISERS' PRODUCTS

Absorption Towers
Duriron Castings Co., N. Y. C.
German-American Stoneware Wks., N. Y. C.
Knight, Maurice A., Akron, Ohio.
Lummus, Walter E., Boston, Mass.
U. S. Stoneware Co., The, Akron, O.

Acetylene and Oxy-Acetylene Generators and Equipment
International Oxygen Co., N. Y. C.

Acid and Alkali Resistant Apparatus
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.

Acid Eggs
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Jacoby, Henry E., N. Y. C.

Acid Pitchers
Bausch & Lomb Optical Co., Rochester, N. Y.
Knight, Maurice A., Akron, Ohio.
U. S. Stoneware Co., The, Akron, O.

Acid Proof Brick
Bausch & Lomb Optical Co., Rochester, N. Y.
German-American Stoneware Works, N. Y. C.
Knight, M. A., Akron (East Side), Ohio.
Thermal Syndicate, Ltd., New York City.
U. S. Stoneware Co., The, Akron, O.

Acid Valves
Chadwick-Boston Lead Co., Boston, Mass.
Cleveland Brass Mfg. Co., The, Cleveland, O.

Agitators, or Mixers
Dorr Cyanide Machy Co., Denver, Col., & N.Y.C
General Filtration Co., Inc., Rochester, N. Y.
Pfaudler Co., Rochester, N.Y., Detroit & N.Y.C.
Werner & Pfleiderer Co., Saginaw, Mich.

Air Compressors
Abbé Engineering Co., N. Y. City.
Crowell Engineering Co., Brooklyn, N. Y.
Hubbard's Sons, Norman, Brooklyn, N. Y.

Ammonia
Unger, John S., Chicago, Ill.

Analysis—Gas Apparatus
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Heil Chem. Co., Henry. St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sarco Co., Inc., New York City.
Scientific Materials Co., Pittsburg, Pa.

Analytical Apparatus
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Buffalo Dental Mfg. Co., Buffalo, N. Y.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.

Analytical Laboratories
Columbus Laboratories, Chicago, Ill.
Dearborn Chemical Co., Chicago, Ill.
Sadtler & Son, Samuel P., Philadelphia.

Asphalt Flow Plates
Howard & Morse, N. Y. C.

Bakelite
General Bakelite Co., New York City.

Balances and Weights
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco Cal.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H. ,Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.

Boilers
Sowers Mfg. Co., Buffalo, N. Y.

Boiler Water Treatment
Dearborn Chemical Co., Chicago, Ill.
Merck & Co., N. Y. C.

Blowers
Abbé Engineering Co., N. Y. C.
Crowell Mfg. Co., Brooklyn, N. Y.

Bolting Cloth
Abbé Engineering Co., N. Y. C.

Bone Black
Booth Apparatus Co., Syracuse, N. Y.

Books
Chemical Publishing Co., The, Easton, Pa.
Van Nostrand Co., D., N. Y. C.

Briquette Molds
Howard & Morse, N. Y. C.

Brimstone, Crude
Union Sulphur Co., New York City.

Burners—Gas and Oil
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Buffalo Dental Mfg. Co., Buffalo, N. Y.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent, E. H. & Co., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.

Burners—Sulphur (Rotary)
Glens Falls Machine Works, Glen Falls, N. Y.

Calorimeters—Fuel and Gas
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sarco Co., Inc., New York City.
Sargent, E. H. & Co., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.

Capsules
Bausch & Lomb Optical Co., Rochester, N. Y.
Norton Co., Worcester, Mass.
Thermal Syndicate, Ltd., New York City.

Carboy Stoppers
Bausch & Lomb Optical Co., Rochester, N. Y.
Knight, Maurice A., Akron, Ohio.

Castings (Acid and Heat Resisting)
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Duriron Castings Co., N. Y. C.
Jacoby, Henry E., N. Y. C.
Pacific Foundry Co., San Francisco, Cal.

Castings (Chemical)
Bethlehem Fdy. & Mach. Co., So. Bethlehem, Pa.
Buffalo Fdy. & Mch Co., Buffalo, N. Y.
Duriron Castings Co., N. Y. C.
Jacoby, Henry E., N. Y. C.
Pacific Foundry Co., San Francisco, Cal.
Werner & Pfleiderer Co., Saginaw, Mich.

Caustic Pots
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.

Caustic Soda
General Chem. Co., N. Y. C.
Hooker-Electrochemical Co., N. Y. C.

Cement Filler
Toch Brothers, N. Y. C.

Centrifugal Engineers
Sharples Specialty Co., The, West Chester, Pa.

Centrifugals
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
DeLaval Separator Co., N. Y. C.
International Instrument Co., Cambridge, Mass.
Schaum & Uhlinger, Inc., Philadelphia.
Sharples Specialty Co., The, West Chester, Pa.
Tolhurst Machine Works, Troy, N. Y.

Charcoal
Booth Apparatus Co., Syracuse, N. Y.

Chemical Castings
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Duriron Castings Co., New York City.
Werner & Pfleiderer Co., Saginaw, Mich.

Chemical Glassware
Bausch & Lomb Optical Co., Rochester, N. Y.
Caloris Co., Millville, N. J.
Griebel Instrument Co., Carbondale, Pa.
Corning Glass Works, Corning, N. Y.

Chemicals
Badische Company, New York City.
Baker & Adamson Chemical Co., Easton, Pa.
Baker Chemical Co., J. T., Phillipsburg, N. J.
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Dearborn Chemical Co., Chicago, Ill.
Eimer & Amend, New York City
General Chemical Co., New York City.
Heil Chemical Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Mallinckrodt Chem Co ,St. Louis, Mo.
Merck & Co., New York City.
National Aniline & Chemical Co., N. Y. C.
Palo Company, N. Y. C.
Pfizer & Co., Charles, New York City.
Powers-Weightman-Rosengarten Co., Phila., Pa.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Squibb & Sons, E. R., N. Y. C.
Thomas Co., Arthur H., Philadelphia.

Chemical Plants (Complete Installation)
Lummus, Walter E., Boston, Mass.

Chemical Plants (Erected and Supervised)
M. McNamara, Everett, Mass.

Chemical Reagents
Baker & Adamson Chem. Co., Easton, Pa.
Baker Chem. Co., J. T., Phillipsburg, N. J.
Bausch & Lomb Optical Co., Rochester, N. Y.
Mallinckrodt Chem. Co., St. Louis, Mo.
Merck & Co., N. Y. C.

Chloride of Lime
Hooker-Electrochemical Co., N. Y. C.

Chlorine—Liquid
Badische Company, New York City.
Electro Bleaching Gas Co., N. Y. C.

Classifiers
Dorr Cyanide Mach. Co., Denver, Col., & N.Y.C.

Classifiers or Washers
Dorr Cyanide Mach. Co., Denver, Col., & N.Y.C.

Clay (for Stoneware Products)
Woodbridge Ind. & Devel. Co., Woodbridge, N.J.

Coal Tar Products
National Aniline & Chemical Co., N. Y. C.

Cocks—Plug (Acid Proof)
Duriron Castings Co., N. Y. C.

Colorimeters
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.

Colors—Aniline and Alizarine
Farbwerke-Hoechst Co., N. Y. C.
National Aniline and Chemical Co., N. Y. C.

Combustion Tubes and Boats
Bausch & Lomb Optical Co., Rochester, N. Y.
Norton Co., Worcester, Mass.
Thermal Syndicate, Ltd., New York City.

Condensers (Barometric and Surface)
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Jacoby, Henry E., N. Y. C.
Lummus, Walter E., Boston, Mass.

Consulting Chemists and Chemical Engineers
Abbott, W. G., Jr., Washington, D. C.
Foster, A. B., Washington, D. C.
Hall & Paul, Pittsburgh, Pa.
Little, Arthur D., Inc., Boston, Mass.
Munn, W. Faitoute, East Orange, N. J.
Ney, A. H., N. Y. City.
Sadtler & Sons, Samuel P., Philadelphia.
Unger, John S., Chicago, Ill.

Corn Oil (Extracted)
Woolner & Co., Peoria, Ill.

Crucibles
American Platinum Works, Newark, N. J
Baker & Co., Inc., Newark, N. J. (Platinum)
Bausch & Lomb Optical Co., Rochester, N. Y.
Bishop & Co., J., Malvern, Pa. (Platinum)
Buffalo Dental Mfg Co., Buffalo, N. Y.
Dixon Crucible Co., Joseph, Jersey City, N. J.
Duriron Castings Co., N. Y. C. (Acid Proof).
Heil Chemical Co., Henry, St. Louis, Mo.
Norton Co., Worcester, Mass. (Alundum).
Thermal Syndicate, Ltd., N. Y. C. (Vitreosil).

Crushers and Grinders (Industrial and Laboratory)
Abbé Engineering Co., New York City.
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Raymond Bros. Impact Pulv. Co., Chicago, Ill.
Sargent & Co., E. H., Chicago, Ill.
Williams Patent Crusher & Pulv. Co., Chicago.

Cupels
Bausch & Lomb Optical Co., Rochester, N. Y.
Hoskins Mfg. Co., Detroit, Michigan.
Norton Company, Worcester, Mass.

Cylinders (Oxygen and Hydrogen)
International Instrument Co., N. Y. City.

Diaphragms
General Filtration Co., Inc., Rochester, N. Y.

Diffusion Apparatus
General Filtration Co., Inc., Rochester, N. Y.
Lummus, Walter E., Boston, Mass.

Dissolving Tanks—Automatic
Lummus, Walter E., Boston, Mass.
Werner & Pfleiderer Co., Saginaw, Mich.

Distilling Machinery and Apparatus
Badger & Sons Co., E. B., Boston, Mass.
Bausch & Lomb Optical Co., Rochester, N. Y.
Booth Apparatus Co., Syracuse, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Devine Company, J. P., Buffalo, N. Y.
Eimer & Amend, New York City.
Electric Heating Appliance Co., N. Y. C.
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
German-American Stoneware Works, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Lummus, Walter E., Boston, Mass.
Palo Company, N. Y. C.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Sanborn Evaporator Co., N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Stokes Machine Wks., F. J., Philadelphia.
Swenson Evaporator Co., N. Y. C.
Thomas Co., Arthur H., Philadelphia, Pa.
Unger, John S., Chicago, Ill.
Werner & Pfleiderer Co., Saginaw, Mich.
Zaremba Company, Buffalo, N. Y.

Dryers—Vacuum
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine & Company, J. P., Buffalo, N. Y.
Jacoby, Henry E., New York City.
Stokes Machine Co., F. J., Philadelphia, Pa.
Werner & Pfleiderer Co., Saginaw, Mich.

Drying Apparatus and Machinery
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Jacoby, Henry E., New York City.
Werner & Pfleiderer Co, Saginaw, Mich.

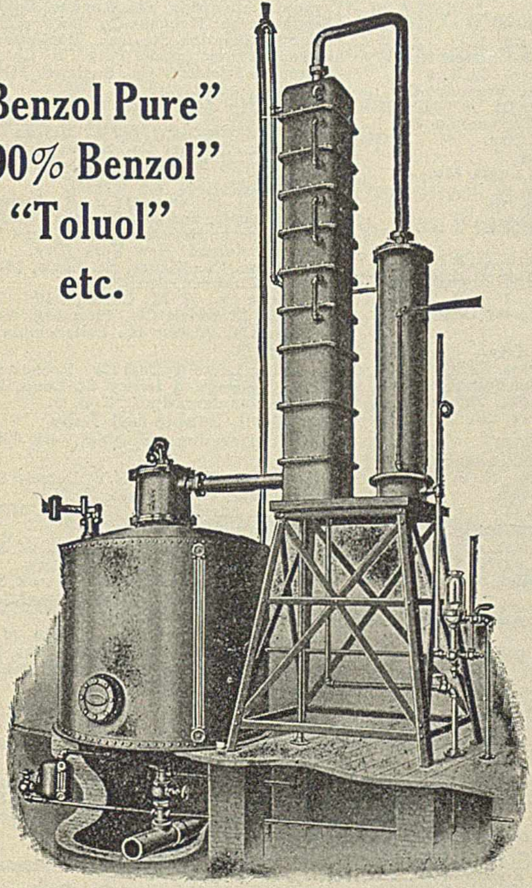
Ductility Machines
Howard & Morse, N. Y. C.

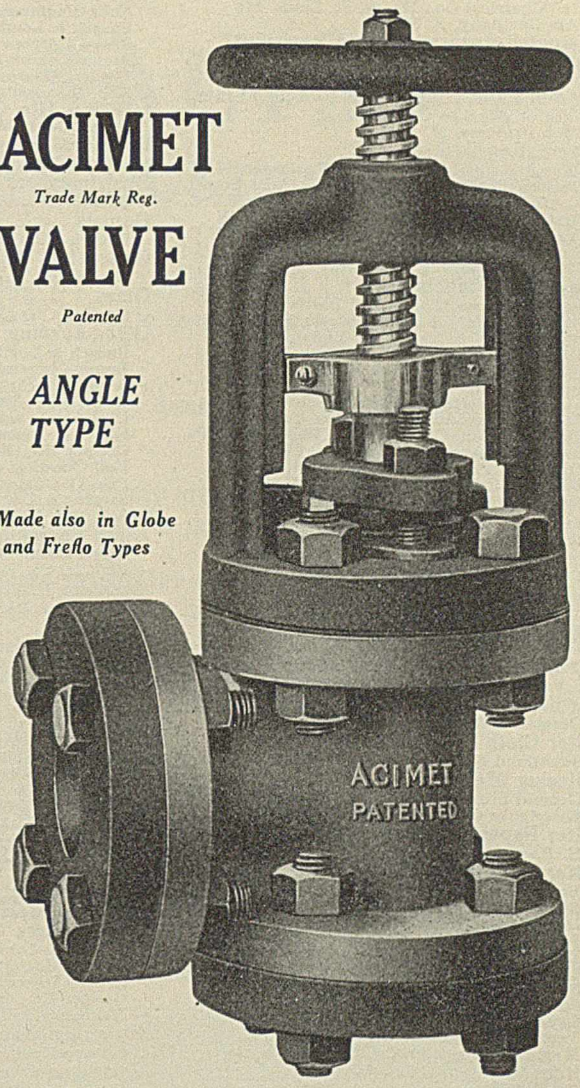
Dyestuffs
Farbwerke-Hoechst Co., New York City.

Electrical Instruments
Thwing Instrument Co., Philadelphia Pa

Electrical Measuring Instruments
Leeds & Northrup Co., Phila., Pa.

Electrodes—Platinum
American Platinum Works, Newark, N. J.
Baker & Co., Inc., Newark, N. J.




ACIMET
PATENTED

  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Bishop & Co., J., Platinum Works, Malvern, Pa.
  - Eimer & Amend, New York City.
  - Engelhard, Chas., New York City.
  - Heil Chemical Co., Henry, St. Louis. Mo.
  - Palo Company, N. Y. C.
- Enameled Apparatus (Acid Resistant)
  - Elyria Enameled Prod. Co., Elyria, O.,&N.Y.C.
  - Pfaudler Co.,Rochester,N.Y., Detroit, &N.Y.C.
- Enamel Paint (Impervious to Acid Fumes)
  - General Bakelite Co., N. Y. C.
  - Toch Brothers, N. Y. C.
- Evaporating Dishes
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Duriron Castings Co.. N. Y. C. (Acid Proof).
  - Elyria Enameled Prod. Co., Elyria, O.,&N.Y.C.
  - German-American Stoneware Works, N. Y.
  - Pfaudler Co.,Rochester,N.Y., Detroit, &N.Y.C.
  - Stuart & Peterson Co., The, Burlington, N. J.
  - Thermal Syndicate, Ltd., New York City.
- Evaporating Machinery
  - Badger & Sons, Co.. E. B., Boston, Mass.
  - Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
  - Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
  - Devine Company, J. P., Buffalo, N. Y.
  - Electric Heating Apparatus Co., N. Y. C.
  - Jacoby, Henry E., N. Y. C.
  - Lummus, Walter E., Boston, Mass.
  - Sanborn Evaporator Co., New York City.
  - Stokes Machine Company,F.J.,Philadelphia,Pa.
  - Swenson Evaporator Company, Chicago, Ill
  - Werner & Pfleiderer Co., Saginaw, Mich.
  - Zaremba Company, Buffalo, N. Y.
- Extracting Apparatus
  - Lummus, Walter E., Boston, Mass.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Extraction Cylinders
  - Lummus, Walter E., Boston, Mass.
- Faucets (Stoneware—Acid Proof)
  - German-American Stoneware Works, N. Y. C.
  - Knight, M. A., Akron (East Side), Ohio.
  - U. S. Stoneware Co., The, Akron, O.
- Fertilizer Industries Equipment
  - Schutte & Koerting Co., Philadelphia.
- Fertilizers
  - German Kali Works, N. Y. C.
- Filter Cloth (Metallic)
  - Sweetland Filter Press Co., N. Y. C.
- Filtering Media
  - General Filtration Co., Inc., Rochester, N. Y.
  - Kieselguhr Co. of America, Los Angeles. Cal.
- Filter Paper (Whatman)
  - H. Reeve Angel & Co., New York.
- Filter Presses (Laboratory & Industrial)
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco,Cal.
  - International Filtration Corp., N. Y. C.
  - Jacoby, Henry E., New York City.
  - Kelly Filter Press Co., Salt Lake City, Utah.
  - Lungwitz, E. E., New York City.
  - Shriver & Co., T., Harrison, N. J.
  - Sperry & Co., D. R., Batavia, Ill.
  - Sweetland Filter Press Co., The, N. Y. C.
  - Swenson Evaporator Co., Chicago, Ill.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Filters
  - General Filtration Co., Inc., Rochester, N. Y.
- Filters—Water
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco,Cal.
  - Booth Apparatus Co., Syracuse, N. Y.
  - Eimer & Amend, N. Y. City.
  - German-American Stoneware Works, N. Y. C.
  - Heil Chemical Co., Henry, St. Louis, Mo.
  - Lenz & Naumann, Inc., N. Y. C.
  - Palo Company, N. Y. C.
  - Sargent & Co., E. H.. Chicago, Ill.
  - Thomas Co., Arthur H., Philadelphia.
- Filtros
  - General Filtration Co., Inc., Rochester, N. Y.
- Fire Brick and Clay
  - Buffalo Dental Mfg. Co., Buffalo, N. Y.
  - Dixon Crucible Co. Joseph, Jersey City, N. J.
  - Kieselguhr Co. of America, Los Angeles, Calif.
- Furnace Linings
  - Kieselguhr Co. of America, Los Angeles, Calif.
- Furnaces—Annealing—(Hardening and Enameling)
  - Abbé Engineering Co., N. Y. C.
  - Buffalo Dental Mfg. Co., Buffalo, N. Y.
  - Electric Heating Apparatus Co., N. Y. C.
- Furnaces (Case Hardening, Rivet and Bolt)
  - Abbé Engineering Co., N. Y. C.
- Furnaces—Electric Laboratory
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co.,San Francisco, Cal.
  - Eimer & Amend, New York City.
  - Electric Heating Apparatus Co., N. Y. C.
  - Engelhard, Chas., N. Y. City.
  - Heil Chemical Co., Henry, St. Louis, Mo.
  - Hoskins Mfg. Co., Detroit, Mich.
  - Lenz & Naumann, Inc., N. Y. C.
  - Palo Company, N. Y. C.
  - Sargent & Co.. E. H. Chicago, Ill.
  - Scientific Materials Co., Pittsburg, Pa.
  - Thomas Co., Arthur H., Philadelphia.
- Furnaces—(Forge)
  - Abbé Engineering Co., N. Y. C.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co.,San Francisco. Cal.
  - Buffalo Dental Mfg. Co., Buffalo, N. Y. C.
  - Electric Heating Apparatus Co., N. Y. C.
- Furnaces (Melting, Oil or Gas)
  - Abbé Engineering Co., N. Y. C.
  - Braun Corporation, Los Angeles. Calif.
  - Braun-Knecht-Heimann Co.. San Francisco,Cal.
  - Buffalo Dental Mfg. Co., Buffalo, N. Y.
  - Electric Heating Apparatus Co., N. Y. C.
  - Heil Chemical Co., Henry, St. Louis, Mo.
- Furnaces—Muffle
  - Abbé Engineering Co., N. Y. C.
  - Bausch & Lomb Optical Co., Rochester. N Y.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco,Cal.
  - Electric Heating Apparatus Co., N. Y C
  - Heil Chemical Co., Henry, St. Louis, Mo.
  - Hoskins Mfg. Co., Detroit, Mich.
  - Lenz & Naumann, Inc., N. Y. C.
- Furnaces—Sulphur
  - Schutte & Koerting Co., Philadelphia.
- Gas Analyzers
  - Bausch & Lomb Optical Co., Rochester, N. Y.
- Gauges
  - Bausch & Lomb Optical Co., Rochester, N. Y.
- Generators (Electro-Oxy-Hydrogen)
  - Shriver & Co., T., Harrison, N. J.
- Glass
  - Corning Glass Works, Corning, N. Y.
- Glass Blowing
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco,Cal.
  - Caloris Co., The, Millville, N. J.
  - Carbondale Instrument Co., Carbondale, Pa.
  - Eimer & Amend, New York City.
  - Greiner Co., Emil, N. Y. City.
  - Heil Chemical Co., Henry, St. Louis, Mo.
  - Palo Company, N. Y. C.
  - Sargent & Co., E. H., Chicago, Ill.
  - Scientific Materials Co., Pittsburg, Pa.
- Glass Enameled Apparatus
  - Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
  - Pfaudler Co., Rochester,N.Y., Detroit, &N.Y.C.
- Graphite Products
  - Dixon Crucible Co., Joseph, Jersey City, N. J
- Grinders
  - Abbé Engineering Co., N. Y. City.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco,Cal.
  - Raymond Bros. Impact Pulv. Co., Chicago, Ill.
  - Williams Patent Crusher & Pulv. Co., Chicago.
- Heating Apparatus (Laboratory)
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Electric Heating Apparatus Co., N. Y. C.
  - Hoskins Mfg. Co., Detroit, Mich.
  - Lenz & Naumann, Inc., N. Y. C.
- Hot Plates (Laboratory Purposes)
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Electric Heating Apparatus Co., N. Y. C.
  - Hoskins Mfg. Co., Detroit, Mich.
- Hydro Extractors
  - Tolhurst Machine Works, Troy, N Y.
- Hydrometers
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Caloris Co., The, Millville, N. J.
  - Griebel Instrument Co., Carbondale, Pa.
  - Greiner Co., Emil, New York City.
  - Heil Chemical Co., Henry, St. Louis, Mo.
- Hydrogen Generators
  - International Oxygen Co., N. Y. C.
- Hydrogen (Pure)
  - International Oxygen Co., N. Y. C.
- Insulation
  - Kieselguhr Co. of America, Los Angeles, Calif
- Jars and Jugs (Acid Storage)
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - German-American Stoneware Works, N. Y. C.
  - Knight, M. A., Akron (East Side), Ohio.
- Kettles (Chemical Castings)
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
  - Duriron Castings Co., N. Y. C.
  - Jacoby, Henry E., New York City.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Kettles (Lined)
  - Elyria Enameled Prod. Co.. Elyria, O., & N.Y.C.
  - PfaudlerCo., Rochester,N.Y., Detroit, & N.Y.C.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Kettles (Steam Jacketed)
  - Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
  - Elyria Enameled Prod. Co.. Elvria. O.. & N.Y.C.
  - Pfaudler Co., Rochester,N.Y.,Detroit, & N.Y.C.
  - Sowers Mfg. Co., Buffalo, N. Y.
  - Sperry & Co., D R., Batavia, Ill.
  - Stuart & Peterson Co., The, Burlington, N. J.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Kettles (Stoneware)
  - German-American Stoneware Works, N. Y. C.
  - Knight, M. A., Akron (East Side), Ohio.
- Kieselguhr
  - Kieselguhr Co. of America, Los Angeles, Calif.
- Laboratory Supplies
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco,Cal.
  - Caloris Co., The, Millville, N. J.
  - Carbondale Instrument Co., Carbondale, Pa.
  - Corning Glass Works, Corning, N. Y.
  - Eimer & Amend, New York City.
  - Greiner Co., Emil, New York City.
  - Heil Chem. Co., Henry, St. Louis, Mo.
  - Lenz & Naumann, Inc., N. Y. C
  - Palo Company, N. Y. C.
  - Sargent & Co., E. H., Chicago, Ill.
  - Scientific Materials Co., Pittsburg, Pa.
  - Thomas Co., Arthur H., Philadelphia, Pa.
- Lacquer
  - General Bakelite Co., New York City.
- Lactic Acid
  - Woolner & Co., Peoria, Ill.
- Leaching Cells
  - Zaremba Co., Buffalo, N. Y.
- Lead Burning
  - M. McNamara, Everett, Mass.
- Lead Lined Pipe and Accessories
  - Schutte & Koerting Co., Philadelphia.
- Lubricants
  - Dearborn Chemical Co., Chicago, Ill.
  - Dixon Crucible Co., Joseph, Jersey City, N. J
- Machinery—Mining and Metallurgical
  - Abbé Engineering Co., New York City.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co.,San Francisco, Cal
  - General Filtration Co., Inc., Rochester, N. Y.
  - Stokes Machine Co., F. J., Philadelphia.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Machinery—Mixing and Kneading
  - Abbé Engineering Co.. New York City
  - PfaudlerCo.,Rochester,N.Y., Detroit, &N.Y.C.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Machinery—Pulverizing
  - Abbé Engineering Co., New York City.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co.,San Francisco,Cal
  - General Filtration Co., Inc., Rochester, N. Y.
  - Raymond Bros. Impact Pulv. Co., Chicago, Ill
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Machinery (Special)
  - Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
  - Duriron Castings Co., N. Y. C.
  - Werner & Pfleiderer Co., Saginaw, Mich.
  - York Electric & Machine Co., York, Pa.
- Microscopes
  - Bausch & Lomb Optical Co., Rochester, N. Y
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco Cal
  - Eimer & Amend, New York City.
  - Heil Chem. Co., Henry, St. Louis, Mo.
  - Lenz & Naumann, Inc., N. Y. C.
  - Sargent & Co., E. H., Chicago, Ill.
  - Scientific Materials Co., Pittsburg, Pa.
  - Thomas Co., Arthur H., Philadelphia, Pa
- Microtomes
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Heil Chemical Co., Henry, St. Louis, Mo.
  - Lenz & Naumann, Inc., N. Y. C.
- Mills—Ball, Pebble and Tube
  - Abbé Engineering Co., New York City.
- Mixers
  - PfaudlerCo., Rochester.N.Y.,Detroit, & N.Y.C.
  - Sowers Mfg. Co., Buffalo, N. Y.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Mixing Tanks
  - Elyria Enameled Prod. Co., Elyria, O., & N.Y.C
  - Lummus, Walter E., Boston, Mass.
  - PfaudlerCo.,Rochester,N.Y., Detroit, & N.Y.C.
  - Werner & Pfleiderer Co., Saginaw, Mich.
- Montejus—Automatic
  - Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
  - German-American Stoneware Works, N. Y. C
  - Schutte & Koerting Co., Philadelphia.
- Nickel-Chromium Gauze
  - Howard & Morse, N. Y. C.
- Nitrating Pots
  - Pfaudler Co.,Rochester,N.Y.,Detroit, & N.Y.C.
- Nitre Pot Acid Pipes
  - Duriron Castings Co., N. Y. C. (Special Alloy)
  - Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
  - Thermal Syndicate, Ltd., N. Y.C. (Silica Ware)
- Nozzles (Acid Proof)
  - Duriron Castings Co., N. Y. C.
- Oil Testing Instruments
  - Bausch & Lomb Optical Co., Rochester, N. Y.
  - Braun Corporation, Los Angeles, Calif.
  - Braun-Knecht-Heimann Co., San Francisco,Cal
  - Lenz & Naumann, Inc., N. Y. C.
- Optical Instruments
  - Bausch & Lomb Optical Co., Rochester, N. Y
- Oxygen Generators
  - International Oxygen Co., N. Y. City
- Oxygen (Pure)
  - International Oxygen Co., N. Y. City.
- Oxygen Testing Apparatus
  - International Oxygen Company, N. Y City
- Packings (Condensing Tower)
  - German-American Stoneware Wks., N. Y. C.
  - Knight, M. A., Akron (East Side), Ohio.
  - U. S. Stoneware Co., The, Akron, O.
- Paints
  - Toch Brothers, N. Y. City.
- Patent Attorneys
  - Brickenstein, John H., Washington, D. C.
  - Foster, A. B., Washington, D. C.
  - Parker, C. L., Washington, D. C.
  - Sieck, Herbert, Chicago, Ill.
  - Townsend, Clinton P., Washington, D. C.
- Penetrometers
  - Howard & Morse, N. Y. City.
- Percolators
  - Elyria Enameled Prod.Co., Elyria, O., &.N.Y.C
  - Kieselguhr Co. of America. Los Angeles, Cal.
  - Pfaudler Co., Rochester N.Y., Detroit, & N.Y.C.
- Photo-Micrographic Apparatus
  - Bausch & Lomb Optical Co., Rochester, N. Y
- Pipe and Accessories
  - Bausch & Lomb Optical Co., Rochester, N. Y
  - Corning Glass Works, Corning, N. Y.
- Pipe and Accessories (Acid Proof)
  - Duriron Castings Co., N. Y. C.
  - Elyria Enameled Prod. Co., Elyria, O., & N.Y.C
  - German-American Stoneware Works, N. Y. C.
  - Knight, M. A., Akron (East Side), Ohio.
  - Schutte & Koerting Co., Philadelphia.
  - Thermal Syndicate, Ltd., N. Y. C. (Fused Silica).
  - U. S. Stoneware Co.. The, Akron, O.
- Pipe and Fittings—Lead or Tin Lined
  - Chadwick-Boston Lead Co., Boston, Mass.

POTASH SALTS

FOR AGRICULTURAL and INDUSTRIAL USES

We sell MURIATE OF POTASH, SULFATE OF POTASH, DOUBLE MANURE SALT, MANURE SALT, KAINIT and KIESERIT, in single cars and upwards, to Chemical Works, Fertilizer Mixers, Jobbers and Dealers.

We also sell direct to Consumers, for agricultural use, any quantity of Muriate, Sulfate or Kainit from one 200-lb. bag up.

Sales to Manufacturers for direct importation from Germany are made by the New York Office. Meyer, Wilson & Co., San Francisco, Cal., are Agents for the Pacific Coast.

Books relating to Production and Uses of Potash in Agriculture sent free on request.

THE GERMAN KALI WORKS

42 Broadway, NEW YORK

BRANCH OFFICES AT CHICAGO, SAVANNAH, NEW ORLEANS AND BALTIMORE

MADE IN U·S·A·

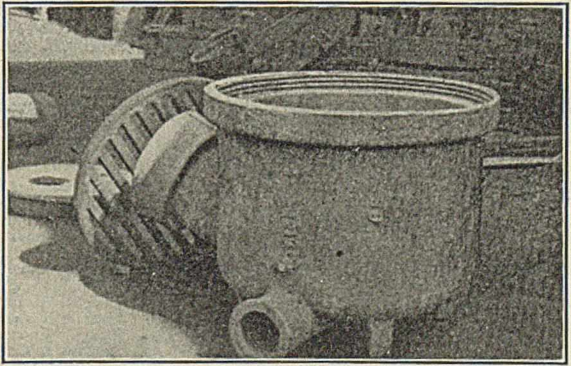
DENATURED ALCOHOL

We can supply every requirement — our facilities permit offering Denatured Alcohol according to any and every approved U. S. Government Formula. This Alcohol is of the highest quality and will stand any test.

Special and prompt attention given to carload shipments. Submit your specifications and we will gladly make quotations.

WOOLNER & CO.

PEORIA ILLINOIS



Test a Sample of

CORROSIRON

MADE IN CALIFORNIA

— the Machinable, Acid-Resisting Alloy

Users of CORROSIRON have proved that it is particularly adaptable to many exacting conditions of requirement. They have been able to cast it in difficult, intricate shapes. It is being cast around steel pipes, shafts, etc., and castings of nearly three inches in thickness have failed to show flaws.

CORROSIRON is deserving of your attention and we are anxious that you submit a sample to your chemical test.

We are making Centrifugal Pumps up to six inches and are carrying Valves and Plug Cocks in stock

Pacific Foundry Company

Harrison and Eighteenth Sts. SAN FRANCISCO, CAL.

CLASSIFIED INDEX TO ADVERTISERS' PRODUCTS.—(*Concluded*)

Platinum (Sheet, Wire and Foil)
American Platinum Works, Newark, N. J.
Baker & Co., Inc., Newark, N. J.
Bausch & Lomb Optical Co., Rochester, N. Y.
Bishop & Co., J., Platinum Works. Malvern. Pa.

Platinum Ware (Laboratory)
American Platinum Works, Newark, N. J.
Baker & Co., Inc., Newark, N. J.
Bausch & Lomb Optical Co., Rochester, N. Y.
Bishop & Co., J., Platinum Works, Malvern. Pa.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Engelhard, Chas., New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann. Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co.. Pittsburg. Pa.
Thomas Co., Arthur H., Philadelphia.

Porcelain Ware—Laboratory
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo
Lenz & Naumann. Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia.

Potash Salts
German Kali Works, N. Y. C.

Pulverizers—Laboratory
Abbé Engineering Co., New York City.
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., SanFrancisco. Cal.
Eimer & Amend, New York City.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.
Williams Patent Crusher & Pulv. Co., Chicago.

Pumps—Acid
Bausch & Lomb Optical Co., Rochester, N. Y.
Bethlehem Fdy. & Mach. Co., So. Beth'm, Pa.
Devine Co., J. P., Buffalo, N. Y.
Duriron Castings Co., New York City.
German-American Stoneware Works, N. Y. C.
Schutte & Koerting Co., Philadelphia.

Pumps (Laboratory Vacuum)
Abbé Engineering Co., New York City.
Bausch & Lomb Optical Co., Rochester, N. Y.
Buffalo Dental Mfg. Co., Buffalo, N. Y.
Crowell Mfg. Co., Brooklyn, N. Y.
Hubbards' Sons, Norman, Brooklyn, N. Y.

Pumps (Vacuum)
Abbé Engineering Co., N. Y. C.
Bethlehem Fdy. & Mach. Co., So. Beth'm, Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Crowell Mfg. Co., Brooklyn, N. Y.
Duriron Castings Co., N. Y. C.
Jacoby, Henry E., New York City.

Pump Parts Metal (Acid Proof)
Duriron Castings Co., N. Y. C.
Schutte & Koerting Co., Philadelphia.

Pyrometers
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Engelhard, Chas., New York City.
Greiner Co., Emil. New York City.
Heil Chem. Co., Henry E., St. Louis, Mo.
Hoskins Mfg. Co., Detroit, Mich.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia.
Thwing Instrument Co., Philadelphia, Pa.

Quartz
Booth Apparatus Co., Syracuse, N. Y.

Quartz Glass
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Engelhard, Chas, New York City.
Greiner Co., Emil, New York City.
Hanovia Chemical & Mfg. Co., Newark. N. J
Heil Chem. Co., Henry. St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thermal Syndicate, Ltd., New York City.
Thomas Co., Arthur H., Philadelphia.

Radium
Eimer & Amend, New York City.
Heil Chemical Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.

Reagents—Chemical
Baker & Adamson Chem. Co., Easton, Pa.
Baker Chem. Co., J. T., Phillipsburg, N. J.
Bausch & Lomb Optical Co., Rochester, N. Y.
Heil Chemical Co., Henry, St. Louis, Mo.
Hoffmann & Kropff Chem. Co., Brooklyn, N. Y.
Merck & Co., N. Y. C.
Squibb & Sons, E. R., N. Y. C.

Refineries—(Oil—Sugar Installation)
Lummus, Walter E., Boston, Mass.

Refractories
Kieselguhr Co. of America, Los Angeles, Calif.
Norton Co., Worcester, Mass.

Resistance Wire
American Platinum Works, Newark, N. J.
Baker & Co., Inc., Newark, N. J.
Bishop & Co., J., Malvern, Pa.

Retorts
Dixon Crucible Co., Joseph, Jersey City, N. J.
Heil Chemical Co., Henry, St. Louis, Mo.
Lummus, Walter E., Boston, Mass.
Thermal Syndicate, Ltd., N. Y. C.

Retorts (Cast Iron)
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.

Retorts—Acid (Cast Iron)
Bethlehem Foundry & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.

Rotary Compressors or Blowers
Abbé Engineering Co., N. Y. C.
Crowell Mfg. Co., Brooklyn, N. Y.

Rotary Lead Fans
Schutte & Koerting Co., Philadelphia.

Screens (Grinding & Pulverizing)
Raymond Bros. Impact Pulv Co., Chicago, Ill.

Separators—Air
Raymond Bros. Impact. Pulv Co., Chicago, Ill.

Separators—Centrifugal
International Instrument Co., Cambridge, Mass.
Schaum & Uhlinger, Inc., Philadelphia.
Tolhurst Machine Works, Troy, N. Y.

Shredders
Williams Patent Crusher & Pulv. Co., Chicago.

Sieve Agitators
Howard & Morse. N. Y. City.

Sieves (Testing)
Howard & Morse, N. Y. City.

Silica—Fused
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Engelhard, Chas., New York City.
Greiner & Co., Emil, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thermal Syndicate, Ltd., New York City.
Thomas Co., Arthur H., Philadelphia.

Solvent Recovery Apparatus (Vacuum)
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
Lummus, Walter E., Boston, Mass.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Werner & Pfleiderer Co., Saginaw, Mich.

Spelter
New Jersey Zinc Co., The, N. Y. C.

Spray Nozzles
Schutte & Koerting Co., Philadelphia.

Steam Engineering Specialties
Sarco Co., Inc., New York City.

Steam Traps and Meters
Sarco Co., Inc., New York City.

Stirring Apparatus
Booth Apparatus Co., Syracuse, N. Y.
Duriron Castings Co., N. Y. C.
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Werner & Pfleiderer Co., Saginaw, Mich.

Stoneware—Chemical (Laboratory)
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
German-American Stoneware Works, N. Y. C.
Heil Chem. Co., Henry, St. Louis, Mo.
Knight, Maurice A., Akron, Ohio.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia.
U. S. Stoneware Co., The, Akron, O.

Stoneware (Acid Proof—Industrial Purposes)
German-American Stoneware Works, N. Y. C.
Knight, M. A., Akron (East Side), Ohio.
U. S. Stoneware Co., The, Akron, O.

Succinic Acid
Woolner & Co., Peoria, Ill.

Sulphur, Crude
Union Sulphur Co., New York City.

Surface Combustion Equipment
Bausch & Lomb Optical Co., Rochester, N. Y.

Syphons—Steam Jet
Duriron Castings Co., N. Y. C. (Acid Proof).
Schutte & Koerting Co., Philadelphia, Pa.
Elyria Enameled Products Co., Elyria, O., and N. Y. C.

Tanks—(For Acid or Basic Reaction)
Elyria Enameled Products Co., Elyria, O., and N. Y. C.
German-American Stoneware Works, N. Y. C
Knight, Maurice A., Akron, Ohio.
Lummus, Walter E., Boston, Mass.
Pfaudler Co., Rochester. N.Y., Detroit, & N.Y.C.
U. S. Stoneware Co., The, Akron, O.

Tanks—(Measuring & Self-decanting)
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
Pfaudler Co., The, Rochester, N. Y.
Lummus, Walter E., Boston, Mass.

Tanks—Pressure
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
German-American Stoneware Works, N. Y. C.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
U. S. Stoneware Co., The, Akron, O.

Tanks (Steel)
Stevens Brothers, N. Y. C.

Tanks (Storage)
Elyria Enameled Prod. Co., Elyria. O., & N.Y.C.
German-American Stoneware Works, N. Y. C.
Knight, M. A.. Akron (East Side), Ohio
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
U. S. Stoneware Co., The, Akron, O.

Temperature Control Instruments
Thwing Instrument Co.. Philadelphia, Pa.

Thermometers
Bausch & Lomb Optical Co., Rochester, N. Y.
Caloris Co., The, Millville, N. J.
Carbondale Instrument Co., Carbondale, Pa.
Engelhard, Charles, New York City.
Greiner Co., Emil, New York City.
Heil Chemical Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.

Thermostats
Bausch & Lomb Optical Co., Rochester, N. Y.
Thwing Instrument Co., Philadelphia., Pa.

Thickeners, or Dewaterers
Dorr Cyanide Mch'y Co., Denver, Col., N. Y. C.
International Filtration Corp., N. Y. C.

Tile (Tower)
German-American Stoneware Works, N. Y. C
Knight, M. A., Akron (East Side), Ohio.
U. S. Stoneware Co., The, Akron, O.

Triangles
Bausch & Lomb Optical Co., Rochester, N. Y.
Thermal Syndicate, Ltd., New York City.

Vacuum Drying Apparatus
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdv & Mch. Co.. Buffalo, N. Y.
Devine Co.. J. P., Buffalo. N. Y.
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
Jacoby Henry E., New York City.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Stokes Machine Co., F. J., Philadelphia.
Werner & Pfleiderer Co., Saginaw, Mich.

Vacuum Pans
Badger & Sons Co., E. B., Boston, Mass.
Devine Co., J. P., Buffalo, N. Y.
Elyria Enameled Prod. Co., Elyria, O., &. N.Y.C.
German-American Stoneware Works, N. Y. C.
Jacoby, Henry E.. New York City.
Lummus, Walter E., Boston, Mass.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Sanborn Evaporator Co., New York City
Sowers Mfg. Co., Buffalo, N. Y.
Sperry & Co., D. R., Batavia, Ill.
Stokes Machine Co.. F. J., Philadelphia.
Stuart & Peterson Co., The, Burlington, N. J.
Swenson Evaporator Co., Chicago, Ill.
Werner & Pfleiderer Co., Saginaw, Mich.
Zaremba Co., Buffalo, N. Y.

Vacuum Pumps
Abbé Engineering Co., N. Y. City.
Bausch & Lomb Optical Co., Rochester, N. Y.
Crowell Engineering Co., Brooklyn, N. Y.
Hubbard's Sons, Norman, Brooklyn, N. Y.
York Electric & Machine Co., York, Pa.

Vacuum Stills
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
Lummus, Walter E., Boston, Mass.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Stuart & Peterson Co., The, Burlington, N. J.
Werner & Pfleiderer Co., Saginaw, Mich.

Valves and Fittings—Lead
Schutte & Koerting Co., Philadelphia, Pa.

Varnish—Coil Impregnation
General Bakelite Co., New York City.

Vats (Rectangular)
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.

Vicat Needles
Howard & Morse, N. Y. City.

Viscosity Floats
Howard & Morse, N. Y. City.

Water Bath (Laboratory)
Bausch & Lomb Optical Co., Rochester, N. Y.
Electric Heating Appliance Co., N. Y. C.

Water Softening Apparatus
Booth Apparatus Co., Syracuse, N. Y.

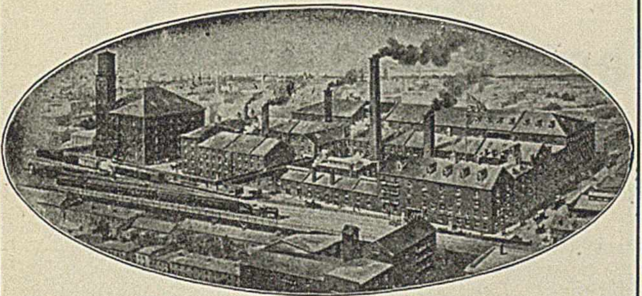
Weighing Machinery—(Automatic)
Werner & Pfleiderer Co., Saginaw, Mich.

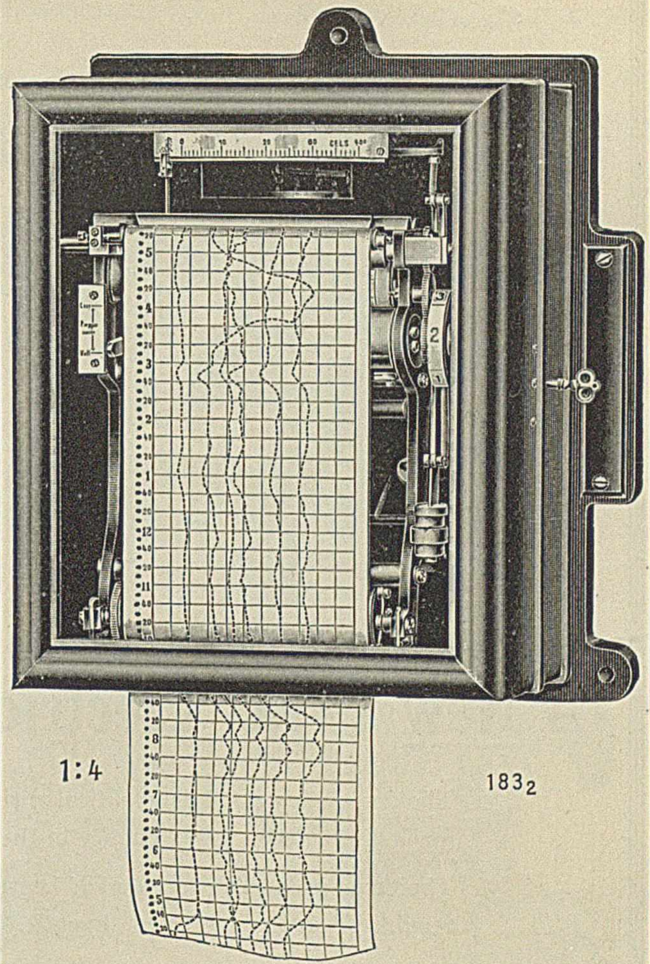
Welding and Cutting Apparatus
International Oxygen Co., N. Y. C.

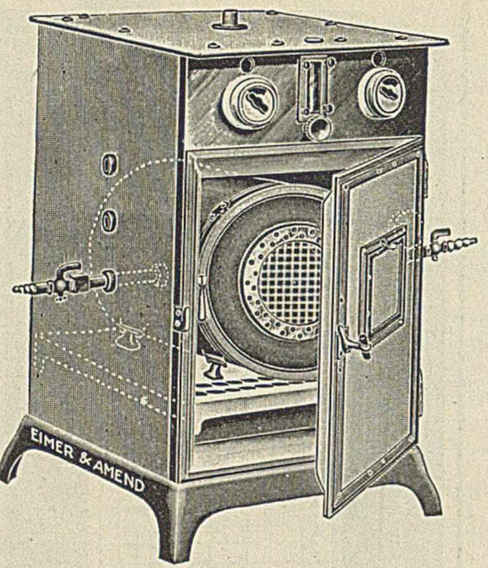
Wire Cloth
Howard & Morse, N. Y. City.

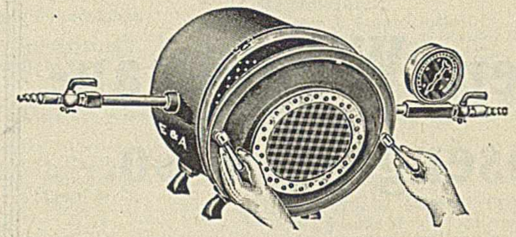
Wire, Resistance
Driver, Harris Wire Co., Harrison, N. J.

Wood Distillation Equipment
Badger & Sons, Co., E. B., Boston, Mass.
Elyria Enameled Prod. Co., Elyria, O., & N.Y.C.
Lummus. Walter E.. Boston, Mass.
Pfaudler Co., Rochester N.Y., Detroit, & N.Y.C.
Swenson Evaporator Co., Chicago, Ill.
Zaremba Co., Buffalo, N. Y.




1:4
183₂





A New Freas Electric Vacuum Oven

The Oven illustrated is identical with the Freas Electric Vacuum Oven except for its size and a slight change in the arrangement of the door.

The Oven proper is constructed, heated and regulated on the same lines as the regular Freas Drying Oven, Type R.

The cast bronze vacuum chamber—internal dimensions 9 inches deep, 9 inches diameter—fits in the oven as illustrated. It is provided with racks for shelves, vacuum gauge and connections for vacuum and for passing in heated air or reducing gases. The ground surfaces of the oven and its door are held together perfectly by sturdy spring clips. This construction allows the surfaces to be easily reground in case of need; it permits also instant removal of the door.

The vacuum chamber is readily removable, permitting the use of the oven proper—chamber dimensions 12 by 12 inches, for regular drying purposes.

The Freas Electric Vacuum Oven is the only oven for use with vacuum that can be maintained accurately at any temperature desired up to 180° C. It is considered the most satisfactory vacuum oven available. Repeat orders received—one recently for four ovens—prove the satisfaction it is giving.

Price	Complete with Vacuum Chamber, inside dimensions 9 x 9 inches, -	net $152.50
	Complete with Vacuum Chamber, inside dimensions 8 x 18 inches, -	net $250.00

SOLE DISTRIBUTORS

EIMER AND AMEND

(Founded 1851)

INDUSTRIAL AND EDUCATIONAL LABORATORY APPARATUS
CHEMICALS AND DRUGS

NEW YORK
N. Y.

PITTSBURGH
PA.