

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume III

SEPTEMBER, 1911

No. 9

BOARD OF EDITORS.

Editor: M. C. Whitaker.

Associate Editors:

Geo. P. Adamson, E. G. Bailey, H. E. Barnard, C. A. Browne, G. E. Barton, Wm. Brady, Wm. Campbell, F. B. Carpenter, Virgil Coblenz, Francis I. Dupont, W. C. Ebaugh, Wm. C. Geer, W. F. Hillebrand, W. D. Horne, Karl Langenbeck, A. D. Little, C. E. Lucke, P. C. McIlhiney, E. B. McCready, Wm. McMurtrie, J. Merritt Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, Geo. C. Stone, Ernst Twitchell, Robt. Wahl, Wm. H. Walker, W. R. Whitney.

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 at the Post-Office, Easton, Pa., as Second-class Matter.

EDITORIALS

THE PURE FOOD LAW.

The country has had several years' operation of the Pure Food Law, and the veriest tyro knows that it is 'doing things'. It is natural to suppose that the five thousand members of the society have a special interest in it, because of their assistance and coöperation in its establishment and of the influence of chemistry upon its operation. Among those who have kept track of its workings through the food inspection decisions and Notices of Judgment, there may be differences of opinion as to the details, but the attempt on the part of the government to make the law meet the conditions would probably be generally recognized.

This is no attempt at a criticism of the working of the law; it is intended more as a suggestion that we chemists pay attention to this particular matter in which we may be presumed to know something, and that we at least support by our interest those who bear the burdens of seeing the law executed. It would seem to the writer a good scheme for local sections to make a point of inducing some one of their members to present at a section meeting a summary of the working of this law. The decisions are available through the department of agriculture. In the Notices of Judgment, now numbering over 800, one readily sees the practical operation of the law. It may be that accounts of watering milk for interstate shipment, putting cottonseed oil in place of olive oil, glucose where sucrose belongs, chaff where wheat and oats belong, mineral oil in turpentine, and good in nothing, does not make uplifting reading, but the general prevalence of schemes to defraud is certainly made evident by the judgments. Those conditions of public opinion which should help cure this trouble will probably be benefitted by more general public knowledge.

If a firm doing a large business is detected in shipping a quart of poison, bearing a label liquid bread,

from one State into another, does confiscation of the shipment constitute adequate punishment? If copper acetate were added to a stock of pickles to produce the same effect as the use of a copper kettle, and such pickles were improperly shipped from one State to another, what would constitute a proper fine? There are hundreds of interesting answers to such questions in the Notices of Judgment of the Department of Agriculture.

The average citizen who depends on the daily press for his information probably has a hazy notion that some one is behind a movement to prevent poisoning of the people by sodium benzoate and poor whiskey. To this knowledge it might be worth while to add a little concerning the actual working of the law. The judgments are the indicators. The average chemist may enjoy questioning whether the penalties have been too severe or not, and whether there is a need in our well advanced and civilized country for the execution of such a law. Enlightened public opinion may be assisted in its growth if our members become acquainted with the Pure Food Law.

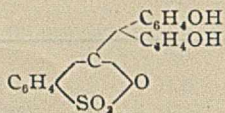
W. R. WHITNEY.

THE SUBCUTANEOUS ADMINISTRATION OF PHENOLSULPHONEPHTHALEIN AS A MEANS OF DETERMINING THE WORKING CAPACITY OF THE KIDNEYS.

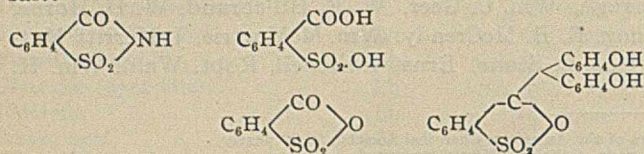
In view of the fact that the phenomena concerned in the process of secretion of urine by the kidneys are still largely a matter of speculation, any method that will accurately demonstrate the working capacity of the kidneys must be hailed with delight by the physician and surgeon.

To the chemistry of the dyestuffs, which has already furnished such valuable materials to medicine, we are again indebted for placing at the disposal of science a substance possessing most wonderful prop-

erties. To add to our pride as chemists we are able to state that the dyestuff in question was discovered by an American chemist, and that American pharmacologists established its application in medicine. This substance is phenolsulphonophthalein, first prepared by Remsen (*American Chemical Journal*, 6, 180), and has the formula:



It is best produced from saccharine over the O-sulphobenzoic acid, obtained from its acid ammonium salt:



John J. Abel and L. G. Rowntree (*Journal of Pharmacology and Experimental Therapeutics*, 1, 260), who determined the pharmacological properties of the product, describe the substance as follows:

"It is a bright red crystalline powder somewhat soluble in water, more so in alcohol, insoluble in ether; its dilute alkaline solution is of a purer red than that of phenolphthalein, while a more strongly alkaline solution is purple. It is readily soluble in solutions of sodium carbonate and has a stronger avidity as an acid than any of the phthaleins hitherto examined by us.

"Solutions of the sodium salt properly made up may be injected under the skin without the slightest evidence of an irritant action. The drug may also be administered by mouth without untoward effects of any kind. Taken into the mouth as a powder it is at first slightly sweetish to the taste, then bitter and rather disagreeable. Applied in this way it stains the mucous membrane of the mouth and tongue a brilliant red which later becomes yellow and then disappears. Given by mouth to healthy human beings in doses of 0.1-0.15 gram the drug is readily absorbed and appears in the urine in the course of an hour or an hour and a half. The urine, if acid, assumes a yellow or reddish yellow color, which immediately gives place to the purple of sulphonephthalein on the addition of an alkali. After injection underneath the skin in doses of 1.6 cc. of a 5 per cent. solution it may be detected in the urine of healthy individuals within ten minutes."

It is interesting to note that the substance is absolutely harmless, manifesting no untoward effects of any kind when taken internally and causing no irritation when injected subcutaneously.

The properties which have made the use of this dyestuff as a diagnostic agent so important are that it is entirely eliminated by the kidneys, and that while it can be detected in the urine of healthy individuals within ten minutes and at the end of two hours from 60-70 per cent. of the amount administered is elim-

inated, its detection and excretion takes a much longer time in cases of renal disease.

Dr. Charles Goodman (*American Medicine*, May, 1911) summarizes the advantages of this substance as follows:

"The drug is not readily decomposed. It can be sterilized by boiling. Dose, 6 mg. injected hypodermically. Recovered in the urine as early as three minutes after injection. Within two hours from 50-70 per cent. of the drug should be recovered in the healthy state, in diseased conditions proportionately less. The drug lends itself to accurate measuring. The flow of urine excreted does not influence the amount of drug excreted. No matter how much urine, the amount of drug recovered will exactly show the index of the derangement of the kidneys. In a case of diabetes insipidus, a patient passed 1,150 cc. of urine within two hours and the drug recovered showed almost the entire amount of the dye. The presence of pus or other extraneous matters does not interfere with the proper colorimeter estimation of the amount of drug recovered. The technique is very simple. The injection is given, the time noted, the patient asked to void every five minutes in order to establish a time when the drug first appears in the urine. If there is no objection to the use of the catheter, the urine is collected for the first hour and for the second hour and the amount of the drug recovered is estimated and in that way we establish the work of the kidney."

Further observations in regard to the value of the phenolsulphonophthalein test in determining the renal function were presented by Drs. E. L. Keyes and A. R. Stevens and by Drs. J. T. Geraghty and L. G. Rowntree in two papers read before the New York Academy of Medicine, May 4, 1911 (*Medical Record*, June 3, 1911).

The results of Keyes and Stevens are practically confirmatory of those obtained by Geraghty and Rowntree. The chief criticism of Keyes and Stevens is that the test serves only as an index of the total kidney capacity, and does not show how each kidney is functioning. If each ureter is catheterized separately to overcome this objection, the mere introduction of the instrument caused a diminution of the phenolphthalein output. For this reason they now make two tests, one with ureteral catheterism and the other without, and confirm the results with other tests.

In Geraghty's and Rowntree's latest study they employed intramuscular and intravenous as well as subcutaneous injections. The chief difference between the new and old method is an increase of 5-10 per cent. output during the first half hour.

There does not seem any doubt, however, as to the value of the test, for even though ureteral catheterism reduces the output of the drug, it gives the index of excretion of each kidney as a basis of comparison. On the other hand, if the catheter is not used it will show the working capacity of both kidneys together.

ORIGINAL PAPERS.

FISH OIL AS A PAINT VEHICLE.

By MAXIMILIAN TOCH.

Received July 20, 1911.

On November 3, 1910, I delivered a lecture at St. Bride's Institute, London, before the Paint and Varnish Society, on "The Newer Paint Materials," in which I outlined briefly the liquids that are used in paint materials, other than linseed oil and turpentine. A very short description was given of fish oil, but this chapter received more attention than any other part of the lecture and was widely copied throughout the United States and Europe.

The subject of fish oil demands so much attention and is so poorly understood that I take this opportunity of enlarging on the subject, not to correct any misapprehensions, but to give information which will enlighten the manufacturer and the consumer.

In the first place, we are all prone to call all oils of a fish nature "Fish oils," and I desire to differentiate between the *real* fish oils and the *pseudo fish oils*, for there are several animal oils which have fishy characteristics but which are not strictly fish oils, and these oils do not serve as good a purpose as those which are strictly extracted from fishes. Some of the fish oils—like cod liver oil—even if they were cheap enough, are not totally adapted for paint use. The animal oils which have always been regarded as fish oils, but which I call pseudo fish oils, and that are in the market and easily purchased at a reasonable price, are whale oil, porpoise oil and seal oil. All of these oils are by no means drying oils, and even if they are admixed with drying oils like tung oil and boiled linseed oil, and an additional amount of drier added, they are peculiarly hygroscopic, and after three months I have noted that although these oils may be apparently dry they become sticky when the humidity rises above 80. I append a list of oils taken out of stock, which represent standard samples, and I have given in each case the specific gravity and the iodine number, and I must say that the iodine number is a characteristic indication of the quality of a fish oil for paint purposes.

FISH OIL CONSTANTS.

	Specific gravity, 20° C.	Iodine No., Hübl, 4 hours.
No. 1 crude whale oil.....	0.9195	136.1
No. 1 filtered whale oil.....	0.9168	125.0
No. 2 filtered whale oil.....	0.9187	142.9
Cod oil.....	0.9196	147.3
Porpoise body oil.....	0.9233	132.3
Seal oil—water white.....	0.9227	143.0
<i>Menhaden oil.</i>		
Extra bleached winter.....	0.9237	150.4
Bleached—refined.....	0.9273	161.2
Regular.....	0.9249	165.7
Dark brown.....	0.9250	154.5

The specific gravities were determined with the aid of the Westphal balance.

The iodine numbers were determined according to the standard method of Hübl.

On a previous occasion I mentioned that the textbooks show the specific gravity of fish oil as approxima-

ting that of linseed oil, but in no instance have I found this to be the case within the last year, for it appears that fish oils freshly made and containing no admixture of other species, but representing the pressing of only one specie, are as a general rule below 927. The oil that gives the best and most lasting results for paint purposes is the Menhaden oil, and the winter bleached variety is the one that should be recommended. This is an oil fairly pale in color, with an iodine number of 150 or over, and with little or no fishy odor; in fact I might say that in the purchasing of fish oil for paint purposes it is well to beware of a fish oil that has the so-called characteristic fishy odor. I have not yet satisfied myself as to the cause of this odor, but as far as I have reached in my investigation I am inclined to believe it is due to phosphorus decomposition compounds. The results which I have obtained from the proper grades of fish oil—and I am glad to say there are several manufacturers sufficiently intelligent to market oils that are very desirable—warrant me in saying that fish oil in the hands of an intelligent manufacturer, and used up to 75 per cent., produces excellent results for exterior purposes. For interior purposes fish oil does not seem to be desirable, for it gives off noxious gases for a long time.

As compared with Soya bean oil, and I have continually refrained from giving any opinion as to the value of this material as an exterior paint oil, as I have not yet had sufficient time to form an opinion, it will be observed that in 1906 I published my first researches on the subject of fish oil, and I have been watching it ever since, and when mixed with linseed oil, even up to 75 per cent. of fish oil, it gives excellent and lasting results and does not show any hygroscopic properties, but when used in the raw state, particularly in conjunction with pigments which in themselves are not catalytic driers, the results are not satisfactory.

Since last year some of the enamel leather and printing ink manufacturers have adopted the use of fish oil as a medium to replace linseed oil, with excellent results, and the enamel leather which is produced, while not so high in gloss as that made entirely of linseed oil, is much more flexible and possesses an unctuousness which prevents it from cracking. But fish oil for leather purposes shows a peculiar defect, and a campaign of education will be necessary if ever this material is to be used for the manufacture of shoes or auto tops, for fish oil, particularly when it originally has a high acid number, seems to effloresce and gives an undesirable bloom to enamel leather, which, however, can be removed from the surface by the ordinary application of either benzine or a mixture of benzine and turpentine. At the same time, enamel leather is very largely used for carriage and automobile tops, and for shoes, and wherever it is used for these purposes these products are continually polished.

I might quote an analogous case of a manufacturer of chocolate who was unable to market his product,

good as it was, for the reason that the excess of cocoa butter which it contained crystallized on the surface and gave it a mildewed appearance. It was almost impossible for him to exploit his material, owing to this peculiar defect, when it occurred to him to explain to his prospective customers that he was the only man who could make chocolate that had this singular efflorescence, and that it was an indication of its quality. The public soon learned to look for chocolate that had a scum over it, and it was not very long before other manufacturers had to make chocolate of a similar appearance. The same thing might be true of enamel or patent leather. If it has a peculiar grayish bloom, due to some of the fatty acids crystallizing on the surface, it might be taken as an indication that such leather does not crack as readily as enamel made entirely of linseed oil.

The manipulation of fish oil simply amounts to this, that the manufacturers of fish oil will probably be compelled to add their own drier and their own boiled linseed oil to the fish oil and market it in that condition as a paint oil, so that the paint manufacturer may be able to buy it according to a certain specification and know he will get certain results.

We are all aware that paint made from fish oil can be applied to hot surfaces and will not blister or peel as readily as that made of linseed oil, and for this purpose—as a smoke stack paint—it is very desirable.

There is a great demand for baking japans which shall be flexible and at the same time so thoroughly baked that they adhere to the surface most tenaciously and form an excellent enamel, and for this purpose we know that the reasonable use of fish oil improves baking japans very much indeed.

We are also aware that along the seacoast, where paint disintegrates very rapidly on account of the sea air, a fairly liberal use of properly treated fish oil serves a useful purpose.

When red lead is mixed *33 lbs. to a gallon of linseed oil* it thickens up after a very short time and becomes unfit for use. A properly neutralized fish oil prevents the hardening or setting of the red lead in the package, and a paste of this material can be transported a great distance and will last many months in a fresh and soft condition.

All the samples herewith submitted and painted on steel, of the various fish oils, pseudo fish oils and linseed oil, are without the admixture of driers, and you will note that the Menhaden fish oil and the linseed oil have dried approximately the same, but the seal oil and whale oil are still sticky after two weeks. This may be an unfair test, for these other oils can be manipulated with the proper driers and they will serve a fairly good purpose, but inasmuch as Menhaden fish oil appears to be satisfactory for this test even without a drier, its superiority over the animal oils is apparent.

Menhaden oil should, of course, be used with a drier, and for that purpose the best results are obtained by means of a Tungate drier. A Tungate drier is one in which tung oil or China wood oil is boiled with a lead and manganese oxide, and when

the solution is complete this is then mixed with a properly made resin of lead and manganese. Such a drier becomes soluble in the oil at temperatures over 100°C ., and hardens the resulting paint very thoroughly. For fabrics, however, fish oil must be heated to a temperature of over 200°C ., and if air is injected at such a temperature the glycerides are expelled and thick oil is produced which, in conjunction with the drier just named, is equally good for printing inks. It is advisable, however, to add at least 25 per cent. of either a heavy bodied linseed oil or a raw linseed oil which does not break before the manipulation just referred to is begun.

For stacks, boiler fronts, etc., I have already pointed out on another occasion that the treatment of fish oil up to 220°C . with litharge makes a heat-resisting medium that is far superior to anything excepting China wood oil, and for both heat-resisting and exposure to the elements fish oil is superior to China wood oil.

THE EFFECT OF PIGMENTS GROUND IN LINSEED OIL.

By HENRY A. GARDNER.

Received July 21, 1911.

In a recent contribution to the technology of drying oils, Sabin¹ describes the peculiar action that various pigments have upon the drying of linseed oil. Pigments such as barytes and China clay, which have always been considered by the paint chemist as inert pigments or pigments developing no chemical action when ground in linseed oil, appeared in Sabin's test to accelerate the drying of linseed oil when ground therein, and spread out to a thin film. The writer has always contended that such action was not due to any chemical effect between the inert pigments and the oil, but rather to the physical action of such pigments in distributing the mass of oil in which they are ground and thus allowing a greater surface to be exposed to the oxygen of the air. Sabin has stated that the action of such pigments may be due to the hindering of peroxidation processes which involve the loss in weight of the oil films. The writer feels, however, that the stimulation of oxidation by catalytic or contact action may more readily account for the effect these pigments have upon the drying of linseed oil.

The point at issue seems to be whether the so-called inert pigments really have any chemical action when enveloped in linseed oil. To determine this point, the writer has conducted a series of tests which seem to conclusively prove that the pigments in question are really chemically inert and have absolutely no such action. The tests were made in the following manner:

Five grams of each of a series of commonly used paint pigments, including those of inert crystalline nature as well as the more valuable amorphous pigments which are considered more or less chemically active, were ground separately in an agate mortar, with 5 grams of raw linseed oil. The ground paste in each case was placed in a marked glass beaker,

¹ "Linseed Oil," by A. H. Sabin, *THIS JOURNAL*, 3, 84, 1911.

and allowed to stand in a dustless section of the laboratory for one month. The oil-pigment paste from each beaker was then separately extracted with benzine to remove the linseed oil from the pigment. The benzine solutions of oil were then heated to remove the benzine and the residue of oil burned to ash in crucibles. The ash from each test was weighed, and if it ran above the percentage of ash determined on a blank sample of linseed oil (namely, 0.003 per cent.), the ash was analyzed qualitatively for metallic constituents. The following table of results shows the percentage increase in ash, as well as the constituents of ash on the various samples tested:

TABLE OF RESULTS.

Pigment in oil.	Per cent. of ash in oil extracted from oil-pigment paste.	Analysis of ash.
Raw linseed oil without pigment.....	0.003
Barytes.....	0.003
Blanc fixe.....	0.003
Silica.....	0.003
Asbestine.....	0.005
China clay.....	0.007
Whiting.....	0.008
Chrome yellow.....	0.025	Lead oxide (PbO)
Lithopone.....	0.031	Zinc oxide (ZnO)
Prussian blue.....	0.032	Iron oxide (Fe ₂ O ₃)
Sublimed white lead.....	0.033	Lead oxide (PbO)
Zinc oxide.....	0.105	Zinc oxide (ZnO)
Corroded white lead.....	0.116	Lead oxide (PbO)
Red lead.....	0.2112	Lead oxide (PbO)

Observation of these results shows that pigments such as barytes, blanc fixe, and silica have no chemical action on the linseed oil. The results on asbestine and China clay also are negative, the extremely slight increase in amount of ash from these samples probably being due to traces carried over mechanically into the oil mixture, the last named pigments being more fluffy and difficult to separate from oil. Slight action seemed to be apparent in the case of whiting, a pigment somewhat alkaline in nature. A longer test might have shown this pigment to have possessed still greater action. Sublimed white lead, a paint pigment considered of great value by the paint grinder, for use with tinted paints which are liable to destruction when ground with alkaline pigments, showed but little action on the linseed oil. Corroded white lead, which is well known to be quite alkaline in nature, showed considerable action, indicating that the formation of lead linoleate or some other organic lead compound takes place when this pigment is ground in oil. Zinc oxide and lithopone, the latter pigment containing 30 per cent. of zinc sulphide, both indicated action on the oil. Chrome yellow (chromate of lead) showed some action, as did also Prussian blue, the ash from the last named pigment showing a heavy percentage of iron oxide. Red lead showed a most astounding gain in these tests, chemical action of the pigment on the oil being apparent soon after the tests were started, as shown by the formation of a hard cake with the linseed oil. The raw linseed oil which was used in these tests had an acid value of 1.84 which is very low. The neutralization of this free fatty acid by some of the

alkaline pigments used may account for part of the increased percentage of ash. It is the writer's belief, however, that in many cases the pigments, and more especially the basic pigments, had a direct saponifying action upon the glycerides of the oil.

Summing up the results, it is fair to say that the inert pigments so-called are really inert chemically, and that the lead and zinc pigments are chemically active. It would seem advisable, therefore, to use in paints made of the chemically active pigments a moderate percentage of the inert pigments, so that any marked saponification would not take place. The saponification of oil by either lead or zinc pigments is apt to result in early disintegration, as shown by exposure tests.¹ These same tests have proved that marked saponification may be prevented by the use of moderate percentages of the inert pigments.

THE INSTITUTE OF INDUSTRIAL RESEARCH,
WASHINGTON, D. C.

CUPFERRON: ITS USE IN QUANTITATIVE ANALYSIS.

BY OSKAR BAUDISCH AND VICTOR L. KING.

Received July 24, 1911.

Under the name "Cupferron" one of us (O. B.) introduced the ammonium salt of nitrosophenylhydroxylamine, C₆H₅(NO)ONH₄, into quantitative analysis as a precipitant for cupric and ferric ions. By means of cupferron, iron and copper may be separated very rapidly and exactly, not only from one another but also from almost all the other metals. The new method exceeds in elegance, simplicity, and rapidity of operation all the methods known up to the present time for the separation of iron and copper, and has already met with great favor in technical chemical analysis in factories and mining and metallurgical plants.

The advantages of precipitating with cupferron are as follows:

I. Iron and copper are precipitated from solutions strongly acid either with mineral or acetic acids. The precipitated iron and copper salts may be very easily and thoroughly washed free from the chlorides, nitrates, sulphates, etc., of any other metals which may be in solution.

II. The precipitates settle rapidly and may be filtered off without loss of time.

III. The separation of the iron from the copper is accomplished simply by washing the precipitate on the filter with dilute ammonium hydroxide solution. The ferric salt is completely insoluble and remains on the filter.

IV. The iron salt is readily soluble in ether, chloroform, acetone, etc., and may be dissolved, on the filter, away from any other metallic salts such as Pb, Ag, Hg, Sn salts, which may have been simultaneously precipitated.

The particular value of the new method lies in the fact that by its means iron may be rapidly separated from aluminum, manganese, chromium, nickel and cobalt. The "cupferron" method has been thoroughly

¹ See *Bulletins* 26 and 28, Paint Mfrs.' Assn. of U. S.

tested from many sides, and the work of H. Nissen, A. Biltz and O. Hödthe, and Fresenius quite confirm our results.

Cupferron will undoubtedly find extensive application in the quantitative analysis of widely different materials, for it has also been discovered that titanium, cerium, and zirconium may be quantitatively precipitated from acid solutions by it.

An example showing the application of the method to a manganese ore may be of value.

Dissolve 5.0 grams of the finely pulverized ore in 60 cc. of conc. HCl, oxidize the iron with KClO_3 , and after expelling the chlorine, dilute to 500 cc. with water. Pipette out 25 cc. into a beaker and add 20 cc. conc. HCl and 100 cc. cold distilled water. Allow a solution of about 3.0 grams of cupferron in 50 cc. of cold water to flow in a fine stream down the side of the beaker, with constant stirring. A brownish red, partly amorphous, partly crystalline precipitate separates out. As soon as a drop of the reagent causes the formation of a snow-white crystalline precipitate, all the iron is down. For certainty's sake add an excess of the reagent, stir well and filter off with suction. In case the last particles of the precipitate cling tenaciously to the beaker, add a little ether to loosen them, and then remove the ether by adding a little boiling water. In this manner it is possible to quantitatively transfer the precipitate to the filter. The precipitate is now washed with cold water until the filtrate is no longer acid with the mineral acid used. Manganese may be determined in the filtrate. The precipitate is now washed twice with dilute ammonia (1 vol. conc. NH_4OH to 1 vol. H_2O) in order to remove the excess of reagent. Wash once more with cold water and fold the wet paper and precipitate together and dry in a weighed platinum or porcelain crucible with a small flame. Then cover the crucible and heat until no more inflammable gases are evolved and then ignite to Fe_2O_3 , cool and weigh.

I. Substance 5.0 grams $\frac{25}{500} = \frac{1}{20}$ taken Fe_2O_3 0.0330 = 13.2%.

II. Substance 5.0 grams $\frac{25}{500} = \frac{1}{20}$ taken Fe_2O_3 0.0331 = 13.2%.

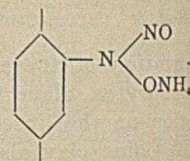
The analysis requires about $1\frac{1}{4}$ hours, but without inconvenience a number may be simultaneously carried out.

PREPARATION OF CUPFERRON.

Sixty grams of nitrobenzol, 1000 cc. of distilled water and 30 grams of NH_4Cl are thoroughly stirred up in a wide-mouthed bottle with an efficient stirring apparatus until a milky emulsion is formed. Into this emulsion (constant stirring) add 80 grams of zinc dust (the amount depends on the quality) in very small portions at a time. During the addition of the Zn dust the temperature must be kept between 15° and 18° C. This may be accomplished by simply throwing pieces of ice into the rapidly whirling liquid from time to time. Continued vigorous stirring and the keeping of the temperature within the pre-

scribed limits are the essentials which determine a good yield. The reduction is continued until the odor of nitrobenzol vanishes. The time required for the reduction depends on the value of the zinc dust. It usually takes half an hour to reduce 60 grams of nitrobenzol. The white zinc hydroxide is now filtered off with suction and the filtrate cooled to 0° C. with ice, and ordinary salt (NaCl) is added to saturation. In a little while a thick mass of snow-white crystals forms. Filter off right away with suction and dry the crystals between filter paper. The yield of phenylhydroxylamine is usually about 70-85 per cent. of the theory. As phenylhydroxylamine solutions are vigorous skin poisons and may pass through the unbroken skin into the blood, the hands should be washed with water and alcohol in case they come in contact with such solutions.

The freshly prepared phenylhydroxylamine is dried for an hour between filter paper and then dissolved in 300-500 cc. of commercial ether. The ether solution is filtered through a dry filter and cooled to 0° C. Into this cold solution dry ammonia gas is passed for about ten minutes and then add somewhat more than the theoretical amount (more than 1 mol.) of fresh amyl nitrite all at once. The clear solution will suddenly get hot and the entire vessel will be filled with snow-white crystals of the ammonium salt of nitrosophenylhydroxylamine,



The brilliant snow-white crystals are filtered off with suction, washed with ether, and dried between filter paper. They are then to be placed in a well-closed bottle with a small piece of solid ammonium carbonate.

The salt prepared and preserved in this manner will be found a welcome and thoroughly satisfactory precipitating and separating agent for copper and iron in any busy laboratory.

UNIVERSITY OF ZURICH,
SWITZERLAND, July, 1911.

THE DETERMINATION OF MANGANESE IN VANADIUM AND CHROME-VANADIUM STEELS.¹

By J. R. CAIN.

Received May 27, 1911.

Watters² has recently described a method for determining manganese in steels containing chromium and tungsten which eliminate the errors caused by using the bismuthate method on such steels, owing to the oxidation of some of the chromium by the bismuthate. The steel is dissolved in sulphuric acid and oxidized with nitric acid, the solution nearly neutralized and the chromium and iron are precipitated with an emulsion of zinc oxide. An aliquot is filtered off, nitric acid added, and the manganese determined

¹ Published by permission of the Director of the Bureau of Standards.
² *Met. Chem. Eng.*, 9, 244 (1911).

by the bismuthate method as usual. This method is very similar to one which the writer devised and has used for this class of materials. There is very little choice between the two, apparently, inasmuch as the time consumed, degree of accuracy, etc., is about the same in each case. However, the method to be described might give better results than that of Watters on high vanadium products, inasmuch as the vanadium in such cases might not always be completely precipitated by his method and this would cause high results. Watters' method was tested as to this point with the Bureau of Standards chrome-vanadium standard, containing about 1.32 per cent. of chromium and 0.20 per cent. of vanadium, and no vanadium was found in the filtrate with the manganese. The percentage of manganese in the standard was found to be identical by the two methods.

It has already been shown¹ that large amounts of chromium and vanadium are completely precipitated from solutions of steel without coprecipitation of manganese, provided the iron is kept mainly in the ferrous condition while the solution is being boiled with the precipitant. To carry out the method for manganese, 1 or 2 grams of steel are dissolved in sulphuric acid (10 per cent. by volume), observing the precautions given in the last-quoted paper, and the chromium and vanadium precipitated by cadmium carbonate as described therein. To the filtrate from this precipitate add 25 cc. of concentrated nitric acid and boil till free from fumes. Cool, oxidize with bismuthate, filter through asbestos, reduce with a measured excess of ferrous solution and titrate as usual.

The method is quite rapid, and its use, or the use of similar methods which eliminate chromium and vanadium during the bismuthate oxidation, seems called for, inasmuch as the results of the cooperating analysts on the above standard were several hundredths of a per cent. high where the bismuthate method was used. Further, the Ford-Williams method also gives high results, apparently due to occlusion of chromic acid. Some precipitates of manganese obtained by the Ford-Williams method from the chrome-vanadium standard were dissolved in sulphuric acid, neutralized with cadmium carbonate and boiled. The precipitate showed appreciable amounts of chromium when dissolved in nitric acid and oxidized with potassium chlorate. A bismuthate determination of manganese in the filtrate gave a result agreeing with the determinations by the method of Watters and that of the writer.

BUREAU OF STANDARDS, WASHINGTON.

ON THE SURFACE TENSION OF MOLTEN GLASSES.

By EDWIN WARD TILLOTSON, JR.

Received June 16, 1911.

Surface tension has been, up to the present time, one of the properties of a glass or enamel of which a comparatively small amount of information is at hand. Owing to the lack of convenient methods for its de-

termination it has been impossible to measure its value and the characteristic effects upon it of each constituent of the glass. This paper is a description of a simple, convenient, and fairly accurate method whereby the surface tension of glasses may be compared.

The method is a variation of that commonly used in the case of liquids, in which the surface tension is calculated from the weight of a drop falling from a tube or a surface of definite size. This method was used by Quincke² for determining surface tension of easily fusible metals, and a modification of it for those having a high melting point. In the latter case, small metallic rods or wires were lowered vertically into the horizontal flame of a blast lamp. From the weight of the drop which was formed and which fell, and the diameter of the wire, the surface tension was calculated by means of the following equation,

$$W = 2\pi rT,$$

in which T is the surface tension, W is the weight of the drop, and $2r$ is the diameter of the rod. Quincke applied this method to a large number of elements and salts, and recorded one experiment with glass fibers. The method has, however, not been extensively used since it is not extremely accurate, but it is useful in instances where other methods are not applicable, especially where simple and rapid measurements are to be made.

The ability of this method to give absolute values for the surface tension is doubtful. At first sight it would appear that the weight of the drop increases until it just overcomes the upward pull of the surface tension, becomes detached and falls. If the problem were as simple as that, the equation given above would hold and the weight of the drops would be proportional to the diameter of the rod, or, in the case of liquids, to the diameter of the tube from which they fall. Tate stated³ this as a law, but Lord Rayleigh showed³ that when water is allowed to drop from various sized glass or metallic tubes, the weight of the drop increases relatively faster than the diameter of the tube up to a certain point, when the weight of the drop remains constant no matter how large the tube or surface from which it falls. Lord Rayleigh also pointed out that the weight of the drop of water is influenced by a number of factors, such as the difference in pressure within the liquid drop from the atmospheric pressure, the physical character of the surface from which the drop is suspended, and the relation of the inner to the outer diameter of the tube. It would seem, therefore, that if metallic or glass rods or fibers were used the last two factors, at least, would be eliminated.

In the experiments described in this paper the glass fibers were lowered in a vertical position with the aid of the machine shown in Fig. 1. In this figure, A is a $3/4$ -inch iron rod 30 inches long, supported by an iron plate 8 inches in diameter and $1/2$ inch thick, which is secured firmly to the table. B is a $1/2$ inch iron rod,

¹ *Pogg. Ann.*, **134**, 356 (1868); *Ibid.*, **135**, 621 (1868).

² *Phil. Mag.*, **27**, 176 (1864).

³ *Ibid.*, [5] **48**, 321.

¹ THIS JOURNAL, **3**, 476 (1911).

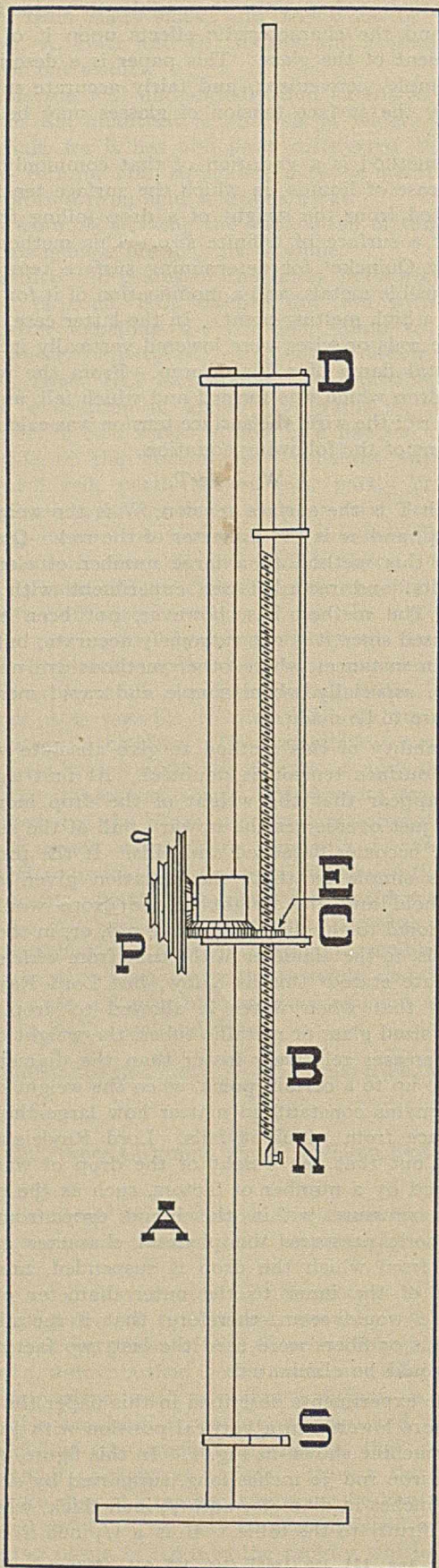


Fig. 1.

passing through the guides C and D and threaded for one-half of its length. It is raised and lowered by the threaded gear wheel E, which is actuated through gears by means of the pulley P. The lower end of B is split, forming a clamp adjusted by the milled head N. The glass fiber is held in this clamp and is kept from swinging by a loop of wire held on the stage S, which is above the blast lamp. The drops of glass were caught in a porcelain dish beneath.

Figs. 2-7 show the results obtained with a variety of silicate glasses. The approximate composition of these glasses expressed in equivalents are as follows:

- A. SiO_2 , 75.3 per cent., CaO 4.4 per cent., Na_2O 20.3 per cent.
- B. SiO_2 , 56.1 per cent., P_2O_5 3.7 per cent., BaO 10.2 per cent., CaO 17.4 per cent., Na_2O 10.7 per cent., K_2O 2.0 per cent.
- C. Composition was not definitely known, except that it contained large percentages of lead and boric oxides.
- D. SiO_2 , 80.1 per cent., BaO 4.7 per cent., Na_2O 15.2 per cent.
- E. SiO_2 , 71.4 per cent., BaO 11.4 per cent., Na_2O 17.2 per cent.
- F. A beaker of Jena laboratory glass.

In the figures given the ordinates represent the weight of the drop expressed in grams and the abscissas the diameter of the fiber in millimeters. If Tate's law were correct, a straight line would be produced, *i. e.*, the weight of the drop would be directly proportional to the diameter of the fiber. It is evident from the results obtained that this is not the case, since for larger fibers the weight of the drop is greater than this law demands. If, however, an empirical factor, proportional to the area of the cross section of the fiber, be introduced, a curve may be obtained which closely approximates the experimental results. Since this new factor is proportional to the areas of the cross section or to the square of the diameter, it is evidently due to the cohesive power which exists throughout the molten glass as distinguished from the phenomena appearing at the surface. Before the drop can fall this cohesion, in addition to the surface tension, must be overcome. The weight of the drop is therefore increasingly greater with the larger fibers. The continuous curves which are shown in the figures are calculated from the following equation,

$$W = \alpha \cdot D + \beta \cdot D^2,$$

in which W is the weight of the drop in milligrams, D is the diameter of the fiber in millimeters, and α and β are constants. This equation was derived by Quincke¹ from one given by Karmarsch and was employed for calculating the surface tension of solids. However, he did not apply it to his results with molten substances. It must be remembered that, while this equation appears to satisfy the condition for small fibers of glass, it cannot be considered to be an absolutely general equation. For, as Lord Rayleigh¹ found in the case of drops of water, there will doubtless be a limit to the size of rod, above which the drops will all be of the same size.

¹ *Loc. cit.*

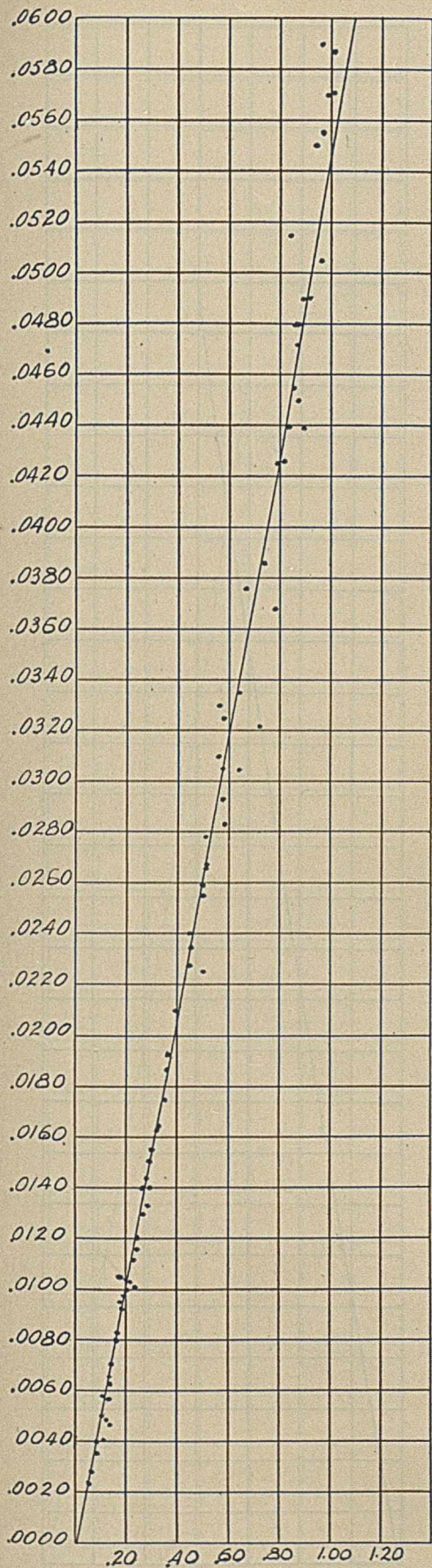


Fig. 2.

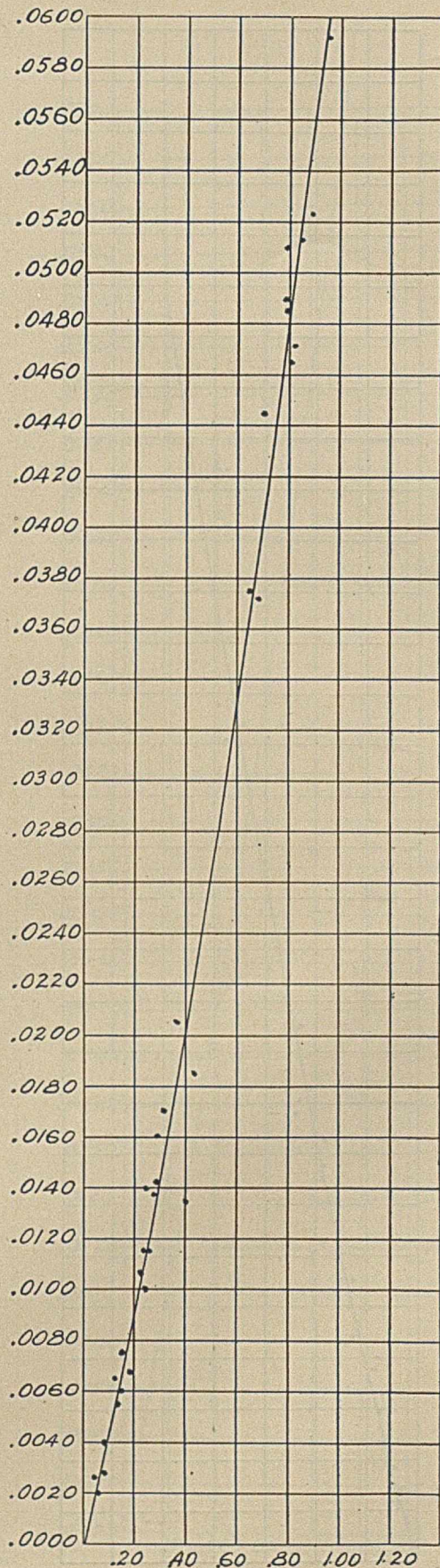


Fig. 3.

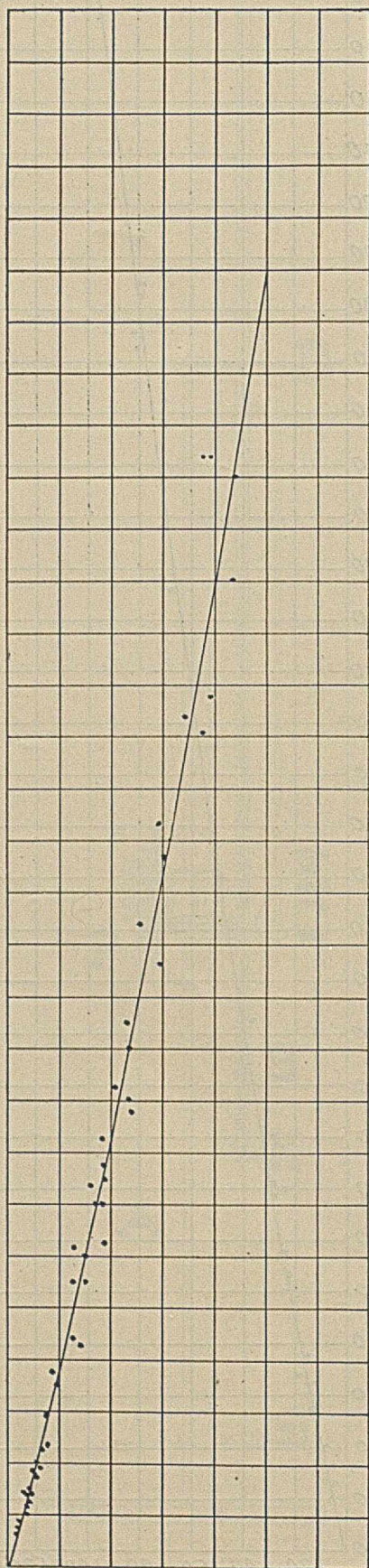


Fig. 4.

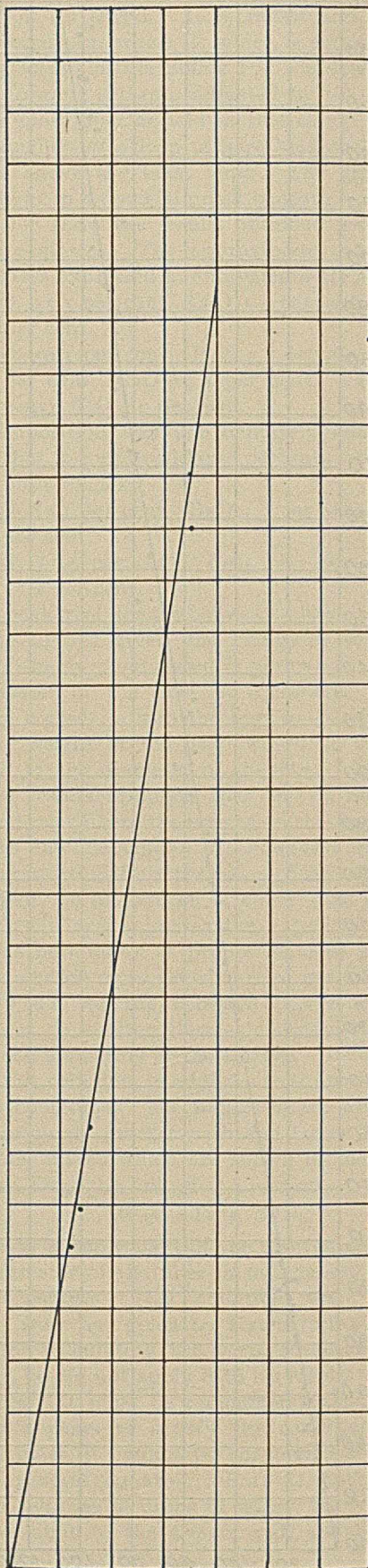


Fig. 5.

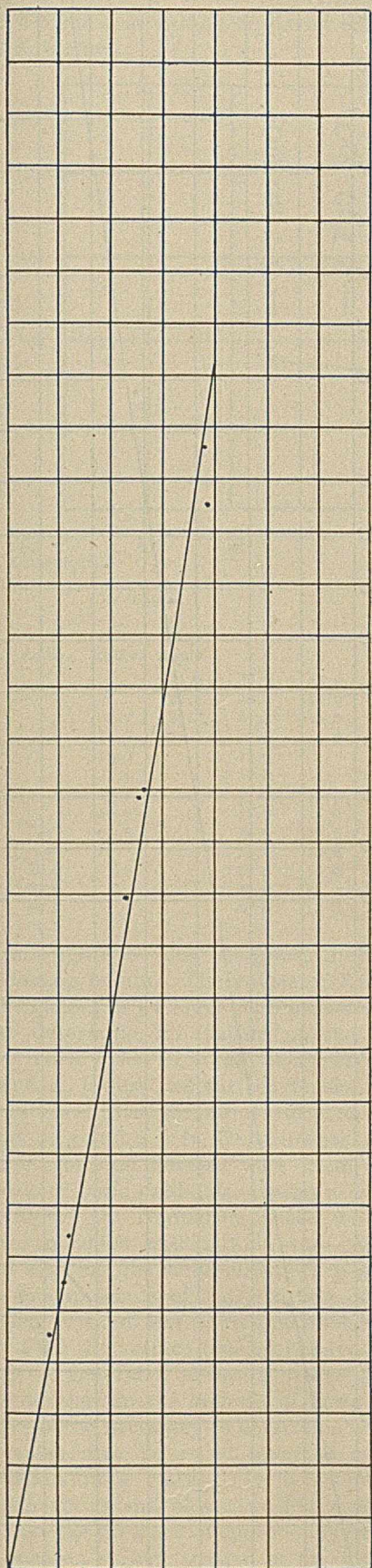


Fig. 6.

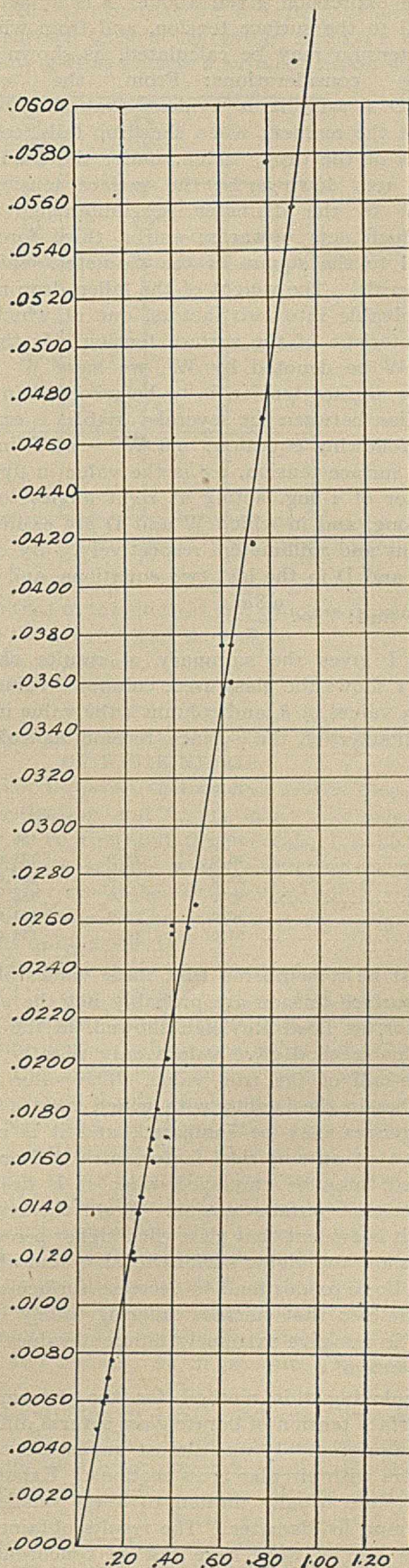


Fig. 7.

In the expression given above, α is a factor proportional to the surface tension, and from which the surface tension may be calculated, as shown by the following considerations: From the equation $W = \alpha \cdot D + \beta \cdot D^2$ it is evident that the forces in action at the moment when the drop falls, consist of the mass of the drop, which, under the influence of gravity, acts downwards; the surface tension, proportional to the diameter (circumference) of the fiber, which acts upwards; and a third force, proportional to the square of the diameter, which also acts upwards. The weight of the fallen drop is therefore resolvable into two factors, one of which, $\alpha \cdot D$, is characteristic of the surface tension. If this fraction of W be denoted by W' , we have $W' = \alpha \cdot D$. Since the surface tension is to be recorded in dynes, the relation between the several variables is expressed by the following equation: $9.8 W' = \pi D T$ in which T is the surface tension, 9.8 is the value in dynes per centimeter of 1 mg. acting at right angles to a line 1 mm. long, and in which W and D are expressed in milligrams and millimeters respectively. By eliminating W' and D in the last two equations, and solving for T we find: $T = \frac{9.8\alpha}{\pi}$.

Table I gives the summary of results obtained. Column 1 shows the glass used, column 2 values of α , column 3 values of β , and column 4 the value in dynes per centimeter of the surface tension as calculated from α .

TABLE I.

Glass.	α .	β .	T .
A.....	50.0	4.5	156.0
B.....	40.0	25.0	125.0
C.....	35.0	15.0	109.0
D.....	50.0	15.0	156.0
E.....	46.0	15.0	143.0
F.....	53.0	10.0	165.0

It must be remembered that these values obtained for the surface tension are probably not the absolute values, for, as Lord Rayleigh showed, in the case of water, this method gave values only slightly greater than one-half of the true value. The value of this method lies in the facility with which surface tension of two glasses may be compared, and it is not improbable that an empirical factor, such as Lord Rayleigh used, may be employed when it is desired to know the true surface tension. From the results of Table I, it is evident that glass with higher percentages of silica show the higher surface tension, and also that lead and boric oxides tend to decrease surface tension. It appears also that silicates differing widely in composition do not give extremely different values for the surface tension.

In employing this method for the determination of the surface tension of borate glass several difficulties were encountered. It was almost impossible to draw large fibers with circular cross sections. Experiments were therefore usually limited to fibers smaller than 0.6 of a mm. in diameter. The results obtained with the same size of fiber were not so concordant and showed in general a greater divergence from the theoretical straight line than those obtained with

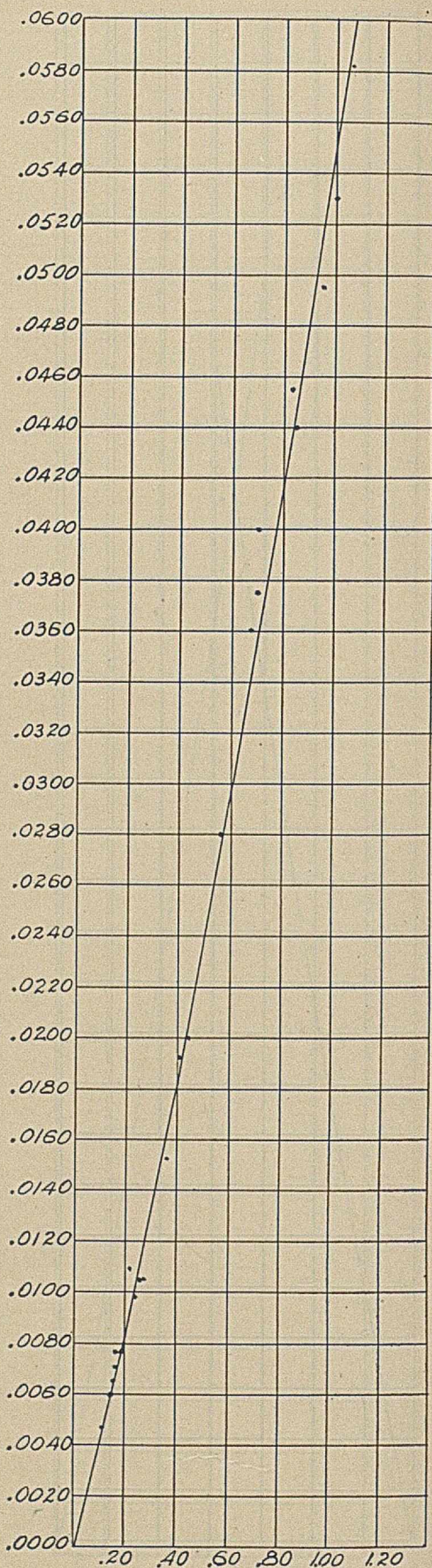


Fig. 8.

silicates. Fig. 8 shows a typical experiment. In Table II is shown the composition of glasses employed and the results obtained.

and it has been shown that for a variety of silicate glasses the surface tension lies within not very wide limits. Borate glasses possess a surface tension which

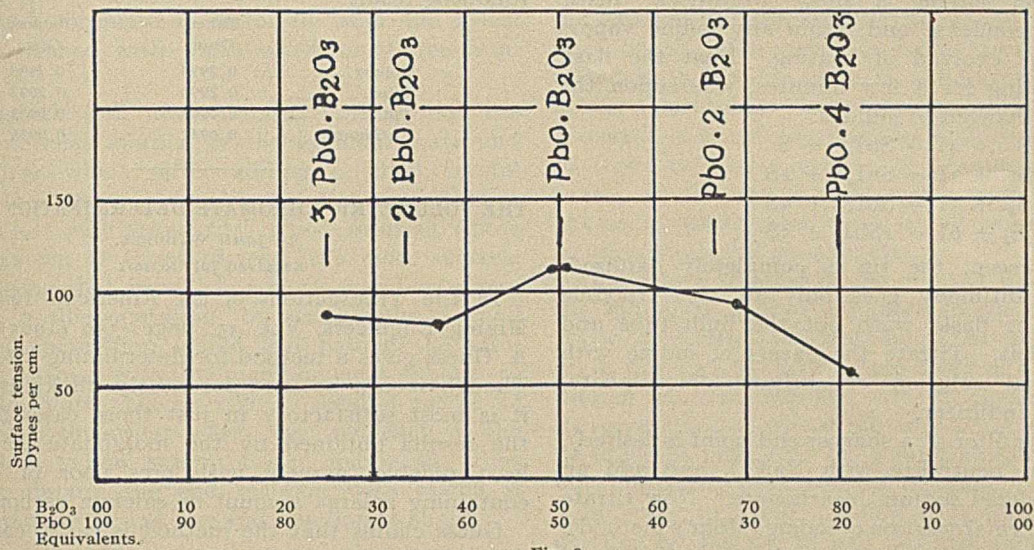


Fig. 9.

is lower than that of the silicates and which is markedly different for the several lead borates.

DEPT. INDUSTRIAL RESEARCH,
UNIVERSITY OF KANSAS.

A RAPID AND ACCURATE METHOD FOR THE ANALYSIS OF WHITE METALS.

By J. C. BENEKER, Metallurgist, Cincinnati Metal Products Company.

After investigating and trying many methods for the analysis of bearing and type metals, I have devised a composite scheme which embodies the best features of other researches and several ideas which I believe are original. The method is rapid and at the same time quite accurate.

Dissolve 1/2 gram of the fine drillings in a mixture of 25 cc. HCl + 5 cc. HNO or 25 cc. HCl saturated with liquid bromine (not bromine water), warm on the steam bath and add about one gram tartaric acid to hold up the antimony. Dilute with hot water to about 400 cc. and slowly add an excess of a solution of NaOH. Now add an excess (about 20 cc.) of a 10 per cent. solution of Na₂S. This is made by saturating half of a 10 per cent. NaOH solution with H₂S and then adding the other half. Allow to settle and filter by decantation a couple of times, using hot, dilute Na₂S solution for washing. Transfer the precipitate to the filter and wash with a hot, dilute Na₂S solution several times. The residue consists of the sulphides of Cu, Pb, Fe and Zn, while the filtrate contains Sn and Sb also As if present (Method of A. Rössing).¹

Dissolve the residue in HNO₃ and run down with H₂SO₄ for the lead. The Cu, Fe and Zn are determined as usual, the copper preferably by A. H. Low's iodometric method.² Add to the filtrate a small excess of HCl and allow to settle on the steam bath about an hour. Filter the precipitate, washing well with luke warm water to remove all H₂S. Place the paper containing the sulphides in an Erlenmeyer flask. Add a measured excess of N/10 iodine solu-

TABLE II.

No.	B ₂ O ₃ Equiv.	BaO Equiv.	PbO Equiv.	Na ₂ O Equiv.	α.	β.	T dynes per centimeter.
1.....	66.7	33.3	38.0	15.0	118.0
2.....	72.8	27.2	34.0	15.0	116.0
3.....	62.1	..	9.7	28.2	34.0	15.0	106.0
4.....	59.0	..	16.7	24.3	30.0	15.0	94.0
5.....	81.1	..	18.9	..	19.0	..	59.0
6.....	68.1	..	31.9	..	31.0	..	96.0
7.....	50.7	..	49.3	..	37.0	15.0	115.0
8.....	49.1	..	50.9	..	37.0	15.0	115.0
9.....	37.2	..	62.8	..	28.0	15.0	87.0
10.....	25.3	..	74.7	..	29.0	15.0	90.0
11.....	80.0	20.0	22.0	15.0	69.0
12.....	78.0	22.0	25.0	15.0	78.0
13.....	65.5	34.5	40.0	15.0	125.0

Although these data are not complete, they bring out some interesting points. The values of β are the same for all the glasses in which enough measurements were made to determine the nature of the curve. The addition of boric oxide to borax, as shown in Experiments 1 and 2, lowers the surface tension. The addition of lead borate has the same effect, as shown in Experiments 1, 3 and 4. In Experiments 11, 12, and 13, in which barium borates were used, an increase in amount of boric oxide also causes a decrease in surface tension. On comparing these with Experiments 5-10, in which lead borates were used, we find boric acid showing the same effect when present in more than one molecule of B₂O₃ to one of PbO. In glasses which contain less than one molecule of B₂O₃ to one of PbO the surface tension behaves irregularly, showing in general a lowering of the surface tension with a decrease in the amount of boric oxide.

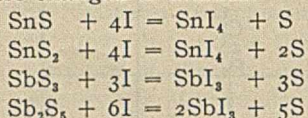
Further work will be necessary to determine whether the surface tension may be relied upon to indicate definite compounds in a glass. The series of lead borates, as given above and plotted in Fig. 9, is sufficient to show that the presence of compounds has considerable influence on surface tension of the glass.

The purpose of this paper has been to bring forward a simple and rapid method measuring the surface tension of certain high-melting substances, especially glasses. A number of experiments have been recorded

¹ Journal Society Chemical Industry, 1902, 191.

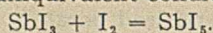
² "Technical Methods of Ore Analysis."

tion, 30-50 cc. conc. HCl, and about two grams of tartaric acid. Never omit the tartaric acid, which serves to hold the antimony in solution. Insert a rubber stopper having a small swan-neck thistle tube in it to condense and retain any iodine vapors that might be evolved in heating. Heat the flask almost to boiling for a few minutes, whereupon the sulphides are changed to iodides:

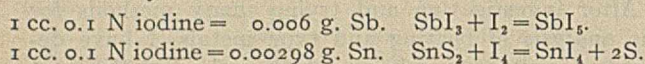


As will be seen, the tin is completely oxidized, whereas the antimony goes only to the triiodide form. Cool the flask, wash out the bulb tube and dilute somewhat. Titrate the excess of iodine with a tenth-normal solution of sodium thiosulphate, using a starch indicator.

Now wash, or filter (if a sharper end point is desired), into a beaker, neutralize with Na_2CO_3 and add an excess of powdered sodium bicarbonate. Now titrate with a tenth-normal solution of iodine (Mohr's method). In this alkaline solution the antimony triiodide is oxidized to the quinivalent condition:



From this last titration the amount of antimony present can be calculated. Multiply the volume of iodine solution used in this titration by $3/2$ and subtract this from the volume of iodine consumed in the first titration. This will give the volume of iodine consumed by the tin alone.



This method of getting the tin and antimony by the titration of the sulphides is, as far as I know, original and for it I can claim several advantages. One is that the antimony is put in just the stage of oxidation that is required for Mohr's titration. Another is that it does not matter in what condition of valency the sulphides are, even free sulphur does not interfere. This fact was ascertained by taking two samples of tin of 0.1 gram each, dissolving one in conc. HCl, forming SnCl_2 , and the other in HCl + HNO_3 , forming SnCl_4 . Analyzing as above, gave almost identical results.

The separation of the insoluble sulphides from the tin and antimony can be made almost absolute by dissolving these sulphides of Cu, Pb, Fe and Zn in hot HCl and reprecipitating by means of NaOH and Na_2S . In this manner any traces of Sb or Sn that may have been retained by the first precipitate are removed and added to the main filtrate.

To test the above method of titrating the sulphides by means of iodine, I have weighed out samples of pure tin and run them through with this method and have obtained the following close results, using the theoretical tin factor for the iodine:

Tin taken.	Tin obtained.
Gram.	Gram.
0.0664	0.0669
0.0702	0.0705
0.0923	0.0922
0.1132	0.1135

To further test the method, known amounts of pure copper, lead, tin and antimony were dissolved together and tested in the above manner with the following result:

	Taken.	Obtained.
	Gram.	Gram.
Copper.....	0.2995	0.2996
Lead.....	0.2990	0.2997
Tin.....	0.0946	0.0953
Antimony.....	0.0942	0.0936

THE VOLUMETRIC CHROMATE DETERMINATION OF LEAD.

By JOHN WADDELL.

Received July 10, 1911

In the Transactions of the American Institute of Mining Engineers, Vol. 35, page 359 (1905), Mr. H. A. Guess gives a method for determining lead in ores. Though it can be used for nearly all kinds of ores, it is most satisfactory in just those cases for which the results obtained by the molybdate method are least reliable, namely, with ores poor in lead and containing a large amount of calcium carbonate.

Guess claims that the method is easily carried out and I understand that it is employed at the Traill Smelter in British Columbia.

It does not seem, however, to have become at all general. I have not found it in any of the books on quantitative analysis nor have I seen it described in any of the chemical periodicals. Guess describes the method as follows:

"To the ore charge of from 1 to 5 grams in a 250 cc. flask add from 3 to 5 cc. of strong nitric acid and 15 cc. of strong hydrochloric acid; digest until everything is in solution and the excess of acid has been reduced to about 8 cc. The whole operation on the hot plate requires but 15 minutes. The flask is then removed, and slightly diluted ammonia is added slowly in slight excess, the neutralizing action being sufficiently vigorous to render the contents of the flask quite hot. Acetic acid of 80 per cent. strength is then added slowly, the flask being shaken vigorously until the smell indicates a decided excess of acetic acid. Then 5 cc. of strong ammonium acetate are added to insure the solution of any lead compounds remaining undissolved by the ammonium acetate already formed in the flask.

If the ore contains no antimony or separated gelatinous silica and if the siliceous residue in the bottom of the flask is only in slight amount (as is usual with heavy lime ores or with concentrates) add to the hot, undiluted and unfiltered solution an excess—about 10 cc.—of a ten per cent. potassium chromate solution. Under these conditions the bulk of the contents of the flask will not exceed 50 cc., and after shaking and letting the precipitated lead chromate settle for about five minutes the contents are filtered through an 11 cm. filter of any fairly rapid and close paper. If these directions are carried out the lead chromate will be quite granular and will show no tendency to run through. The precipitate in the flask and on the filter is washed several times with hot water containing about 0.5 per cent. of acetic acid until free from soluble chromates. The funnel

with the filter is then set over the original flask and hot, dilute hydrochloric acid (1 : 1) poured through the filter, dissolving the lead chromate. Further additions of hydrochloric acid are made if necessary and all lead chromate is dissolved from the filter; then it is washed with warm water until free from chromate.

The original flask now contains nothing but the hydrochloric acid solution of the lead chromate and the washings which, after adding a small crystal from 0.5 to 2 grams in weight of potassium iodide, is titrated direct with standard "hypo" solution whose value is known in terms of lead, the most suitable strength being that in which 1 cc. is equal to 5 mg. of lead. In this operation, by using only a small quantity of potassium iodide and having the solution fairly strong with hydrochloric acid (about 50 cc. of hydrochloric acid 1 : 1 in a total of 200 cc. of solution) and somewhat warm, any tendency of the lead to form yellow scales of lead iodide and thus somewhat obscure the end reaction with starch is completely checked and the end reaction is sharp.

The sharpness of the end point with starch, as opposed to the indistinctness of the end point in the molybdate method, is given as one of the special features.

Students working in my own and other laboratories have found difficulties with this method. Sometimes the blue color of the starch disappeared on addition of thiosulphate, only to come back in a minute or two; in other cases the precipitate of lead chromate seemed not to be washed free from soluble chromate in the course of an hour or more; sometimes even when no error was visible the results were not concordant. Owing to the difficulties experienced by my students last winter, I ran through a couple of determinations of an ore myself and obtained 23.61 per cent. and 24.10 per cent., a difference of half a per cent.

Since the method is especially interesting from an instructional point of view, I decided to investigate the points of difficulty. I may say incidentally that treatment of the ore with hydrochloric acid before the addition of nitric acid is to be recommended, since it lessens the tendency to form a globule of sulphur which may enclose some lead.

The effect of varying the strength of acid used in the titration was first tried. To about 10 cc. of a solution of chromate (9.4 grams per liter) 200 cc. of a mixture of strong hydrochloric acid and water in which the acid varied between 5 cc. and 100 cc. were added, and after addition of potassium iodide the iodine was titrated with thiosulphate. With small quantities of acid the blue color of the starch, after being first discharged, came back after a minute or two. With 5 cc. of acid the color was discharged and reproduced several times, and even with 20 cc. the color came back once. It seems that there should be at least 25 cc. of acid present.

Titration in which the chromate had been heated with acid for varying lengths of time between 60° and 80° C. showed in general partial decomposition,

though the variations were not always of the order that might be expected.

As there is evidently a time reaction between the chromate, hydrochloric acid and potassium iodide, the effect of varying amounts of iodide, up to 1 gram, were tested. The most concordant results were obtained by using one gram of iodide, and by running in the thiosulphate drop by drop, about three drops a second, 1 cc. of chromate in that case being equal to 1.968 cc. and 1.976 cc. of thiosulphate in duplicates. In this set of experiments 25 cc. of acid and 175 cc. of water were added to 15 cc. of a chromate solution measured by a pipette.

One source of error in the method was found to be the solubility of lead chromate in the 0.5 per cent. acetic acid used for washing. The addition to 50 cc. of this acid of two or three drops of a solution containing less than one per cent. of chromate rendered its solvent action almost nil, and hence the acid may be used till nearly all the soluble chromate is washed out, but finally pure water is required.

In order to avoid possible error from setting free chlorine by the use of half and half hot hydrochloric acid, I dissolved the lead chromate with a cold mixture of 25 cc. of hydrochloric acid and 75 cc. of water, washing alternately with this mixture and with cold water. From time to time 5-10 cc. of hot water were used for the more perfect dissolution of the lead chloride.

The precipitate having been all dissolved and washed into the flask as Guess describes, the liquid was made up to about 200 cc. and one gram of potassium iodide was added, followed immediately, to avoid loss of iodine, by thiosulphate from the burette at the rate of two or three drops a second. After the brown color had nearly disappeared and had given place to a dark green, starch was added and the thiosulphate run in, a few drops at a time, with vigorous shaking. When the blue color was nearly discharged I added 10 cc. of strong hydrochloric acid and heated the flask to 40° C., after which two or three drops of thiosulphate were sufficient to bring the clear green color of the chromic salt, which constitutes the end point.

The following results were obtained, using the modified method:

Twenty-five cubic centimeters of a solution of pure lead containing 0.150 gram of lead required in duplicate determinations 30.65 and 30.51 cc. of thiosulphate. A student who made a check determination used 30.50 cc. The average is 30.55 cc.; or 1 cc. thiosulphate equals 0.00491 gram lead.

A solution of ore was made, such that 25 cc. would require somewhere about 30 cc. of thiosulphate. In four determinations, the figures obtained were 28.73, 29.25, 29.25 and 29.25 cc. A student made a check determination, dissolving the lead chromate in 50 cc. of 1 : 1 cold hydrochloric acid and using half a gram of chromate. He required 29.04 and 28.97 cc. of thiosulphate.

Afterwards I made four determinations, taking half a gram of ore and required 28.30, 28.40, 28.28

and 28.30 cc. of thiosulphate. The lowest and highest figures give respectively 27.76 and 27.88 per cent. of lead.

The difference between the Guess method of solution of lead chromate and the one which I adopted was tested by sprinkling basic lead chromate upon two filters and dissolving one quantity with nearly boiling 1 : 1 acid and the other in the manner I have described. In the first case 1 cc. thiosulphate = 0.01516 gram chromate; in the second 1 cc. thiosulphate = 0.01446 gram chromate.

Assuming that the second determination was correct, the 0.4336 gram of chromate used in the first case should have required 29.99 cc. of thiosulphate instead of 28.60 cc., which was actually used. With starch iodide paper, chlorine can be readily detected when hot 1 : 1 hydrochloric acid is put upon lead chromate.

In the presence of large quantities of iron, say 20 per cent., the tendency to form basic acetate gives difficulty in dissolving the lead. Of course, any ferric acetate precipitated along with lead chromate is fatal. Guess points out that the presence of antimony, bismuth, silver or gelatinous silica interferes with the process, but says that if the lead is first changed to sulphate and, after separation from the soluble sulphates, dissolved in ammonium acetate as for the molybdate determination, the rest of the process may be carried out as before. In this case the only advantage in the chromate method is its delicacy; it takes a longer time, but duplicate determinations should check within a tenth of one per cent., and often do check within two or three hundredths.

I wish to acknowledge help given by several students, particularly by Mr. H. Bradley and Mr. W. Agassiz.

SCHOOL OF MINING,
KINGSTON, ONT.

NOTES ON THE DETERMINATION OF ACIDS IN SUGAR CANE JUICE.

By P. A. YODER.

Received May 22, 1911.¹

In a previous report² reference was made to an investigation of the acid constituents in sugar cane juice and its products, which I commenced at the Louisiana Sugar Experiment Station, and I mentioned some of the analytical difficulties encountered in determining certain of these constituents, reporting in detail the development and application of a polariscopic method for the determination of malic acid (and incidentally also of tartaric acid). While work upon the general problem of the acid constituents was interrupted before it was sufficiently rounded off to admit of a report being made on the subject as a whole, yet, besides the work on malic acid already reported, there are other results among those thus far obtained, both on analytical methods and in the

examination of cane products, which I deem should be made available to others who may be working on the same or on similar problems. I shall present, therefore, in the following some notes on analytical operations and some determinations and approximate estimations of acid constituents in the cane juice, without presuming in this to report a satisfactory scheme of analysis or the results of ultimate determinations of all the acids present.

In the early stages of the work, after finding the usual methods of determining and identifying commonly occurring organic acids not to work satisfactorily, a number of other methods described in textbooks and the periodical literature and modifications and combinations of these methods were tried. In these preliminary tests of methods, I was assisted by Mr. W. G. Taggart, assistant chemist, who, under my direction, applied them variously—to cane juice, to solutions of molasses or molasses and sugar, to such solutions with added known amounts of certain acids, to solution of definite quantities of sucrose, dextrose, and levulose with or without additions of the acids in question, and to solutions of one or more of the acids alone in water.¹

With the exception of a method of Behr² for the separation of the aconitic acid as its acid ammonium salt, practically all the methods described in the literature which we tried were worked out by their authors primarily for the analysis of wines and other fermentation products and fruit juices, and none of them take into consideration the possible presence of

¹ Among the methods receiving special consideration in our experiments are the following:

1. The method of G. Jörgensen (*Z. Unters. Nahr.-Genusssm.*, **13**, 241-257 (1907); *Chem. Abstr.*, **1**, 1448-52 (1907)), for tartaric, succinic, citric, and malic acids, in which, after separating the acids from some of the other matters by means of the lead salt, the tartaric acid is separated as the acid potassium tartrate, the succinic then shaken out with ether and subsequently the citric and the malic acids converted to the barium salts and their separation effected by a procedure based on a difference in their solubility in 50 per cent. alcohol.

2. The method of R. Kunz (*Z. Unters. Nahr.-Genusssm.*, **6**, 721 (1903); **12**, 641-5 (1906); *Chem. Zentr.*, **II**, 854 (1903); **I**, 418 (1907)), for the succinic acid, involving the extraction with ether by an extraction apparatus according to Schacherl, and the subsequent oxidation by potassium permanganate of other acids than succinic.

3. The method of Möslinger (*Z. Unters. Nahr.-Genusssm.*, **4**, 1120-30 (1901); *Chem. Zentr.*, **I**, 231 (1902); **II**, 1386 (1903)), for lactic acid, in which its separation from malic and tartaric acids is based upon the solubility of its barium salt in 75 per cent. alcohol.

4. The method of C. Schmidt and C. Heipe (*Z. anal. Chem.*, **21**, 534 (1882)), for tartaric, succinic, and malic acids, making use of the calcium salts to separate the tartaric acid from the others, and of the barium salts to separate the succinic from the malic acids. Also a modification of this method ("Official and Provisional Methods of Analysis," U. S. Dept. of Agriculture, Bureau of Chemistry, *Bull.* **107** (revised), p. 80) in which succinic acid is disregarded and citric acid is separated from the malic acid by heating the water solution of the calcium salts of the two.

5. The method of F. Mutlet (*Annales des Falsifications*, **2**, 383-6), for tartaric, citric and malic acids, in which the tartaric acid is separated as the acid potassium salt and the other two are separated from each other as the barium salts, by a half volume of alcohol.

6. The method for tartaric acid by J. von Ferentzy (*Chem. Ztg.*, **31**, 1118 (1907)), as applied by L. Gowing-Scopes (*Analyst*, **33**, 315-9 (1908)), in which the tartaric acid is precipitated as a basic salt by the magnesium mixture and thus separated from the malic or succinic acids.

7. The method for separating aconitic acid by A. Behr (*Ber. d. chem. Ges.*, **10**, 351 (1877)), in which the acids are first separated in a free state by means of the lead salts and hydrogen sulphide, then the acid ammonium aconitate formed, which proved to be a suitable compound for its further purification, liberating the acid finally with sulphuric acid and shaking out with ether.

¹ This paper is an abridgement of a paper by the author on the same subject presented at the 42nd General Meeting of the American Chemical Society, July 12, 1910.

² THIS JOURNAL, **3**, 563-574 (1911).

² Loc. cit.

aconitic acid. The aconitic acid, however, has been found present in cane juice and its products by Behr,¹ in sugar beet products by v. Lippmann,² and in sorghum by Parsons.³ My own investigations, as will be shown further on, proved this acid to be not only present in Louisiana cane juice and molasses, but to be the predominating one of the acids. As aconitic acid and its salts are, in most of their properties which are involved in the analytical operations, very similar to some of the other acids commonly occurring in plant juices, its presence in the cane products especially complicates the problem of determining which of the other acids are present and in what quantities. The methods available, even in the absence of aconitic acid, are sadly deficient as means of sharp-cut separations. These circumstances led me to make many preliminary experiments on the properties of some of the salts, and the behavior of the acids under various possible treatments for their separation. The results from some of these lines of preliminary experiments are submitted in the following:

I. SOME RESULTS FROM PRELIMINARY TESTS.

1. *Extractibility of the Free Acids with Ether.*—In the method of Jørgensen⁴ in its original form, which method first of all I attempted to apply, we are directed to shake out with ether, repeating two or three times. This proved to be insufficient to extract even 90 per cent. of the succinic acid, as may also be calculated from theoretical grounds, basing the calculations on the relative solubilities of the acid in water and ether. By trial with a solution of succinic acid, making three extractions with equal volumes of ether each time, we recovered less than half the acid. More recently Jørgensen has published a modification of his method⁴ in which he requires more thorough extraction. As aconitic acid is also readily extracted with ether, it is evident that with the cane products it would not suffice simply to titrate this extract with a standard alkali to determine the succinic acid in it. Kunz⁵ offers a procedure with the ether extract to get the true amount of succinic acid, involving the oxidation of the acids other than succinic acid with potassium permanganate in an acid solution, then precipitating the succinic acid with standard silver nitrate solution and titrating back the excess of silver nitrate. He also suggests a more satisfactory way of extracting the solution with ether, using a form of what some German writers⁶ have chosen to call "perforation apparatus." Kunz used the Schacherl⁶ apparatus. Not having this apparatus on hand, I improvised a substitute which was more efficient and at the same time very simple in construction, using it on an ordinary ether extraction flask, and with a tin spiral condenser (see Fig. 1).

The tube *B* to hold the liquid to be extracted may

be chosen of a size to suit the volume, increasing also the size of the outside tube *A*, if necessary. Tube *A* has three indentations around the conical part at the bottom to prevent tube *B* from sealing off the communication with the ether flask below. To avoid too rapid a delivery of ether while filling or under irregular returning from the condenser, so as to cause some of the water solution to be carried over, the openings

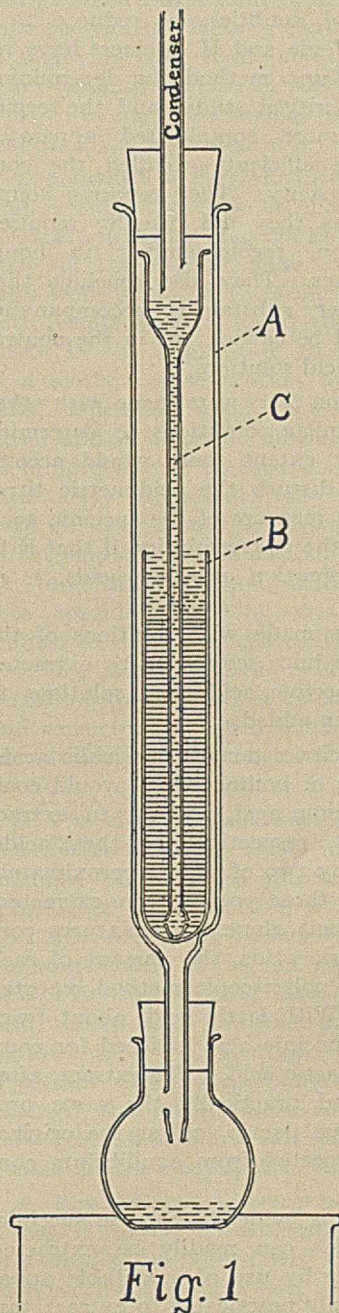


Fig. 1



Fig. 2

at the bottom of the delivery tube *C* should be suitably constricted. Evidently a similar apparatus could be used for extraction (or "perforation") with a heavier liquid like chloroform. For *B* we could substitute one like that represented in Fig. 2 and tube *C* can be omitted or else shortened and suspended with its lower end at the surface of the liquid in *B*. The

¹ *Loc. cit.*

² *Ber. d. chem. Ges.*, **12**, 1649 (1879).

³ *Am. Chem. J.*, **4**, 39; *Ber. d. chem. Ges.*, **15**, 1763 (1882).

⁴ *Z. Unters. Nahr.-Genussm.*, **17**, 396 (1909). *Chem. Abstr.*, **3**, 1781 (1909).

⁵ C. v. d. Heide and H. Steiner, *Z. Unters. Nahr.-Genussm.*, **4**, 114-6 (1902).

⁶ *Ibid.*, **4**, 174-6 (1902).

solutions with which I had occasion to deal showed little or no tendency to emulsify, therefore I could hurry the extraction as much as the efficiency of my condenser allowed. A tin spiral condenser with an inside diameter of only $\frac{1}{4}$ inch proved too small for the return flow during rapid boiling, yet even with such and with the cooling water at 20 to 23°, 10 hours sufficed to extract practically all the succinic acid. With $\frac{3}{8}$ -inch tin tubes for condensers to this apparatus, the time could doubtless be reduced to 5 or 6 hours. C. v. d. Heide and H. Steiner¹ have recently subjected the Kunz method for determining the succinic acid to a critical study, and the former of these describes a more complicated apparatus which should be more efficient provided the condenser has sufficient capacity. They report 9 hours, when boiling as fast as they did, usually required for complete extraction, recommending 12 hours for certainty in all cases. They also conclude that the oxidation of other substances accompanying the succinic acid should be carried out in the neutral solution instead of the acid solution.

A number of extraction tests were made with other organic acids under similar conditions to determine approximately to what extent these would accompany succinic acid, to disturb the acidimetric titration of the extract as a measure of the succinic acid, or to occasion losses in the water solution if that is to be used for the determination of other acids, *e. g.*, citric and malic.

Aconitic acid in tests made with solutions of the acids derived from cane juice seemed to be extracted about as rapidly as succinic acid from solutions to which the latter had been added.

In tests with 0.1 *N* citric, tartaric, or malic acids, the same rate and time of boiling which would completely extract the succinic acid, sufficed to extract 37, 23 and 53 per cent., respectively, of these acids, and with mixtures of any two of these approximately the same proportions of those present were extracted, as when each was present alone. In mixtures containing malic and tartaric acids, the amount of each was determined by the polariscopic method reported in a previous paper.² With lactic acid, about twice the time required for succinic acid sufficed for complete extraction of the lactic acid. The extract, after dissolving in water, had practically the same proportion of lactid to actual lactic acid as the original solution, as may be expected from equilibrium considerations.

From the foregoing it is evident that the succinic, aconitic, and lactic acids can readily be extracted quantitatively with ether by use of a suitable apparatus, but that it is hardly practicable to extract tartaric, citric, or malic acids quantitatively from their solutions in water. The tests show, also, that the first three acids, if extracted from a solution containing also one or more of the last three, will not thereby be separated free of the last three, and that the residual water solution will not contain the total

of the last three. The separation may, of course, be accomplished more nearly quantitatively by redissolving the ether extract in water and reextracting, and repeating this as often as necessary to attain the degree of accuracy desired.

2. *Solubility or Precipitability of the Acids as Calcium Salts.*—In the first series of tests under this heading, the salts were formed by the addition of calcium acetate in excess to solutions of the free acids. In these, of course, acetic acid is a by-product. In later tests with a few of the acids, the salts were formed by the addition of milk of lime and lime water to the acid, in some cases just to neutrality and in others in excess. In the first series only broad approximations were aimed at, no very definite conditions as to temperature, agitation, and time of standing being maintained. The results from either series have no value as accurate physical constants, but can serve the purpose of suggesting methods for the separation of the acids, allowing, of course, also for the possible modifying influence of other substances present in natural products upon the solubility of these salts. The tests were made by trying different concentrations until a strength of the acid was reached which would just suffice to call forth a precipitate with the excess of calcium acetate, or calcium acetate and 95 per cent. alcohol sufficient to make it 50 per cent. alcohol or 85 per cent. alcohol. Unless otherwise stated, the results given in the accompanying table represent upper limits in strength (in grams per 100 cc. before the addition of alcohol) which do not suffice to give precipitates immediately or very soon, and without rubbing the sides of the tube or inoculating with crystals of the same salts.¹

TABLE I.—UPPER LIMITS, IN GRAMS ACID IN 100 CC. WATER WITH EXCESS OF CALCIUM ACETATE, WHICH DOES NOT CAUSE A PRECIPITATE.

Acids used.	In water alone.	With addition of alcohol to 50 per cent.	With addition of alcohol to 85 per cent.
Tartaric acid	Less than 0.1 if stirred for some time	0.13 for immediate precipitation	0.01
Citric acid	More than 0.32 if cold Less than 0.32 if hot	0.08	0.008
Aconitic acid	More than 5.00 cold or hot ²		
Malic acid	More than 5.00	0.14, less if heated	0.0025
Succinic acid	More than 5.00	0.88	0.03
		2.5, but after starting much ppt. formed	0.05

Calcium acetate alone in water solution, if too concentrated, will gelatinize or form a jelly-like precipitate on addition of alcohol. Between 5 and 6 $\frac{2}{3}$ per cent. was found to be the upper limit in concentration of the water solution which will not give a precipitate when 95 per cent. alcohol is added until an alcoholic concentration of 85 volume per cent. is reached.

In a series of tests in which the calcium salts of citric, aconitic, and malic acids were formed by the addition of calcium hydroxide to the free acid, and

¹ The supply of alcohol from which I used was later discovered to have a considerable acidity, due to volatile acids, which may have exerted some influence in keeping more of the salts in solution.

² See, however, the discussion of aconitic acid below for the behavior of its calcium salt in a neutral solution when heated.

¹ *Z. Unters. Nahr.-Genussm.*, 17, 291–307, 315–320 (1909).

² *THIS JOURNAL*, 3, 563–574 (1911).

in which the alcohol used was absolute alcohol, results were obtained differing in some particulars from those given above, and showing also, in the cases tried, a marked difference in the solubility of the salt in a solution exactly neutral (to phenolphthalein) and one having an excess of calcium hydroxide.

With tartaric acid: The concentration in a neutral water solution which, without addition of alcohol, fails to give a precipitate within 20 hours, lies between 0.025 and 0.05 per cent. With the addition of an equal volume of alcohol, the limit is between 0.025 and 0.033 per cent. for immediate precipitation and between 0.0033 and 0.0045 per cent. for precipitation on standing 20 hours. The mother liquor, from which calcium tartrate was precipitated by addition of an equal volume of alcohol and standing 20 hours, contained in two trials the equivalent of 0.0021 per cent. and 0.0030 per cent., respectively, of tartaric acid, computed on the volume of water exclusive of the alcohol.

With citric acid: The limit in water solution with calcium hydroxide to exact neutrality was about 1.42 per cent. in the cold and between 0.25 and 0.3 per cent. in the boiling hot solution, and in each case it was less with an excess of calcium hydroxide.

With aconitic acid: A 10 per cent. solution of the acid in water, neutralized with dry calcium hydroxide, was insufficient to give a precipitate in the cold. Heated to boiling, a 1 per cent. solution, calculated as free acid, sufficed to call forth a precipitate of the calcium salt. In other experiments it developed that the water adhering to the precipitate of (impure) calcium aconitate, on decanting from the precipitate formed on boiling, sufficed to dissolve the precipitate on cooling.

With malic acid: 0.25 per cent. of the acid, exactly neutralized with calcium hydroxide, just sufficed to bring forth a precipitate upon addition of an equal volume of absolute alcohol. With an excess of calcium hydroxide, considerably less sufficed.

With lactic acid: A 10 per cent. solution, neutralized with calcium hydroxide, did not give a precipitate, even when an equal volume or when 8 volumes of absolute alcohol were added.

From the foregoing notes on aconitic acid, we can correct the impression that is current and is frequently reproduced in text-books,¹ that the citric acid is the only one of the natural organic plant acids whose calcium salt is less soluble in hot than in cold water. The difference between the solubility of the calcium salt in cold and in hot water is in fact greater in the case of the aconitic acid than in the case of the citric acid.

With lactic acid: A solution of the acid, neu-

tralized with calcium hydroxide and made up to a 15 per cent. solution, gave no precipitate when an equal volume of 95 per cent. alcohol nor any immediate precipitate when 14 volumes of 95 per cent. alcohol were added.

The solubility of the malate of lime in 50 per cent. alcohol is so much greater than that of the lime salts of the other acids mentioned, excepting lactic acid, and so much less soluble in 85 or 90 per cent. alcohol than the calcium lactate, that this affords us a means of removing from malic acid the main bulk of these other acids, if present in sufficient quantity to interfere with my polariscopic method for estimating malic acid, as suggested in my report on that method.²

3. *Solubility or Precipitability of the Acids as Barium Salts.*—The properties of the barium salts of these acids are in many respects known to be analogous to those of the calcium salts. With lactic acid direct tests were made on the solubility of the barium salt with results same as noted above for the calcium lactate. In the application to the acids of cane juice of a method of separation by means of the barium salts, depending upon their different solubilities in water and in alcoholic mixtures of different strength, as in Jørgensen's³ method above referred to, the aconitic acid, if present, may be precipitated partly with citric acid and partly with malic acid. Thus in an attempted determination of the cane juice acids by Jørgensen's method, before this fact was taken into consideration, we obtained results indicating from 0 to 0.033 per cent. citric acid and from 0.059 to 0.094 per cent. malic acid from the same sample, according to the number of times we would redissolve and reprecipitate, when in fact, as afterward proved, the sample had but traces or none of these two acids present.

4. *The Acid Ammonium Salts of Aconitic, Citric, and Succinic Acids.*—Behr⁴ made use of an acid ammonium salt for the purification of aconitic acid, forming it by saturating a portion of the aconitic acid with ammonia, boiling to drive off the excess of ammonia, then adding an equal amount of the free acid. In my work on cane juice acids this method also served this purpose admirably. However, in parallel tests with solutions of succinic acid (which, if present, might accompany aconitic acid in an ether extract) the results were so nearly analogous that this acid ammonium salt could hardly serve as a means for the quantitative separation of these two.

5. *Von Stahre's⁵ Pentabrom Acetone Reaction and Denige's⁵ Acetone Dicarboxylic Acid Reaction as Means of Detecting and Identifying Citric Acid.*—The former of these reactions did not, in our hands, prove a very delicate test for citric acid. The latter reaction, however, is very delicate. Denige's reagent is 5 g. mercuric oxide in 20 cc. concentrated sulphuric acid and 100 cc. water. To 4-5 cc. of the solution (which

¹ Fresenius, "Anleitung zur qualitativen chemischen Analyse," 16th Ed., p. 437; Allen, "Commercial Organic Analysis," 3rd Ed., Vol. I, p. 530. (Into the latter treatise has crept the misleading statement: "Aconitate of calcium, $\text{Ca}_3(\text{C}_6\text{H}_3\text{O}_6)_2 + \text{H}_2\text{O}$, forms small crystals which require 100 parts of cold water for solution, but are much more soluble in boiling water. Hence aconitic acid gives no precipitate with lime water either in the cold or on boiling, a behavior which distinguishes it from citric acid." The latter statement may be true for so dilute a solution as lime water, but could not be said to apply to a much stronger solution, such as might be obtained by adding milk of lime to aconitic acid.)

² THIS JOURNAL, 3, 563-574 (1911).

³ Z. Unters. Nahr.-Genussm., 13, 241-257 (1907); Chem. Abstr., 1, 1448-52 (1907).

⁴ Ber. d. chem. Ges., 10, 351 (1877).

⁵ Chem. Zentr., II, 418 (1895).

⁶ J. Soc. Chem. Ind., 1898, 802; Chem. Zentr., II, 134 (1898).

should be very dilute in citric acid) is added 1 cc. of Denige's reagent and heated to boiling, then 5 to 6 drops of a 2 per cent. potassium permanganate solution are added. With citric acid in quantities down to mere traces, the first drop of potassium permanganate solution would always call forth a cloudiness due to a very finely divided, readily subsiding precipitate. The test was tried upon the following other substances: aspartic, malic, oxalic, tartaric, lactic, glycolic, fumaric, and succinic acids, and upon pure sucrose. None of these gave a reaction likely to be mistaken for that from citric acid. Oxalic acid gave a white precipitate with the mercury reagent alone, but when this was filtered off, and the potassium permanganate added to the filtrate, no additional precipitate was formed. The test revealed citric acid also in the presence of any of these substances.

When, however, the test was applied to a sample of aconitic acid, which we had on hand, it gave apparently the same reaction as citric acid, differing only in that it was usually not until the second or third drop of potassium permanganate solution was added that the fine pulverulent precipitate formed. Another preparation of aconitic acid, supplied by Messrs. Eimer and Amend, likewise gave the reaction. Whether this was due to contaminations with citric acid, from which the aconitic acid was presumably prepared, remains undetermined. Considering, however, the close relation in constitution, of the aconitic to the citric acid, on the one hand, and to the acetone dicarboxylic acid on the other, I think there is but little doubt that the aconitic acid itself is capable of giving this reaction. We may likewise expect the tricarballic acid to give this reaction. Since aconitic acid and possibly also tricarballic acid are present in the cane juice, the fact that we got the reaction in cane juice with Denige's reagent does not prove either the presence or the absence of citric acid. The fact that here also not the first drop of potassium permanganate called forth the precipitate is some evidence that it is not present.

II. EXAMINATION OF SAMPLES OF CANE JUICE.

From the many samples of juice, molasses, and unrefined sugars examined by one or another course of procedure, I shall here report merely a few of the more definite or conclusive findings from one of the samples, with a few references to results from other samples for comparison.

The sample consisted of 6 liters of juice pressed from cane harvested at the beginning of the season, about Oct. 1, a mixture of the four varieties, D74, D95, La. Purple, and La. Striped.

The initial operations were as follows: The juice was neutralized with sodium hydroxide, precipitated with neutral lead acetate and an equal volume of 95 per cent. alcohol, filtered next day and the precipitate washed with 50 per cent. alcohol, then suspended in hot water, decomposed with hydrogen sulphide, filtered, and the filtrate concentrated upon the water-bath to a small volume. A small portion of this was titrated with normal potassium hydroxide. It indicated acidity in the total residue equivalent to 125.1

cc. normal acid. The titrated portion was united with the rest, the whole diluted with water and precipitated with an excess of calcium acetate and alcohol to an alcohol concentration of 85 per cent. After standing a day it was filtered. The precipitate of calcium salts was treated three times with water, twice with 200 cc. and once with 50 cc. The water solutions were each treated first with alcohol to 50 per cent., filtering after one or more days, then the filtrates further treated with alcohol to 85 per cent., filtering after one or more days. The insoluble residue (which I shall designate A), the precipitates from 50 per cent. alcohol (B, B', and B''), and those from 85 per cent. alcohol (C, C', and C'') were each investigated further by a different course of procedure. Many different operations were applied to these residues and products from them, some of which will be mentioned in the following paragraphs in connection with individual acids reported upon.

1. *Oxalic Acid.*—This acid, if present, should have been in the residue A, of calcium salts which failed to dissolve in water. This residue was treated with acetic acid; the portion not dissolved in acetic acid was dissolved in hydrochloric acid, then reprecipitated with ammonium hydroxide and calcium acetate, acidifying again with acetic acid. A small precipitate was hereby obtained, equivalent to 0.0027 gram oxalic acid. With manganese dioxide and sulphuric acid this residue evolved carbon dioxide, thus verifying the conclusion that it is an oxalate.

2. *Phosphoric Acid.*—This made its appearance in three different residues, two of them from residue A above, which had failed to dissolve in water, and one from a combination of B and B' precipitates from 50 per cent. alcohol. Residue A was treated with acetic acid, the solution in acetic acid was treated with alcohol to 50 per cent., and both precipitate and filtrate examined for phosphoric acid. The precipitate had 0.1586 gram, computed as P₂O₅. The acidified alcoholic filtrate, after conversion by means of potassium carbonate to the potassium salts and examining for tartaric acid, proved to contain 0.0241 gram phosphoric acid as P₂O₅. From the residue B and B', obtained by dissolving in water and reprecipitating from 50 per cent. alcohol, I separated 0.0060 gram as P₂O₅. Thus a total of 0.1887 g. phosphoric acid as P₂O₅ was found.

3. *Sulphuric Acid.*—No effort was made to trace this out quantitatively in all the residues in which it might occur, *viz.*, A, B, B' and B''. In a product from C', the precipitate from 85 per cent. alcohol, I also found a trace of sulphuric acid. From residues B and B', after further operations that might have occasioned small losses, I found 0.0305 g. sulphuric acid as SO₃.

4. *Tartaric Acid.*—The calcium tartrate, if present in large quantity, should have appeared in A; or if present in small quantity, it should have appeared only in residues B, B', and B'', or possibly in small traces in residues C, C', and C''. Products from A, B, and B', tested in small volume for tartaric acid by conversion to the acid potassium salt, gave nega-

tive results, hence tartaric acid cannot be present in more than mere traces. In other more direct tests made upon cane syrup it also proved to be absent there, in that the acids from 100 grams syrup, separated by use of the lead salts, gave no precipitate from 50 cc. solution in water after neutralizing with calcium hydroxide. This was further verified by the polariscopic method with the uranium compound, in that the uranium produced little or no change in the optical activity.

5. *Malic Acid*.—This, if present, should have appeared in residues C, C', and C'', precipitated from the 85 per cent. alcohol, but principally in C. From this residue the acids were set free by converting them into the lead salts and decomposing the lead salts with hydrogen sulphide as in the initial operations with this sample of juice. The acids thus liberated were examined by the polariscopic method with the uranium salt¹ and showed a mere trace of malic acid present, *viz.*, 0.0170 gram. C' and C'' similarly yielded 0.0101 and 0.0040 gram, respectively. From B and B' combined, there were recovered additional traces, 0.0095 and 0.0054 gram. The total in these five portions is 0.0461 gram. Tests with cane syrup, as stated in the former report, gave results indicating about 0.01 to 0.03 per cent. malic acid in the syrup.

6. *Succinic Acid*.—This should be found principally in residue B, B' and B''. B and B', combined and dissolved in water, was divided into two portions. The first portion of $\frac{1}{3}$ was acidified and extracted with ether by use of the apparatus previously described. In the first five hours, with slow boiling, 0.7438 gram was extracted; in the next 15 hours, 0.1489; and in the next 12 hours, 0.0212 gram. Each residue was dissolved in 25 cc. ether and $\frac{1}{3}$ of each taken. These portions were combined, the ether evaporated, the residues dissolved in water, acidified with sulphuric acid, oxidized with an excess of potassium permanganate, again extracted, the extract residue neutralized and tested with silver nitrate according to Kunz.² It gave no precipitate, hence there was no succinic acid present. The other $\frac{2}{3}$ of the above extracts, after first separating the main bulk of the aconitic acid by heating the solution of the calcium salts, was also tested by Kunz's method for succinic acid and none found.

7. *Aconitic Acid*.—This acid should be mainly in residues B, B', and B'' with smaller amounts also in C, C', and C''. Being readily soluble in ether when free, it should appear along with succinic acid, if the latter were present, in the ether extracts. By conversion of a portion of these residues into the acid-ammonium salt, the crystallization took place so readily and so completely as to make it evident that it was almost pure aconitic acid. The first crystals of brownish color were recrystallized several times from 50 per cent. alcohol to purify a portion, then, when quite colorless, were decomposed with sulphuric acid, extracted with ether, and a melting point determination made. The purified specimen melted at

183–184°, commencing to decompose at the same time. Because of incipient decomposition, and possibly incomplete purification of so small a sample, the melting point was not very sharp, but was near enough to that found by Behr, *viz.*, 187–188°, that this taken in connection with the other properties makes the conclusion that it is aconitic acid a safe one. The first and second residues, mentioned in the preceding paragraphs on succinic acid, extracted by ether from $\frac{1}{3}$ of the solution from B and B' combined, proved on titration to have total acids equivalent to 14 cc. normal acid, which, computed as aconitic acid, amounts to 0.8123 gram (out of 0.8027 gram air-dried residue) or for the total from residues B and B', 2.437 g. No further tests were made to determine the degree of purity of the aconitic acid in these extracts than the indications furnished by the crystallization of the acid ammonium salt above referred to, nor were the smaller residues B'', C, C', and C'' further examined for aconitic acid. Each of these was, in all probability, mainly aconitic acid, except for the small traces of malic acid found in C, C', and C''. Acidimetric titrations of the several acid residues examined from malic acid showed a total acidity, not accounted for as malic acid, equivalent to 0.625 gram aconitic acid, computed upon the whole of the sample. The indications from all these crude acid residues point to about 3 grams, or 0.05 per cent., as the total of aconitic acid in the sample.

In another sample of 5 liters of juice from the same cane, the acids were similarly separated in the free state by means of the lead salts. This acid residue was subjected to ether extraction more directly than was the case in the sample above reported. The total extraction residues after the evaporation of the ether were 2.1542 grams from the first 9 hours, 0.4082 gram from the next 11 hours, and 0.0785 gram from the next 6 hours, a total of 2.6409 grams, or 0.05 per cent. These residues gave the same evidence of being almost wholly aconitic acid, when a pure specimen was prepared from them by means of the acid ammonium salt. The indication as to quantity of aconitic acid in the juice is therefore about the same in this as in the other sample.

8. *Citric Acid*.—This acid, if present, should have appeared in residues B, B', and B'', precipitated as calcium salts from 50 per cent. alcohol. Some products from B and B' which should have contained accumulations of citric acid, if present, could not be made to yield the characteristic crystals of the barium salt. From a new sample of 200 grams cane syrup the acids were separated by means of the lead salts and hydrogen sulphide as in this sample. The acids were converted to the calcium salts, and the solution treated with an equal volume of alcohol. The precipitate thus formed, dissolved in 450 cc. cold water, was heated to boiling and filtered hot. The precipitate thus separated was converted to the barium salt, but did not yield the characteristic barium citrate crystals. I conclude that the citric acid is not present in the juice nor in the syrup used in these tests.

¹ THIS JOURNAL, 3, 563–574 (1911).

² *Loc. cit.*

TABLE II.—SUMMARY OF CONCLUSIONS ON ACIDS IN CANE JUICE ANALYZED.

Names of acids.	Amount from	Gram acid per 100 cc. juice.
	the 6 liters of juice. Grams.	
Sulphuric acid (as SO ₂), total not determined.....	0.0305	0.00051
Phosphoric acid (as P ₂ O ₅).....	0.1887	0.00314
Oxalic acid.....	0.0027	0.00004
Tartaric acid.....	none	none
Malic acid.....	0.0461	0.00077
Succinic acid.....	none	none
Aconitic acid, not determined but indications of about.....	3.0	0.05
Citric acid.....	none	none
Total determined or indicated.....	3.2680	0.05447

Remarks.—If we compare the total of acids accounted for in this summary, equivalent to 60.2 cc. normal solution, with the amount of acidity found in the residue of acids after their separation from the juice by means of the lead salts and hydrogen sulphide, viz., 125.1 cc. normal solution, we find that about half of the acids there present are unaccounted for. Doubtless part of this was acetic acid from lead acetate not completely washed out of the precipitate. Lactic acid was not looked for. If present it would have been left as a calcium salt in the 85 per cent. alcohol which was discarded. Nor was any account taken of tricarballic acid, which v. Lippmann¹ found in sugar beets, along with citric acid and aconitic acid. Some work started on the volatile acids was interrupted before it was finished and no report of interest can at present be made on these nor on such other acids as may be present which are not precipitated with lead acetate. It seems clear from the work thus far accomplished that aconitic acid is the predominating one among those precipitated with lead salts in a neutral 50 per cent. alcohol mixture. The only others thus far identified that are present in significant amounts are phosphoric and sulphuric acids. Oxalic, tartaric, succinic, citric, and malic acids are either completely absent or are present in such small quantities as to have no practical significance to the manufacturer. These facts may have important significance to the sugar chemist and manufacturer, who is seeking to improve the sugar house and refinery operations so as to secure more complete exhaustion of the molasses or to prevent the formation of scale in the evaporation apparatus. This relatively high percentage of aconitic acid is a special characteristic of sugar cane juice and its unpurified products. The suggestion that it occasions the peculiar cane flavor in these products, however, finds no support in the taste of the purified acid, nor in odor or taste developed in heating aconitic acid or its salts, or mixtures of these, with sugar. The free acid facilitates the browning of sugar upon heating, as do also other acids, e. g., tartaric, citric or malic. The phosphoric acid is doubtless removed in part in the clarification process if the juice is limed to neutrality. Such of the phosphate and the sulphate of lime as remains in the clarified juice may become the cause of the formation of scale. With reference to the extraction of sucrose from the molasses, it would

be interesting to know what are the "molassigenic values" of the aconitic acid and its several salts, i. e., their power of preventing or facilitating the crystallization of sucrose. The high solubility of the lime salt of aconitic acid, even in the hot solution, makes it improbable that any notable quantity of the aconitic acid is removed in the clarification process in which lime is used, or that it is deposited as a scale or sediment during the evaporation in the "effects" or the "pan," unless the presence of sugars to the point of saturation materially reduces the solubility of the calcium aconitate. The aconitic acid therefore accumulates in the molasses, where it is usually present in extraordinary large amounts.

BUREAU OF CHEMISTRY,
WASHINGTON, D. C.

THE OCCURRENCE OF LEVAN IN SUGAR.

By W. G. TAGGART.

Received July 3, 1911.

Greig Smith and Thomas Steele² obtained from sucrose solutions inoculated with *Bac. levaniiformans* a new gum which they named levan, and of which they made a complete chemical study.

In conjunction with W. L. Owen, bacteriologist for the Louisiana Sugar Experiment Station, in his work on "The Bacterial Deterioration of Sugars"² it became necessary to study this same gum. The results agree with Smith and Steele in that levan hydrolyzes quantitatively into levulose according to the reaction $(C_6H_{10}O_5)_n + n(H_2O) = n(C_6H_{12}O_6)$; that its specific rotary power is about $[\alpha]_D = -40$; that it melts at 200° C.; does not reduce Fehling's solution; and is not precipitated by lead subacetate. Although Smith and Steele found the gum-forming organism to be present in nearly pure cultures and believed that the organism is responsible for the greater part of the deterioration of sugars in storage, they were unable to show by analysis that levan is formed in sugars.

Comparison of results obtained by analyses made monthly of a large number of raw sugars proved that the relation between the fall in single polarization and in sucrose (Clerget) could not be accounted for by inversion. In some cases, while the single polarization was found to decrease the sucrose (Clerget) would slightly increase. Bacteriological examination showed all of these sugars to contain large numbers of the gum-forming organism, and it may readily be seen that should levan be present in a sugar the single polarization would be decreased 0.6° v. for every 1 per cent. gum, and at the same time the sucrose (Clerget) would be increased 0.67° v. by the levan hydrolyzing to levulose during inversion.

To prove that levan was responsible for the unusual changes found to take place in these sugars, attempts were made to separate the gum from solutions of these sugars by precipitating it with alcohol made slightly alkaline with sodium hydroxide. This method, however, brought down so much of the other gummy matter that it was found impossible to separate small

¹ *Ber. d. chem. Ges.*, 11, 707 (1878); 12, 1649 (1879).

² *J. Soc. Chem. Ind.*, Nov. 29, 1902.

³ *Louisiana Bulletin*, No. 125.

quantities of levan from such sugars, even where it had been added.

By adopting special methods, however, a separation of the levan from inoculated sugars was effected, thus bringing the deterioration process of sugars in line with that found to take place in sugar solutions. For this work inoculated Peruvian crystals were used. Two solutions of 14 per cent. sugar of 5 liters each were thoroughly sterilized, and then inoculated with yeast and allowed to ferment. When most of the sugar had fermented, the solutions were filtered and evaporated to 1 liter. The gum was precipitated from the concentrate by adding 3 liters of alcohol made alkaline with sodium hydroxide. After the gum had been dissolved and precipitated four times, a small quantity was obtained which was polarized, hydrolyzed, and the resulting levulose polarized:

	No. I.	No. II.	Control 99.8 sugar.
Polarization of gum.....	-0.35	-0.24	00.0
Polarization of hydrolyzed product.....	-0.72	-0.51	00.0
Theoretical polarization.....	-0.78	-0.53	00.0

Attempts have been made to find a means of avoiding the error in analysis which is caused by the presence of levan. The invertase method was tried and found unsatisfactory, and likewise the Andrlik urea method. In making the direct polarimetric reading in acid and urea solutions it was found that the rate at which the gum hydrolyzed was slower than the rate of sucrose inversion.

THE DETECTION OF SUBSTITUTION OF SPIRITS FOR AGED WHISKEY. A DISCUSSION OF THE CHEMICAL DATA PRESENTED IN THE TRIAL OF U. S. vs. NINE BARRELS OF WHISKEY.¹

By A. B. ADAMS, Chief Chemist, Internal Revenue Bureau.

Received April 24, 1911.

In this country when it is intended to age new whiskey, it is, as a rule, placed in Government Bonded Warehouses for the purpose. When it enters the warehouse it is stamped with what is called the "warehouse stamp" which bears the date of inspection and gauge. When the owner desires to withdraw the package, the tax is paid and a tax-paid stamp placed upon the stamp head, denoting the fact, stating also the time of tax payment and number of gallons content. This is called a "double stamped package."

The integrity of the stamp and the Government marks and brands is guaranteed by law, or rather, the Statutes provide a heavy fine and imprisonment for changing the contents of a package, unless the marks and brands are destroyed.

For many years it has been a common custom among certain dealers to take such a double stamped package, dispose of a portion, or all of its contents, and then refill the package with either an inferior grade of whiskey or alcohol diluted to the proper proof and artificially colored and flavored. This is a violation, as stated above, of Section 3455 R.S.

The past several years the Commissioner of Internal Revenue has claimed that the substitution of

other spirits in a double stamped package could be ascertained by chemical examination. This claim was vigorously disputed by the attorneys who represented the Wholesale Liquor Dealers' Association before the Bureau of Internal Revenue, it being claimed by them that packages of whiskey varied too much from one another in their chemical constituents to make such a comparison reliable.

At their request it was arranged that a case be tried before a jury, and from the many packages under seizure thirteen barrels were selected for trial. These had been seized on the premises of _____ Wholesale Liquor Dealers, Cincinnati.

As four of the packages were libeled later than the others they became two cases, namely, "U. S. vs. Nine Barrels of Whiskey" and "U. S. vs. Four Barrels of Whiskey."

The libel alleged that the barrels were substituted, or did contain other spirits than those tax-paid therein. The first part of the libel read as follows:

"First: That said _____ doing business under the firm name of _____ Co., did then and there receive and have in their possession with intent to defraud, the said nine distillers' original packages (barrels) of whiskey, which said packages had then and there contained distilled spirits other than the contents which were therein when such packages (barrels) were labeled, stamped, branded and marked by a duly appointed officer of the Internal Revenue."

As the thirteen barrels were owned and claimed by the same parties, for convenience sake, the cases were combined for trial and heard as one case.

The thirteen packages under seizure, according to the marks and brands, contained whiskey which had been produced by two reputable distillers at different periods, stored in the respective U. S. Bonded Warehouses for different periods, in order to properly age the whiskey.

NOTE.—It must be understood that the Government had absolutely no suspicion that the distillers had tampered with the packages. The proceedings were what are called "in rem"; that is, the suit was for the forfeiture of the packages and not a criminal action, the Government making no allegation as to who changed the contents of the barrels.

For several years the Division of Chemistry of the Bureau of Internal Revenue had been collecting analytical data on whiskey, in order to see if the chemical experts of the office were justified in deciding that a package of whiskey found on the market was not the identical whiskey indicated by the marks and brands. The method of procedure was as follows:

Upon the receipt, in the laboratory, of the sample of whiskey suspected by a Revenue officer of being other spirits than those indicated by the marks and brands on the package, orders would be sent to the Government officer at the bonded warehouse of the distillery, whose marks and brands were on the suspected package, to obtain from the bonded warehouse one or two samples as near as possible to the same date of inspection as the suspected sample.

The suspected and genuine would then be analyzed and the comparison of the different chemical constituents made. If the results were fairly close the sample was reported as genuine; if there was a marked

¹ Published by authority of the Commissioner of Internal Revenue.

discrepancy the sample was reported as containing other spirits than those tax-paid therein.

A large number of samples whose history was known were analyzed in the Bureau, a careful study made of the results, convincing the officials that a comparison could be made between packages of whiskey produced by the same distillery under approximately the same conditions of manufacture, storage and of age.

As the cases in suit were the first of their kind, and would, if decided favorably, be of great importance to the Government, it was decided to spare no expense or effort in developing unmistakably the truth or falsity of these conclusions. Instructions were therefore issued to the revenue officers, in whose districts the two distilleries were situated, to obtain a series of samples representing each year of the eight years of storage, about five for each year. To obtain the five samples as near as possible to the same date of inspection, and at least three samples of goods not more than a few days old but representing the production of different days.

The officers were told to select for the years in which the suspected samples were produced packages as near as possible to the date of inspection of the suspected samples. This was the only specific instruction to the officers as to particular packages.

This series of samples was desired for the following reasons:

The three samples of new goods to show that there was practically no difference in the analytical data between samples produced from different mashes and different dates of production when first distilled.

The five samples of each year as near as possible to the same date of inspection because such packages would, as a rule, have been stored under identically the same conditions, and, therefore, the differences due to the individual container (barrel) could be clearly shown if such existed.

The samples from each year to show the change in the different constituents, due to the length of storage.

No samples were obtained from packages but one year old as the data from these would have no real bearing on the case, all of the suspected samples having been from packages purporting to contain well matured whiskey.

The genuine and suspected samples were subjected by the same analyst, at the same time, to the following examination:

Proof determined by the regular Internal Revenue hydrometer (2° of proof representing 1 per cent. of alcohol by volume at 60° F.):

Solids.—50 cc. of whiskey were evaporated to dryness on the water bath, in platinum, dried for one hour at 100° C. and weighed.

Color.—Determination in Lovibond's tintometer using the Brewer's scale. The results were calculated to a one-half inch cell.

Acids, Etc.—The methods for the determination of acidity, ethereal salts or esters, aldehydes, furfural and higher alcohols were such as given in *Bulletin 107*, revised, Bureau of Chemistry, Department of

Agriculture, in the chapter on "Analyses of Distilled Spirits," pages 95-6-7 and 8, the Allen Marquardt method being used or the determination of the higher alcohols, results being expressed as amyl alcohol.

Color Insoluble in Water.—Color insoluble in water was determined by taking 50 cc. of the whiskey, evaporating to dryness, taking up the evaporated portion in 10 cc. of hot water, filtering, thoroughly washing the paper, bringing to the 25 cc. mark with water, adding sufficient alcohol to reach the 50 cc. mark or original volume. The color of this solution was then read in a Schreiner colorimeter against the untreated whiskey, the result being reported as the per cent. of color insoluble in water, a genuine whiskey seldom reading less than 70 per cent.

Color Soluble in Amyl Alcohol.—It was determined by shaking the original whiskey with amyl alcohol and estimating color dissolved in this menstruum. In the genuine whiskey the per cent. of color soluble in amyl alcohol seldom falls below 70 per cent. (the Marsh test using phosphoric acid in the amyl alcohol gives readings in excess of 90 per cent.; this test, however, was not used on these samples).

Qualitative Color Tests, Chloroform Test.—About 5 cc. of the whiskey were shaken with 5 cc. of chloroform, the major portion of the natural color being dissolved by the chloroform, artificial colors, such as burnt sugar or aniline dyes, appearing in the upper layers.

Amyl Alcohol Test.—About 5 cc. of the whiskey are shaken with 2 cc. of water and 3 cc. of amyl alcohol, the amyl alcohol dissolving the major portion of the natural color, artificial colors appearing in the watery or lower layer.

Paraldehyde Test.—The Amthor test as modified by Lasche, see description, page 101, of *Bulletin 107*, revised, for caramel.

On the accompanying sheets of analyses the results as obtained on the original samples are given. In parallel columns are also given these results calculated to 100 proof, in this way affording an equitable basis for comparing the chemical data on each sample regardless of its real proof.

The composition of the mash, as stated, is taken from official distillery records.

The serial number of the package is the number given each package, at the particular distillery, when it is inspected.

The date of inspection is the date when the package is gauged and entered in the warehouse; this is generally the day following the final distillation.

The age, by years and months, is the time elapsed between the date of inspection and the date of taking the sample, samples having been placed in glass (careful tests have proved that spirits do not change appreciably when kept in glass bottles securely stoppered); this is, therefore, the age in wood.

The degree of color soluble in amyl alcohol, column 23, in analytical table, is obtained by multiplying the depth of color, column 10, by the per cent. of color soluble in amyl alcohol, column 22.

DISTILLERY A.—Grams per 100 Liters.

Line No.	Composition of mash.		Serial No. of package.	Date of inspection.	Age by years and months.	Proof.	Solids.		Color.		Acids.		Esters.		Aldehydes.		Furfural.		Fusel Oil.	Per cent. color insoluble in water.	Per cent. color soluble in amyl alcohol.	Depth of Gen. Col. cal. from cols. 2, 10.	Chloroform.	Color tests.		Sum of Cong. of cols. 12, 14, 16, 18, 20.
	Malt	Rye					Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.						Original.	Calculated to proof.	
1	Malt	Rye	26497	11-9-00	7 yrs. 3 mo.	116/325	280	21.0	18.0	108.0	93.1	99.9	86.1	12.0	10.3	5.2	4.5	188/162	73	76	13.7	Genuine	Genuine	Genuine	356.0	
2	Malt	Rye	26498	"	"	113/254	220	18.0	15.9	98.4	87.1	96.0	83.0	8.0	7.1	3.0	2.6	192/170	75	82	11.4	"	"	"	351.8	
3	"	"	26499	"	"	113/259	220	17.5	17.3	98.4	87.0	96.0	79.7	8.0	8.9	2.6	2.8	193/172	75	76	13.0	"	"	"	361.4	
4	"	"	26500	"	"	116/284	247	20.0	17.7	103.6	90.5	95.0	81.9	12.2	10.4	3.2	3.8	202/169	77	76	13.3	"	"	"	358.9	
5	Malt	Rye	29047	3-18-01	6 yrs. 11 mo.	113/249	220	18.0	15.9	99.6	88.2	92.0	81.4	11.6	10.3	2.8	2.5	173/153	71	83	13.2	"	"	"	335.4	
6	"	"	29049	"	"	112/227	203	17.0	15.2	93.6	83.6	87.0	77.7	12.0	10.7	2.4	2.2	154/173	75	86	13.1	"	"	"	347.2	
7	"	"	29310	4-1-01	6 yrs. 10-3 mo.	111/142	128	12.75	11.5	34.8	31.9	31.7	28.6	5.2	4.7	0.8	0.7	51/46	9	52	3.7	"	"	"	111.3	
8	"	"	29311	"	"	113/178	157	16.0	13.3	40.8	36.1	33.4	29.6	6.6	3.9	0.6	0.6	63/56	13.5	33	4.0	"	"	"	127.2	
9	"	"	29312	"	"	111/158	142	12.25	11.0	34.8	31.3	30.8	27.7	4.4	3.9	0.4	0.4	70/67	17.0	27	3.6	"	"	"	130.3	
10	"	"	29326	4-2-01	"	111/187	168	14.8	14.0	36.0	32.4	32.4	28.5	4.8	4.3	1.0	0.9	66/50	29.0	27	3.8	"	"	"	120.1	
11	"	"	29328	"	"	110/170	154	14.8	13.2	36.0	32.7	31.2	28.3	5.2	4.8	1.1	1.1	67/61	17.0	26	3.8	"	"	"	120.1	
12	"	"	29330	"	"	110/163	148	14.0	12.7	36.0	31.2	31.2	28.3	5.2	4.8	1.1	1.1	76/68	5.0	33	4.3	"	"	"	134.9	
13	Malt	Rye	30940	6-25-01	6 yrs. 8 mo.	114/221	238	20.0	17.5	114.0	100.0	108.6	94.7	13.3	11.7	2.2	2.8	224/196	77	83	14.5	"	"	"	405.2	
14	"	"	30941	"	"	114/257	225	19.8	17.3	105.6	92.1	105.8	94.0	12.6	11.1	2.2	2.1	262/230	79	80	13.8	"	"	"	429.3	
15	"	"	30942	"	"	113/239	211	17.5	15.7	102.6	90.3	103.8	91.2	12.0	10.6	2.4	2.1	215/190	77	84	13.2	"	"	"	384.2	
16	"	"	30943	"	"	113/241	209	17.3	15.2	96.6	83.5	91.6	79.6	12.0	10.4	2.4	2.1	250/217	76	82	12.4	"	"	"	392.6	
17	"	"	30944	"	"	113/259	229	18.0	15.9	103.2	91.3	108.0	93.6	10.0	8.9	1.5	1.3	220/193	72	84	13.3	"	"	"	430.7	
18	"	"	30883	"	"	111/216	195	15.75	14.2	102.0	91.9	102.0	91.9	12.0	10.8	2.8	2.5	259/233	74	83	11.1	"	"	"	420.1	
19	"	"	30884	"	"	111/210	185	15.0	13.5	97.2	87.6	96.4	86.8	11.3	10.2	2.8	2.3	259/233	74	82	11.1	"	"	"	420.1	
20	Malt	Rye	38923	6-14-02	5 yrs. 8 mo.	109/239	219	17.5	15.0	87.6	80.4	86.2	79.1	19.3	17.7	2.2	2.0	183/168	79	76	11.5	"	"	"	347.2	
21	"	"	38924	"	"	109/207	190	15.0	13.8	86.4	79.3	87.1	79.9	18.5	17.0	1.8	1.7	183/170	79	76	11.5	"	"	"	347.2	
22	"	"	38926	"	"	109/208	191	15.3	14.0	96.0	88.0	87.1	79.9	18.5	17.0	2.0	1.8	195/179	74	80	11.2	"	"	"	365.5	
23	"	"	38927	"	"	109/220	202	15.8	14.5	88.8	81.5	82.3	75.5	17.0	15.6	2.0	1.8	227/208	76	80	11.6	"	"	"	382.4	
24	"	"	38932	"	"	109/217	199	16.0	14.7	94.8	87.0	87.6	80.4	16.0	14.7	2.2	2.0	216/198	75	78	11.4	"	"	"	382.4	
25	"	"	38959	6-17-02	5 yrs. 8 mo	109/148	136	14.0	12.8	87.6	85.3	84.3	79.7	4.8	4.2	0.4	0.6	60/55	9	26	3.3	"	"	"	126.8	
26	"	"	38959	"	"	108/130	120	11.5	10.6	30.0	27.8	31.2	28.9	3.0	2.6	0.4	0.4	60/55	9	28	2.6	"	"	"	114.7	
27	"	"	38959	"	"	108/130	120	11.5	10.6	30.0	27.8	31.2	28.9	3.0	2.6	0.4	0.4	60/55	9	28	2.6	"	"	"	114.7	
28	Malt	Rye	47099	6-27-03	4 yrs. 8 mo.	112/227	243	20.5	18.3	116.4	103.9	129.8	115.8	12.8	11.4	3.6	3.2	250/223	82	78	14.3	"	"	"	457.2	
29	"	"	47100	"	"	112/227	243	17.0	15.2	100.8	96.4	104.7	93.5	12.4	11.4	3.6	3.2	262/234	79	80	12.2	"	"	"	438.2	
30	"	"	47101	"	"	117/17.0	212	17.0	14.9	103.2	90.4	100.8	88.4	12.0	10.5	3.8	3.3	257/225	79	80	11.9	"	"	"	417.6	
31	"	"	47102	"	"	112/229	204	16.5	14.7	112.8	100.7	120.5	107.5	12.8	11.4	3.6	3.2	266/238	76	80	11.7	"	"	"	440.8	
32	"	"	47103	"	"	112/249	222	17.0	15.2	105.6	94.5	110.4	98.6	12.0	10.7	3.6	3.2	269/240	81	74	11.2	"	"	"	446.8	
33	Malt	Rye	50715	1-16-04	4 yrs. 1 mo.	109/131	125	13.0	12.4	22.8	21.7	20.5	11.6	2.4	2.3	trace	trace	54/51	0.4	17	2.1	"	"	"	101.1	
34	"	"	50723	"	"	105/159	151	13.0	12.4	80.4	76.6	74.0	70.5	1.6	1.2	1.2	1.2	139/133	74	80	9.9	"	"	"	291.3	
35	"	"	50724	"	"	105/176	168	14.0	13.3	85.2	81.1	82.6	69.1	12.8	12.2	1.5	1.4	144/137	74	76	10.1	"	"	"	298.9	
36	"	"	50725	"	"	105/177	167	13.8	13.1	88.8	84.6	84.6	79.1	11.6	11.0	1.5	1.4	171/163	77	76	10.0	"	"	"	337.7	
37	"	"	50726	"	"	104/159	153	11.0	10.6	79.2	75.1	70.4	67.7	11.2	11.1	1.4	1.1	148/142	77	83	9.2	"	"	"	308.1	
38	"	"	50727	"	"	104/160	154	12.0	11.5	73.2	70.4	68.6	65.9	11.2	10.8	2.0	1.9	158/152	74	87	9.5	"	"	"	298.0	
39	Malt	Rye	59773	5-10-05	2 yrs. 9 mo.	106/141	133	11.0	10.4	82.8	78.1	80.9	76.3	10.4	9.8	2.4	2.2	143/135	77.0	74	7.7	"	"	"	301.4	
40	"	"	59774	"	"	106/148	140	10.3	10.4	75.6	71.3	78.7	74.2	10.0	9.4	2.8	2.6	169/159	79.0	80	8.1	"	"	"	316.5	
41	"	"	59775	"	"	105/141	134	10.3	9.8	72.0	68.6	77.2	73.5	12.8	12.2	2.6	2.5	164/156	83.0	78	8.2	"	"	"	312.8	
42	"	"	59776	"	"	106/140	132	10.5	9.9	72.0	67.9	78.5	74.1	7.6	7.2	2.2	2.0	167/157	72.0	76	8.0	"	"	"	308.1	
43	"	"	59777	"	"	106/140	142	10.8	10.2	73.2	69.0	76.5	72.1	11.6	10.9	2.4	2.1	164/155	72.0	78	8.4	"	"	"	311.2	
44	Malt	Rye	73112	7-4-07	7 1/2 mo.	101/91	90	7.0	6.9	54.0	53.5	53.7	53.2	11.6	11.5	2.0	2.0	120/119	72.0	"	"	"	239.2	
45	Malt	Rye	75152	11-8-07	3 mo.	100/70	70	5.3	5.3	34.8	34.8	60.3	60.3	4.4	4.4	1.7	1.7	139/139	65.0	"	"	"	240.2	
46	Malt	Rye	77502	3-11-08	8 days	100/29.0	29.0	2.5	2.5	10.8	10.8	42.6	42.6	5.2	4.8	1.2	1.2	127/127	"	"	"	188.6	
47	"	"	77550	3-11-08	6 days	100/29.0	29.0	2.5	2.5	10.8	10.8	46.9	46.9	4.8	4.8	1.2	1.2	134/134	"	"	"	183.9	
48	"	"	77559	3-12-08	5 "	100/18.0	18.0	3.0	3.0	9.6	9.6	38.7	38.7	4.8	5.6	0.8	0.8	148/144	"	"	"	198.7	
49	"	"	77613	3-14-08	5 "	100/44.0	44.0	3.0	3.0	12.0	12.0	37.4	37.4	5.6	5.6	1.0	1									

In the last column of the analytical sheet is recorded the sum of the congeneric substances.

The data for the samples taken from the packages in suit, or as they will be spoken of from now on, the suspected samples, is printed in heavy type.

The data for the samples taken from packages in the U. S. bonded warehouses of the respective distilleries, and, therefore, authentic samples, which will be spoken of as genuine samples, is recorded in light type.

The experimental work in this office had proved the following point: that when whiskey is stored in charred oak barrels in dry storage, the proof, solids, color and the different congeneric substances increase in proportion to the time stored. While this basic principle was admitted by nearly every one interested, it was contended by the attorneys for the wholesale liquor dealers, before mentioned, that while the increase was proportional to the time stored, yet there was no relation between the increase in different packages of the same age, or any age. In other words, their claim was that while these constants did increase, yet the increase was not regular, and because one package four years old contained certain amounts of acids, esters, etc., another package of the same age would contain entirely different proportions and amounts of acids, esters, etc.

An examination, by the writer, of the two distilleries whose marks and brands were on the packages under seizure showed that at that time, Fall of 1908, every effort was being made to produce a clean new whiskey; that this was reduced to proof and bonded in charred white oak barrels of the best cooperage obtainable; that the usual warehouse care was given the whiskey the moment it was placed in the warehouse; that the warehouses were subjected to a normal temperature of from 70° to 80° F.; that the aim of the distillers, in each case, was to produce a whiskey commercially as near as possible to their own standard.

Samples from Distillery "A" are divided into nine groups, representing whiskey of different ages. The suspected samples are placed in the group where they belong according to the age indicated by the marks and brands.

In the group which is four years and one month old we were fortunate in obtaining five samples which were inspected the same date as one of the suspected samples, namely, package No. 50,715, and, therefore, the contents of these packages were taken from the same cistern on the date they were inspected, and on that date, if the contents of the cistern had been thoroughly mixed, the whiskey in each package had identically the same composition as each and every other package. As the proof in each package was the same, the contents of the cistern had been thoroughly mixed, otherwise the proof would have varied.

Taking the packages of new whiskey we find a trace of solid matter, no color, a very small amount of acids, a larger quantity of esters, a small amount of aldehydes, practically only a trace of furfural and a considerable amount of higher alcohols. Between the two samples produced on different days and nearly

a month apart there was no appreciable difference in any of the constants, the sum of the congenics being 161.7 for one, 175.0 for the other.

In the sample one day old (which means one day in wood) we find no distinction between this and the samples just produced, except that the package one day in wood contained an appreciable amount of color.

In the sample three days old we find the solids to have increased several times more than in the samples just produced, the color is twice as much as in the sample one day in wood, the other constituents are approximately the same, a constant amount of furfural appearing in each sample (entirely due to the fact that furfural is largely extracted from the charred oak package).

The remaining samples of the new goods, namely, those of five, six and eight days old bear the same relation as the samples just discussed, an appreciable increase in the solids, color and furfural, the other constants remaining the same. The minimum amount of congenics for this group is 161.7, maximum 198.7.

In addition to these a sample three months, and one seven and a half months old were taken; these admirably assisted in showing the process of aging. The solids have increased to 70 and 90 parts; the color to 5.3 and 6.9 degrees; the acids have changed to 34.8 parts for the three-month sample and 53.5 for the seven and a half months. The esters have increased to 60.3 and 53.2, the aldehydes to 11.5, the furfural showing a steady increase over the very new goods. The higher alcohols are approximately the same as when first produced. The total sum of the congenics is 240.2 and 239.2, an appreciable increase over the new goods.

These results prove: first, the uniform content of the different determinable constituents in whiskey just distilled: second, with the exception of the higher alcohols the congenics immediately begin to show an increase.

The next group of samples is two years and nine months old. Considerable time having elapsed, decided increases would be expected. The proof has increased to 105 and 106, four of the samples being 106 and one 105. The solids have increased to 132 minimum and 142 maximum, the color increased to a very appreciable degree, namely, 9.8 minimum and 10.4 maximum. The acids 67.9 minimum and 78.1 maximum, a difference between the five samples of only 10.2. The esters to 72.1 minimum and 76.3 maximum, a difference of 4.2. The aldehydes 7.2 minimum and 12.2 maximum; furfural 2.0 minimum and 4.1 maximum; higher alcohols 135 minimum and 159 maximum, a difference of 24. The total sum of the congenics is 301.4 minimum and 316.5 maximum, a difference of 15.1.

For the five samples the percentage of color insoluble in water ranges from 72 per cent. to 83 per cent. Depth of color soluble in amyl alcohol, calculated to Brewer's Scale, varies from 7.7° to 8.4°. The quantitative tests for color gave positive reaction for genuine

color, that is, there was no apparent trace of caramel or other color than that extracted from the barrels.

In the group just discussed an important change is noted, namely, an equilibrium seems to be established between the acids and the esters, it will be observed that this condition is maintained to the end of the bonded period.

The proportion between the aldehydes is fairly constant although tending to show that in some cases the influence of the package is stronger than the influence of the storage, as indicated in the one case of the aldehydes dropping to 7.2. The furfural in one package increased to 4.1 as against an average of the four packages of 2.1. It would be expected that the amount of this constant would depend upon the package, more so than upon the storage, and, that while there would be shown a general increase and ratio between the different packages, yet the maximum and minimum would vary considerably, due to the fact that the content of furfural in the charred package varies.

The next group of samples consist of six, each bearing inspection marks of the 16th of January, 1904. Five of these samples, namely, 50,723-27 inclusive, were taken from the respective packages at the U. S. Bonded Warehouses, and were four years and one month old when taken. Sample package No. 50,715 was taken from a package on the premises of the claimant of the litigation. As was mentioned previously, all packages inspected on the same day are necessarily taken from the same cistern which has been thoroughly mixed and reduced to the proper proof before a single package is filled. On this day, namely, January 16, 1904, the contents of each and every package inspected would have analyzed the same, as each was an aliquot portion of the cistern.

Four of the six samples have a proof of 105 and two a proof of 104. The solid content of the genuine samples varies from 151 to 168; the solid content of the suspected sample is 125. The depth of color in the genuine varies from 10.6 to 13.3; the color of the suspected sample is 12.4. (It is expected that in these cases when substitution has been effected, that artificial color will be added and the depth of color brought back to that of the original whiskey, at least.)

The acids of the genuine samples analyzed vary from 70.4 to 84.6, a difference of 14.2; the acids of the suspected samples 21.7, or about 48.7 points less than the minimum sample of the genuine.

The esters of the genuine vary from 65.9 to 79.1, a difference of 13.2; the esters of the suspected sample are 26.1 or 39.8 less than the minimum genuine.

The aldehydes of the genuine vary from 10.8 to 12.2; the suspected sample contains 2.3 parts.

The furfural of the genuine varies from 1.1 to 1.9; only a trace of furfural appears in the suspected.

The content of higher alcohols, of the genuine samples, varies from 132 to 163, a difference of 31; the content of the suspected samples in higher alcohol is 51 parts, or 81 parts less than the minimum genuine.

The claim is made that as the higher alcohol content

of these six packages on the day of inspection was the same, and any difference at the time of the analysis was due to evaporation and osmotic action which changes tend to increase the higher alcohol content and never diminishes it, then these results clearly show that package 50,715 contained only about one-third of the fusel oil that should be expected.

In studying the composition of the color, we find that the "color insoluble in water" of the genuine samples varies from 74 to 77 per cent.; there is no color insoluble in water in the suspected samples, all of the color dissolving in this menstruum.

The "color soluble in amyl alcohol" for the genuine varies from 76 to 87 per cent. The same test on the suspected shows only 17 per cent soluble. The depth of color soluble in amyl alcohol varies from 9.2 to 10.1; the depth of color soluble in amyl alcohol of the suspected sample is 2.1. The qualitative test for artificial coloring matter proved the color of the genuine samples to be genuine color, derived from the oak package; the same tests on the suspected samples proved a heavy artificial coloration.

The sum of the congeneric substances in the genuine samples vary from 291.3 to 337.1, a difference of 45.8 between the maximum and minimum, or samples taken from packages known to be unsophisticated; the sum of the congeners in the suspected sample is 101.1, or only one-third as much as the genuine samples.

The next group of samples analyzed are five samples taken from packages four years and eight months old, on the premises of the U. S. Bonded Warehouse. The proof in four of the samples is 112, in one 114. The solids vary from 204 to 243. The color from 14.9 to 18.3. The acids from 90.4 to 103.0. The esters from 88.4 to 115.8. The aldehydes from 10.5 to 11.4. Furfural 3.2 to 3.3. Higher alcohol 225 to 224. The color insoluble in water 76 to 82 per cent. Color soluble in amyl alcohol 74 to 80 per cent. The depth of color soluble in amyl alcohol 11.2° to 14.3°. The qualitative tests for color proved in each case to be genuine. The sum of the congeneric substances varies from 417.6 to 460.8.

The next group of samples analyzed contains whiskey five years and eight months old. Five samples inspected 6-14-02, taken from U. S. Bonded Warehouses; two samples, namely, 38,959 and 38,965, inspected three days after the samples just mentioned were taken from packages found on the premises of the claimant of the whiskey, being two of the packages in litigation. The proof of the genuine sample is 109; of the suspected samples 109 and 108 respectively. The solid contents of the genuine samples vary from 190 to 219; of the suspected samples 120 and 136. The depth of color of the genuine varies from 13.8 to 16; of the suspected 12.8 and 10.6. The acids of the genuine vary from 79.3 to 88.0; of the suspected 25.3 to 27.8. The esters on the genuine vary from 75.5 to 90.4; of the suspected 29.7 and 28.9. The aldehydes of the genuine vary from 14.7 to 17; in the suspected 4.2 and 2.6. Furfural from 1.8 to 2.2 in the genuine, and in the suspected 0.6 and 0.4. The

fusel oil found in each genuine sample varies from 168 to 208, and in the suspected samples 67 and 55, or about one-third of that amount found in the whiskey known to be genuine.

Examining the composition of the color we find that the color insoluble in water in the genuine varies from 74 to 79 per cent., on the suspected it is 90 per cent. In each case the color soluble in amyl alcohol, in the genuine, varies from 72 to 80 per cent.; in the suspected samples 26 and 25 per cent. is soluble. The depth of color soluble in amyl alcohol, in the genuine, varies from 10.5 to 11.6; in the suspected it is 3.3 and 2.6. Qualitative tests for color in the genuine prove all the color to be that extracted from the oak packages. The same tests show a heavy artificial coloration in the suspected packages.

The sum of the congenics in the genuine varies from 347.2 to 382.4, a difference of 35.2. The sum of congenics of the suspected samples is 126.8 and 114.7 or 220 points less than in the genuine package containing the smallest amount.

The next group of samples analyzed consists of fifteen samples, nine taken from the Bonded Warehouse, and six from packages found on the premises of the claimants, and therefore part of the packages in litigation.

The samples vary in age from six years and eight months to six years and eleven months.

The proof in the genuine samples varies from 111 to 115; in the suspected from 110 to 113. The solids of the genuine vary from 185 minimum to 238 maximum; the suspected from 128 to 168. The depth of color of the genuine from 13.5 to 17.5; suspected 11.0 to 14.0. The acids of the genuine vary from 83.6 minimum to 100.0 maximum; of the suspected from 34.8 to 40.8. The esters from 77.7 to 95.6, while the esters of the suspected from 27.7 to 32.5, or about one-third as high as the genuine samples of the same age. The aldehydes from 10 to 13.3; the suspected aldehyde content from 3.9 to 5.1. The furfurals varied from 1.3 to 3.1; the suspected from 0.4 to 1.1. The higher alcohols of the genuine from 153 to 233; in the suspected from 46 to 68, about one-third as high as the content of the authentic samples.

The color insoluble in water of the genuine from 72 to 79 per cent.; of the suspected 5.0 to 29 per cent. The color soluble in amyl alcohol from 80 to 86 per cent.; in the suspected from 26 to 33 per cent. The depth of color soluble in amyl alcohol from 11.1° to 14.5° for the genuine, 3.4 to 4.0 for the suspected. The qualitative tests proved no artificial color in the genuine samples, while a large amount of caramel was indicated as present in the suspected.

The sum of the congenics of the genuine vary from 335.4 to 430.7; the suspected from 111.3 to 134.9, or the same difference as indicated in the other comparisons.

The last group analyzed consisted of five samples seven years and three months old in wood.

The proof varies from 113 to 116. The solids from 220 to 280. The depth of color from 15.9 to 18.

The acids from 87.0 to 93.1. The esters from 79.7 to 88.7. The aldehydes from 7.1 to 10.4. The furfurals from 2.3 to 4.5. The higher alcohols from 162 to 174. The color insoluble in water 73 to 77 per cent. The color soluble in amyl alcohol from 72 to 84 per cent. The depth of color soluble in amyl alcohol from 11.4 to 13.7. The sum of the congenics from 348.9 to 361.4.

A careful examination of this résumé of the tables and the curves should convince one of the following points concerning the whiskey taken from the U. S. Bonded Warehouse and described herein as genuine:

1. That there is a general tendency in the proof, color, solids, and the congenics to increase the longer the storage.

2. That the results prove this increase to be uniform and comparable in packages of approximately the same age, the variation being almost negligible, when taking into consideration the possible variation between two different determinations.

3. That the individual package seems to have no other influence (in this connection) than to cause a slight variation in the depth of color and the amount of aldehydes. The content of furfural depends almost entirely on the package and the length of storage.

4. The composition of the color extracted is the same in all the packages, never less than 70 per cent. insoluble in water, or the same per cent. soluble in amyl alcohol (note about Marsh test).

As regards the suspected samples they are not similar to the genuine samples in any points, except proof and depth of color.

The following is the examination of a so-called "Neutral" spirit, or "Blending Goods:":

	Grams per 100 liters.
Acids.....	13.3
Esters.....	20.4
Higher alcohols.....	6.3
Aldehydes.....	0.5
Furfural.....	0.0

This is the class of goods frequently used in this kind of manipulation (substitution) and if used in the proportion of two parts of neutral spirits to one of the *real* whiskey, brought to the proper degree of proof and colored with caramel, until the deficiency in the color, caused by the water white spirit is made up, will give upon analysis figures very similar to the whiskey called *suspected* herein.

I will not consider in such detail the analysis of the whiskey taken from the distillery designated herein as Distillery "B," and of the four packages in litigation bearing marks and brands of this distillery, but suspected of containing other spirits.

These packages were proceeded against in order to introduce evidence in the analytical data of samples from another distillery located in another section of the country where different local conditions might exist. In this case the whiskey in litigation was supposed to be eight years and ten months old, or ten months older than the law permits whiskey to remain in bond; thus it was impossible to obtain samples from the warehouse nearer than ten months

DISTILLERY B.—Grams per 100 Liters.

Line No.	Composition of mash.	Serial No. of package.	Date of inspection.	Age by years and months.	Proof.	Solids.		Color.		Acids.		Esters.		Aldehydes.		Furfural.		Fusel oil.		Per cent. color insoluble in water.	Per cent. color soluble in amyl alcohol.	Depth of Gen. Col. cal. from cols. 10, 22.	Color tests.				Sum of Cong. sub. columns 12, 14, 18, 20.	Line No.
						Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.				Original.	Calculated to proof.	Original.	Calculated to proof.		
1	Rye	28980	4-24-99	8 YRS. 10 mo.	115	164	142	16.5	14.2	49.2	42.8	56.0	48.7	8.0	6.9	2.2	1.9	70.0	61.0	17	29	4.1	Caramel Heavy	161.3	1			
2	"	28981	"	"	115	134	115	17.0	14.8	48.0	41.7	58.1	50.1	7.6	6.5	2.8	2.4	61.0	52.0	17	25	3.6	Caramel Heavy	152.4	2			
3	"	28982	"	"	115	147	147	17.0	14.4	50.4	42.7	55.6	47.1	8.8	7.4	3.8	3.2	65.0	56.0	17	30	3.3	Caramel Heavy	150.7	3			
4	"	28983	"	"	115	146	134	17.5	14.8	50.4	42.7	55.6	47.1	8.8	7.4	3.8	3.2	65.0	56.0	17	29	4.3	Caramel Heavy	159.4	4			
5	191	32984	2-23-00	8 YRS.	118	197	167	15.0	12.7	105.6	89.5	99.4	84.2	12.0	10.2	4.2	4.2	128.0	109.0	17	76	9.7	Genuine	297.1	5			
6	191 bu.	34443	4-28-00	7 YRS. 10 mo.	117	230	196	16.0	13.7	105.6	90.2	94.6	80.8	8.8	7.5	6.8	5.8	135.0	115.0	78	80	11.0	Genuine	298.0	6			
7	"	34444	"	"	117	230	202	16.5	14.1	102.0	87.2	96.8	82.7	8.8	7.5	6.8	5.8	135.0	132.0	70	74	12.2	Genuine	315.2	7			
8	"	34447	4-26-00	"	119	250	210	16.75	14.1	109.2	91.7	111.1	93.4	11.6	9.7	5.2	4.7	128.0	108.0	75	82	11.6	Genuine	307.1	8			
9	"	34448	"	"	118	262	222	17.0	14.4	108.2	91.7	103.4	87.6	14.0	11.9	5.6	4.7	137.0	116.0	78	80	11.5	Genuine	311.9	9			
10	340 bu.	36967	2-6-01	7 YRS.	119	227	192	16.0	13.5	100.8	85.4	105.1	89.0	11.2	9.4	4.2	3.5	122.0	109.0	74	82	11.0	Genuine	296.3	10			
11	"	36968	"	"	119	234	197	15.0	13.2	99.6	83.7	102.5	86.1	8.8	7.4	3.2	2.6	122.0	102.0	77	76	10.0	Genuine	281.8	11			
12	"	36969	2-7-01	"	121	257	212	18.0	14.9	102.0	87.4	108.2	89.3	8.8	7.3	4.2	3.5	133.0	101.0	77	76	11.3	Genuine	285.4	12			
13	"	36970	"	"	121	241	199	15.7	13.0	93.6	77.4	91.0	75.0	10.0	8.3	4.2	3.5	133.0	110.0	75	76	9.9	Genuine	274.2	13			
14	"	36971	"	"	120	258	215	18.0	15.4	100.8	84.0	105.6	88.0	9.2	7.6	4.4	3.7	137.0	114.0	76	80	12.3	Genuine	297.3	14			
15	170 bu.	41679	2-6-02	6 YRS.	113	207	183	13.5	12.1	81.6	72.2	85.3	75.5	12.4	11.0	4.2	3.7	107.0	95.0	72	76	9.1	Genuine	257.4	15			
16	"	41680	"	"	113	210	186	13.7	12.1	82.4	81.8	85.3	75.5	13.2	11.3	4.2	3.7	106.0	94.0	72	72	8.7	Genuine	266.3	16			
17	"	41681	"	"	114	197	173	13.0	12.0	84.0	73.7	89.7	78.7	12.8	11.3	4.6	4.9	117.0	103.0	69	80	9.6	Genuine	271.9	17			
18	"	41682	"	"	116	271	182	15.0	12.9	93.6	80.7	82.7	71.3	13.9	12.0	4.0	3.4	118.0	102.0	74	80	10.3	Genuine	269.4	18			
19	"	41683	"	"	113	196	173	14.0	12.4	84.0	74.3	78.2	69.2	10.8	9.5	4.4	3.8	122.0	108.0	73	80	9.9	Genuine	264.8	19			
20	340 bu.	45982	1-30-03	5 YRS.	113	192	170	15.0	13.3	82.4	74.3	77.9	68.9	12.0	10.6	4.4	3.8	158.0	140.0	74	72	10.1	Genuine	267.7	20			
21	"	45983	"	"	114	209	183	15.5	13.6	84.0	81.1	80.5	69.0	11.6	10.2	4.4	4.4	126.7	111.0	75	74	9.8	Genuine	276.7	21			
22	"	45984	"	"	116	248	214	18.0	14.0	102.0	88.0	87.0	75.5	12.0	10.3	5.0	4.3	135.0	116.0	75	80	11.2	Genuine	284.4	22			
23	"	45985	"	"	116	271	234	18.0	15.5	102.0	88.0	87.0	75.5	12.0	10.3	5.0	4.3	135.0	117.0	80	80	12.4	Genuine	280.6	23			
24	"	45986	"	"	115	212	193	17.7	15.4	92.4	80.4	79.2	68.9	13.3	11.5	3.2	2.8	117.0	117.0	76	76	11.2	Genuine	281.1	24			
25	192+	49310	12-12-03	4 YRS. 5 mo.	112	224	191	16.0	14.3	90.0	80.3	84.5	75.4	15.2	13.6	3.2	2.8	234.0	209.0	80	80	10.2	Genuine	381.1	25			
26	"	49340	"	"	114	184	161	15.0	13.1	84.8	73.2	92.4	81.1	14.2	12.9	4.8	3.8	250.0	223.0	79	76	10.5	Genuine	378.1	26			
27	"	49495	"	"	114	202	177	15.0	13.1	84.8	73.2	76.4	67.1	14.2	13.2	4.8	3.8	250.0	223.0	79	76	10.5	Genuine	379.7	27			
28	"	49553	"	"	111	168	151	14.0	12.6	84.4	72.4	67.8	61.1	15.0	13.2	4.8	3.8	246.0	216.0	78	78	10.2	Genuine	369.9	28			
29	192, 31	49425	12-26-03	"	112	198	177	14.0	12.6	84.4	72.4	80.9	72.1	12.0	10.7	4.8	3.8	250.0	219.0	75	82	10.3	Genuine	368.9	29			
30	"	49428	12-19-03	4 YRS. 2 mo.	112	200	179	15.0	14.0	85.2	79.1	86.6	77.2	11.2	10.1	4.8	3.8	250.0	219.0	75	76	10.6	Genuine	378.0	30			
31	"	49430	"	"	112	191	170	15.0	14.0	85.2	79.1	86.6	77.2	11.2	10.4	4.8	3.8	250.0	219.0	75	76	10.6	Genuine	378.0	31			
32	"	49432	"	"	111	198	178	15.0	13.5	90.2	82.7	81.0	72.2	10.4	9.4	4.2	3.5	257.0	231.0	71	76	10.6	Genuine	360.8	32			
33	"	49434	"	"	111	197	176	15.0	13.5	85.2	82.7	83.0	74.3	11.6	10.4	4.2	3.5	257.0	231.0	71	76	10.6	Genuine	360.8	33			
34	"	49434	"	"	114	204	179	15.0	13.8	87.0	79.8	79.0	70.8	11.6	10.4	4.2	3.5	252.0	222.0	80	80	11.2	Genuine	381.1	34			
35	"	49427	"	"	113	199	176	15.0	13.8	87.0	79.8	81.0	70.8	11.6	10.4	4.2	3.5	252.0	222.0	80	80	11.2	Genuine	381.1	35			
36	"	49429	"	"	112	212	189	15.0	13.8	87.0	79.8	84.8	76.6	12.8	11.6	4.8	4.3	250.0	210.0	74	83	11.0	Genuine	370.8	36			
37	"	49426	"	"	112	192	171	15.0	13.4	93.6	83.2	84.4	75.3	11.2	10.7	4.2	3.5	242.0	210.0	74	74	10.7	Genuine	370.8	37			
38	"	49433	"	"	111	193	174	15.2	13.7	84.0	75.2	78.8	75.3	11.2	10.7	4.2	3.5	242.0	210.0	74	80	10.7	Genuine	380.0	38			
39	192, 16	53673	2-4-05	3 YRS.	102	193	174	15.2	13.7	84.0	75.2	78.8	75.3	11.2	10.3	4.2	3.5	196.0	196.0	71	76	10.4	Genuine	381.9	39			
40	"	53674	"	"	102	192	161	14.7	13.7	84.0	78.3	96.0	61.8	9.2	8.6	0.9	0.8	94.0	88.0	80	80	10.9	Genuine	237.6	40			
41	"	53675	"	"	108	192	164	13.7	13.5	86.4	80.0	70.0	61.8	11.2	10.4	1.0	0.9	78.0	72.0	73	78	11.3	Genuine	228.1	41			
42	"	53676	"	"	108	213	187	16.0	14.3	90.0	83.2	99.3	64.3	10.4	9.2	3.0	2.8	87.0	80.0	80	80	10.6	Genuine	229.9	42			
43	"	53677	"	"	108	199	184	14.0	14.3	94.8	82.8	92.1	66.7	8.8	8.2	2.2	2.0	90.0	83.0	71	71	10.6	Genuine	247.7	43			
44	340	53677	2-1-06	2 YRS.	107	194	181	13.5	14.3	80.4	75.1	62.7	58.6	8.8	8.2	1.4	1.3	82.0	78.0	72	72	10.7	Genuine	221.2	44			
45	"	57912	"	"	109	149	137	11.5	10.5	61.2	56.1	37.4	34.3	8.4	7.7	1.8	1.6	92.0	84.0	80	80	8.4	Genuine	182.7	45			
46	"	57913	"	"	109	169	155	14.5	13.2	72.0	66.1	43.5	39.9	9.2	8.4	3.2	2.9	99.0	91.0	76	76	10.6	Genuine	208.3	46			
47	"	57914	"	"	110	174	158	12.5	11.3	66.0	60.0	43.6	39.6	8.4	7.6	3.2	2.9	118.0	101.0	77	77	8.6	Genuine	217.1	47			
48	"	57915	"	"	108	187	170	14.0	12.7	62.8	56.7	38.5	35.2	7.2	6.5	2.8	2.5	120.0	109.0	84	84	10						

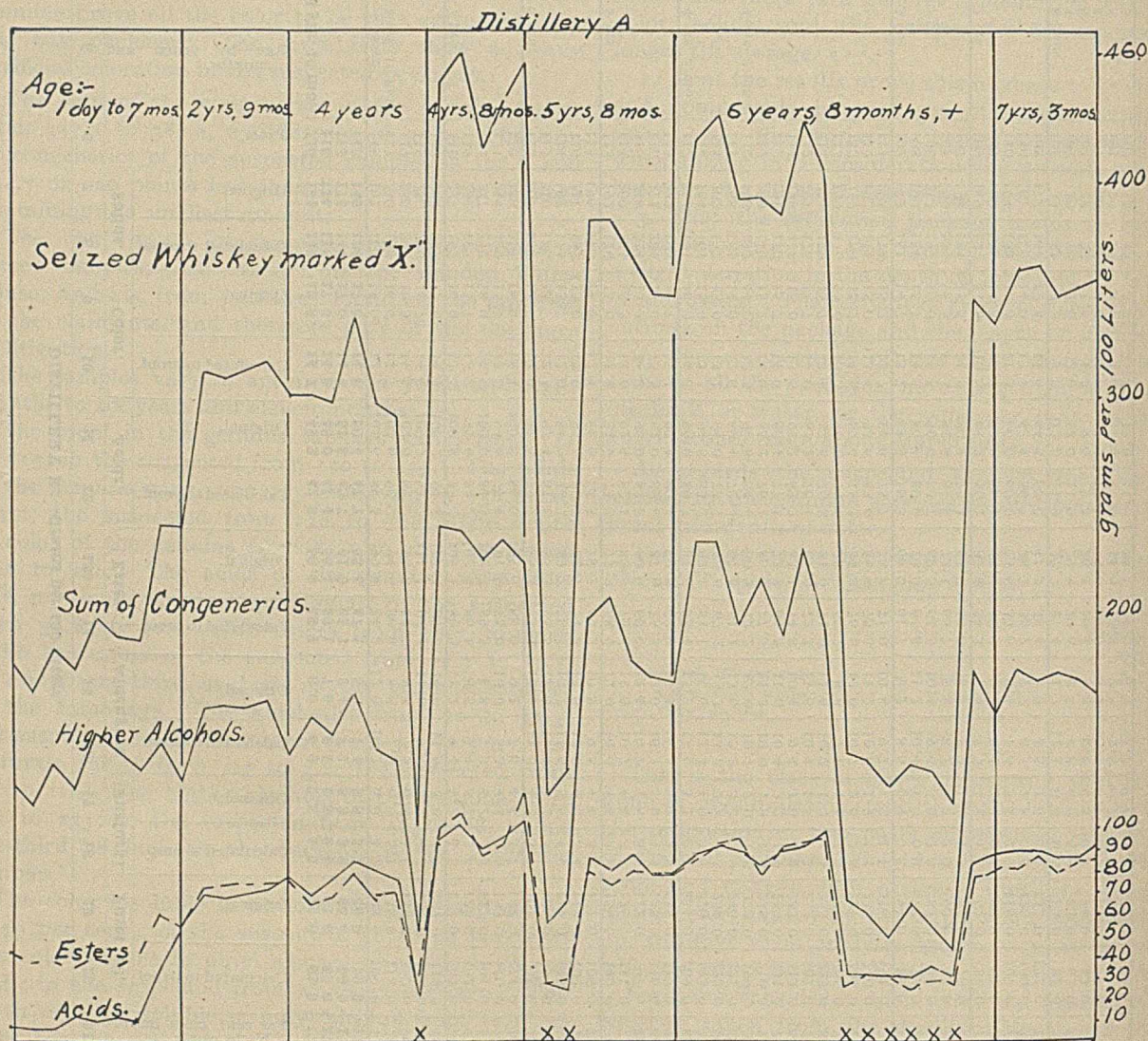
or a year; the proposition, therefore, evolved itself into proving that the product of this distillery when aged in its own warehouse contained certain amounts of color, solids and the different congeners, and that the contents of one package were comparable chemically to the contents of another package of approximately the same age.

A careful perusal of the analytical table and the curves proves essentially the same points as for Distillery "A." One marked variation developed, namely, in the higher alcohol content in the samples produced during the Fall of 1903, when nearly twice as much

A comparison of the *suspected* and the *genuine* will prove that the spirits in the four packages are not similar to the genuine and younger goods analyzed. The content of acids in the suspected is less than in the two-year goods. The content of esters less than in the three-year goods. The higher alcohols are less than for even the new goods.

All comparison ceases here and the differences become more glaring the older the whiskey becomes.

In conclusion it should be stated that in work of this kind, the acids, esters and color form the points which should be used to determine the authenticity of



higher alcohols were produced as at any other period. (The distiller, Mr. —, suggested that as the rye was of poor quality that year, this might account for the high amount. I am inclined to think his suggestion is a good one.) This exception, of course, is repeated in the sum of the congeners. This result would tend to show that while storage has an effect on the quantity of the higher alcohols (they increasing by concentration), yet the amount present depends more on the fermentation and the method of distillation.

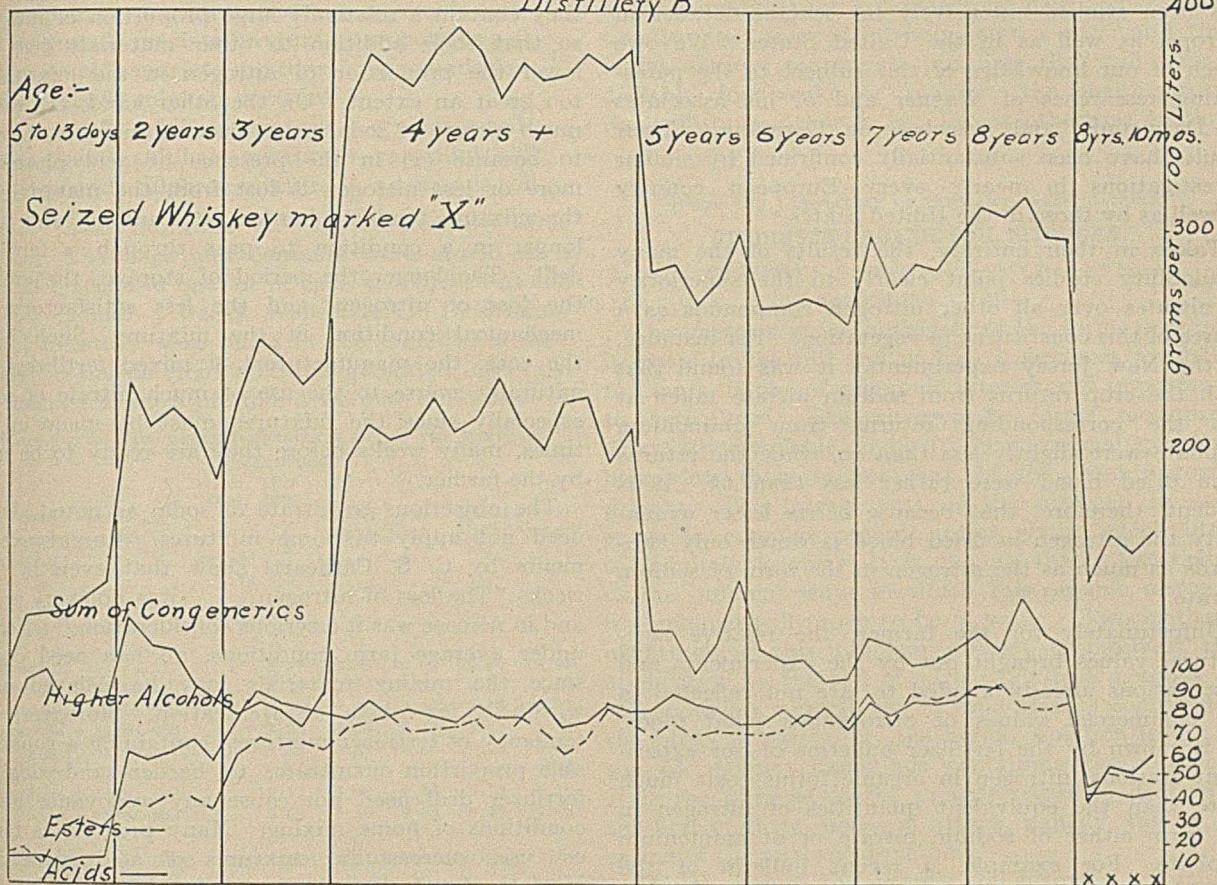
the contents of a package of whiskey. The content of solids, higher alcohols, aldehydes and furfural will assist in arriving at a conclusion, but should not be relied upon solely, as can be done in the case of the acids, esters and color.

HISTORY OF THE CASE.

Trial began April 6, 1909, and ended April 14, 1909.

Jury returned verdict for the Government deciding that the packages did contain other spirits than those tax-paid therein.

Distillery B



Submitted to Circuit Court of Appeals, June 15, 1910, decided by Circuit Court of Appeals, July 13, 1910. Reported in "Federal Reporter," Vol. 181, pages 296-306.

The Higher Court decided that:

"We are satisfied that under the evidence the jury was warranted in finding that the nine barrels in question contained distilled spirits other than the contents which were in them when they were lawfully stamped, etc.....if the testimony offered by the Government is competent." Further on in the opinion: "We conclude that the conditions under which the contents of the seized barrels and the contents of the barrels taken for comparison were produced and handled were sufficiently similar to justify the admission of the evidence objected to."

The case was remanded for a new trial as the Government did not prove that the claimants received the packages in the illegal condition as stated in the libel. The case will not be retried, the Government having obtained a favorable decision on the two main points at issue, namely:

1. Can the presence of other spirits in a package of double stamped whiskey be proven by chemical analysis?
2. Are the analyses of samples taken from packages in the same warehouse proper evidence against similar whiskey under seizure?

THE RELATION OF NITRATE OF SODA TO THE MECHANICAL CONDITION OF COMMERCIAL FERTILIZERS.¹

By JACOB G. LIPMAN.

Received May 1, 1911.

The increasing cost of organic ammoniates and the inert character of a considerable proportion of the materials (used in the making up of commercial mixtures) are forcing progressive farmers to resort, more and more, to home mixing. Those who have learned to use purchased plant food with discretion have realized that the better sources of animal and vegetable nitrogenous substances like dried blood, concentrated tankage, dried and ground fish, and cottonseed-meal have become economic luxuries. But, expensive as are these so-called high-grade materials as a source of nitrogen to crops, they are cheap as measured against the lower grades of tankage, dried blood, and, more particularly, of garbage tankage, leather scrap, hair and wool waste and peat.

It is a fact, indisputably established by almost innumerable experiments and observations, that different materials used as sources of nitrogen to crops vary in their *availability*. Otherwise, stated, some of these substances furnish a large part of their nitrogen to growing crops; that is, they are *readily available*, while others yield up but a small portion of their nitrogen within one or two growing seasons; that is, they are *slightly available*. The question of the rela-

¹ Laboratory New Jersey Agricultural Experiment Station.

tive availability of different nitrogenous plant foods has been studied extensively for several decades in Europe, as well as in the United States. We owe much of our knowledge of this subject to the painstaking researches of Wagner and of his associates at Darmstadt, and elsewhere in Germany.¹ Their results have been substantially confirmed by similar investigations in nearly every European country as well as by those in the United States.²

Taken in their entirety, the results of the many availability studies point clearly to the superiority of nitrates over all other nitrogen compounds as a source of this constituent to vegetation. For instance, in the New Jersey experiments³ it was found that with the crop returns from sodium nitrate taken at 100 the corresponding returns from ammonium sulphate were slightly less than 70, while the returns from dried blood were rather less than 65. It is evident, therefore, that because of its lesser availability the nitrogen in dried blood is worth only two-thirds as much as the nitrogen in the form of sodium nitrate.

Unfortunately for the farmer, the relative agricultural values brought out by the experiments and observations already alluded to are not reflected in the commercial values of nitrogenous plant foods. As is shown by the fertilizer bulletins of our experiment stations, nitrogen in organic forms costs much more than the equivalent quantities of nitrogen in the form either of sodium nitrate or of ammonium sulphate. For example, a recent bulletin of the New Jersey Experiment Station⁴ shows that nitrate nitrogen was purchased in the state in 1910 at an average price of 15.77 cents per pound, and ammonia nitrogen at an average price of 15.54 cents per pound. On the other hand, dried blood nitrogen was purchased at an average price of 20.25 cents per pound, and dried fish and tankage nitrogen at an average price of nearly 20 cents per pound. In some instances the purchase price exceeded 25 cents per pound. To make matters worse, the same and higher prices are charged in mixed goods for nitrogen derived from inert materials, whose relative availability is at times as low as 10 or 20 when the returns from equivalent amounts of nitrate nitrogen are taken at 100.

In view of the facts outlined above it is pertinent to ask why organic ammoniates, some of them of questionable utility, continue to command (in the open market) prices entirely out of keeping with their true agricultural value. To understand the answer to this question it should be remembered: (1) That a large quantity of such materials is purchased by the manufacturers of mixed fertilizers; (2) that they are valuable in imparting a desirable

mechanical condition to the mixed goods; (3) that they contain a relatively large proportion of nitrogen so that their addition to other materials does not lower the proportion of nitrogen in the mixture to too great an extent. On the other hand, the use of much nitrate of soda in fertilizer mixtures is objected to because (1) in the presence of acid phosphate more or less nitrogen is lost from the material; (2) the mixture tends to harden on standing, and is no longer in a condition to pass through a fertilizer drill. The longer the period of storage, the greater the loss of nitrogen, and the less satisfactory the mechanical condition of the mixture. Such being the case, the manufacturers of mixed fertilizers are naturally averse to the use of much nitrate of soda, especially since the mixtures must be made up, at times, many weeks before they are ready to be used by the farmer.

The objections to nitrate of soda, as noted above, need not apply to home mixtures. Recent experiments by C. S. Cathcart⁵ show that even in four weeks "The loss of nitrogen was not very great, and in no case was it a serious consideration." Hence, under average farm conditions, no loss need occur, since the mixing materials may be delayed until within a few days of application. Moreover, the tendency of fertilizer mixtures, containing a considerable proportion of nitrate, to harden and clog the fertilizer drill need not cause any annoyance under conditions of home mixing. Many progressive farmers use, successfully, mixtures of acid phosphate, muriate of potash and nitrate of soda, by giving due heed to climatic conditions and by delaying the mixing until within a few days of applying the fertilizer. Where, occasionally, the fertilizer mixture does harden, the material may be again crushed or ground to a fine powder without difficulty.

In order to secure additional data on the mechanical condition of mixtures of acid phosphate, muriate of potash and nitrate of soda, a number of such mixtures were prepared and tested with a view toward answering the following questions:

1. How long will mixtures of these materials remain drillable?
2. Would the addition of small amounts of dry sifted soil improve the mechanical condition of these mixtures?
3. How long will the mixtures with or without soil remain drillable?
4. Could mixtures of acid phosphate, muriate of potash, and nitrate of soda be crushed again, and made drillable, after they had hardened in storage?

The three materials were mixed in the following proportions:

- 260 pounds nitrate of soda.
- 540 pounds acid phosphate.
- 200 pounds muriate or sulphate of potash.

The mixed material was divided into 50-pound lots as follows:

¹ "The Use of Nitrate of Soda in Commercial Fertilizers," *This Journal*, 3, 30.

¹ See "Die Stickstoffdüngung der landwirtschaftlichen Kulturpflanzen," Berlin, 1892; "Die Düngung mit Schwefelsauren Ammoniak und organischen Stickstoffdüngungen in Vergleich zum Chilisalpeter," Heft 80, "der Deutschen Landwirtschafts-Gesellschaft; Versuche über die Stickstoffdüngung der Kulturpflanzen," *Ibid.*, Heft 129.

² See "Investigations Relative to the Use of Nitrogenous Materials 1898-1907," *Bull.* 221, N. J. Expt. Sta.

³ *Loc. cit.*, p. 34.

⁴ "Analyses and Valuation of Commercial Fertilizers," *Bull.* 233, N. J. Expt. Sta.

- (1) 50 pounds muriate mixture.
- (2) 50 pounds muriate mixture + 5 pounds soil.
- (3) 50 pounds muriate mixture + 10 pounds soil.
- (4) 50 pounds muriate mixture + 15 pounds soil.
- (5) 50 pounds sulphate mixture
- (6) 50 pounds sulphate mixture + 5 pounds soil.
- (7) 50 pounds sulphate mixture + 10 pounds soil.
- (8) 50 pounds sulphate mixture + 15 pounds soil.

Each of these mixtures was represented by three portions. The bags and contents were stored in a dry, cool place, and one lot of each was drilled at the end of 1, 2 and 3 weeks, respectively. Determinations of moisture were made in the ingredients used and also in the different mixtures at stated intervals. The amounts of moisture found were as follows:

MOISTURE CONTENT OF SINGLE INGREDIENTS AND OF THE MIXTURES.		Calculated.			
		Per cent.	Per cent.		
Samples taken.	Samples marked.	2/11/11	2/18/11	2/25/11	3/4/11
		2/14/11	2/20/11	2/27/11	3/6/11
Acid phosphate.....	13.05
K ₂ SO ₄	9.18
KCl.....	1.53
NaNO ₃	3.98
Soil.....
KCl mixture.....	8.39	10.36	10.00	10.00	9.95
50 lbs. mixture + 5 lbs. soil..	8.33	9.70	9.61	9.03	9.58
50 lbs. mixture + 10 lbs. soil..	8.26	9.55	9.15	9.18	9.23
50 lbs. mixture + 15 lbs. soil..	8.20	9.38	9.27	9.13	8.82
K ₂ SO ₄ mixture.....	9.92	10.48	10.08	9.75	10.00
50 lbs. mixture + 5 lbs. soil..	9.84	10.33	9.65	9.45	9.80
50 lbs. mixture + 10 lbs. soil..	9.77	9.98	9.45	9.75	9.10
50 lbs. mixture + 15 lbs. soil..	9.69	9.56	9.35	9.43	9.03

As shown by the moisture determinations, the mixtures of acid phosphate, muriate of potash and nitrate of soda, with or without soil, gained a slight amount of water over the calculated. On the other hand, the corresponding mixtures containing their potash in the form of sulphate lost a slight amount of water in some instances. The differences were not great, however.

At the end of 1, 2 and 3 weeks, respectively, 50 pounds of each mixture were passed through a McWhorter fertilizer drill. No difficulty was experienced in drilling the material at any time, but it was noticed that where soil was added to the fertilizer, the mixed material passed somewhat more rapidly through the drill. A further examination of the mixtures was made at the end of 8 weeks, and it was found then that the contents of the bags could be readily crushed into fairly small particles.

In view of the foregoing statements it appears entirely feasible to make up home mixtures of acid phosphate, muriate of potash and nitrate of soda, a combination that, under average climatic and soil conditions, is sure to give the farmer the greatest amount of available plant food, for the money invested. Beyond that nitrate of soda should find more extensive use at the factory provided that slovenly methods be eliminated and wet mixing restricted. It is to be hoped, at any rate, that nitrate of soda, sulphate of ammonia, cyanamid and organic nitrogenous substances will be used in the future with rather more discrimination as to their relative agricultural values. It is to be hoped also that the

consumer of fertilizers will realize more strongly than he does to-day that a satisfactory mechanical condition is often secured, at too great a cost; and that in his anxiety to provide mixtures that will remain drillable for weeks or months, the manufacturer uses substances that he would not otherwise employ.

[FROM THE LABORATORY OF FERTILITY INVESTIGATIONS]

STUDIES IN ORGANIC SOIL NITROGEN.¹

By ELBERT C. LATHROP AND BAILEY E. BROWN.

Received May 15, 1911.

The question of soil nitrogen, of the forms in which it exists in the soil and of how it becomes available to plants, is one of economic interest and importance to agriculture. The nitrogen in forms recognized as readily available to plants is in normal soils low, being less than 10 per cent. of the total nitrogen present. The largest part of the nitrogen in soils exists in complex organic forms about which little is definitely known. It is obvious that a knowledge of the different ways in which this organic nitrogen is combined will prove to be of value. Two methods of attacking this problem present themselves: the application to the soil of such analytical methods as will show in a general way in what class of compounds the nitrogen exists, or, the actual isolation from the soil of organic compounds containing the nitrogen. It is the purpose of the present paper to deal with the first of these modes of attack, namely, the application of the analytical method.

The sources of the organic soil nitrogen are many and varied. Each year a large amount of organic matter, consisting of plants, plant roots, leaves, organic material in manures and in fertilizers, etc., finds its way into the soil. It is safe to say that a large part, if not all, of the nitrogen in this organic matter has been a component part of the protoplasm of the plant or animal. As soon as such organic material becomes incorporated in the soil and becomes subject to the many transforming agencies in the soil, it begins to undergo decomposition. We have, therefore, to deal with protein decomposition products in the soil. When protein undergoes decomposition, the break occurs along distinct lines of cleavage. Under the influence of chemical agents, the action of dilute acids, heat, bacteria, etc., hydrolysis takes place and the complex protein molecule breaks down into compounds of a less complex nature and finally into a number of primary and secondary dissociation products. Such being the case, one should expect a parallelism between the protein dissociation products obtained by the digestive action of dilute acids on soils in the laboratory and those products formed from plant and animal constituents in the soil under field conditions.

By heating protein material with dilute acids or superheated steam, the following kinds of nitrogenous decomposition products have been recognized for the purpose of analytical classification: ammonia, diamino acids, monoamino acids, and indefinite

¹ Published by permission of the Secretary of Agriculture.

"humic" bodies. We should, therefore, expect to find some or all of these classes of compounds or forms of nitrogen in the soil or in a solution from the soil after treatment with acid or steam.

A review of the literature shows that some work has been done on the subject of nitrogenous compounds in soils or allied material and should be briefly considered. Loges¹ in 1886 found that a hydrochloric acid extract of the soil gave a precipitate with phosphotungstic acid, which is generally recognized as a precipitant for nitrogenous compounds. Eggertz² found that the nitrogen content in thirteen samples of humus varied from 2.59 per cent. to 6.43 per cent. and states that the nitrogen was present in organic form and not as ammonia. Baumann³ suggested the presence of amino compounds in the soil because of the fact that by boiling the soil with hydrochloric acid, ammonia compounds not originally present in the soil were formed. Bertholet and Andre⁴ concluded that the nitrogenous bodies were chiefly insoluble amides which are easily split into ammonia and soluble amides. Warrington⁵ reports the presence of small quantities of amides in the soil. Sestin⁶ reports that a portion of the soil nitrogen was present as amino acids. Dojarinko⁷ working with the humus from seven Russian soils obtained large quantities of amino-nitrogen, 1.34 to 1.96 per cent. of the soil. In 1905, Shorey,⁸ working with an Hawaiian soil with a view to classifying the decomposition products of the nitrogenous bodies in the soil, applied the method of Osborne and Harris,⁹ a modification of the method of Hausmann,¹⁰ to the soil. He obtained in the acid solution 8.5 per cent. of the total nitrogen in the soil, more than half of which existed as "humic" nitrogen and the remainder as ammonia, diamino acids and monoamino acids. More recently, Jodidi,¹¹ working with Michigan peat, using methods of much the same nature, concludes that "the bulk of the organic nitrogen, namely, two-thirds to three-fourths, calculated upon the nitrogen in solution by boiling with acids, is present in the form of monoamino acids, about one-fourth in the form of amides and the rest of the nitrogen represents diamino acids."

Suzuki¹² reports results obtained by treating "humic" acid with boiling hydrochloric acid and then subjecting the solution obtained to esterification and fractional distillation according to Fischer's¹³ method. By such treatment he separated and identified the esters of several of the monoamino acids and obtained tests for some of the other dissociation products of protein material. Recently, Robinson¹⁴ has isolated from Michigan peat, by means of hydrolysis with

boiling acid, leucine and isoleucine. From an alkaline extract of the soil, Schreiner and Shorey in these laboratories have reported the isolation of the following nitrogenous compounds: picoline carboxylic acid,¹ xanthine,² hypoxanthine,³ arginine,⁴ histidine,⁵ cytosine⁶ and creatinine.⁷ These compounds exist in the soil as such and are not products obtained by hydrolyzing the protein material of the soil by laboratory treatment, as is the case in the above-cited investigations, but are products formed in the soil by the decomposition of organic material.

In view of the fact that the number of nitrogenous compounds isolated from soils is rather small and that the procedure for such isolation is not only difficult, but also requires very large amounts of soil, a complete study of the organic nitrogen in many soils would be almost impossible. Therefore an effort was made to see if some analytical method of deriving such knowledge could be applied so that soils might be examined more readily and the examination made on a small sample.

Five soils were selected for this examination. The soils belong to the type known as Hagerstown loam and were collected from plats of the Pennsylvania State College Experiment Station. They have been under continuous cropping and treatment since 1881.⁸ Table I shows the kind of fertilizer treatment they have received for this time. The soils were sifted through a coarse sieve, air-dried and finally passed through a one-half mm. sieve. The calculations are figured on the basis of oven-dried soil. In obtaining the data for this investigation, unless otherwise stated, the methods of analysis of the Association of Official Agricultural Chemists⁹ were used. For the determination of nitrates in the soil solution the colorimetric method was used.¹⁰

TABLE I.—FERTILIZER TREATMENT OF PLATS 20, 21, 22, 23 AND 24.

Plat No.	Fertilizer added per acre.
20.....	10 tons of manure added every other year.
21.....	N as dried blood = 72 pounds N. P as dissolved bone-black = 48 pounds P ₂ O ₅ . K as muriate = 100 pounds K ₂ O. Added every other year.
22.....	Manure, 6 tons; every other year. Limestone, burnt, 2 tons; every four years.
23.....	Limestone, burnt, 2 tons; every four years.
24.....	Check plat, nothing added.

A study of Table II shows that the amounts of total nitrogen in these soils does not vary widely, there being a difference of less than 320 p. m. in the extremes. The soils which have received nitrogenous fertilizers are slightly higher in total nitrogen than the other two plats not so treated. The difference in total nitrogen between plats 20 and 24 is small, still plat 24 contains only about 75 per cent. as much nitrogen as plat 20. It is the nitrogen in the form

¹ *Landw. Vers. Sta.*, **32**, 201 (1886).

² *Centrlb. f. agr. Chem.*, **1889**, 175.

³ *Landw. Vers. Sta.*, **33**, 247 (1887).

⁴ *Compt. rend.*, **103**, 1101 (1886).

⁵ *Chem. News*, **55**, 27 (1887).

⁶ *Landw. Vers. Sta.*, **51**, 513 (1889).

⁷ *Ibid.*, **56**, 311 (1902).

⁸ "Agr. Invest. Hawaii in 1905." *Rept. Chem.*, p. 34.

⁹ *J. Am. Chem. Soc.*, **25**, 323 (1903).

¹⁰ *Z. physiol. Chem.*, **27**, 5 (1899).

¹¹ *J. Am. Chem. Soc.*, **27**, 396 (1910).

¹² *Bull. Coll. Tokio*, **7**, 513 (1907).

¹³ *Z. physiol. Chem.*, **33**, 151, 412 (1901).

¹⁴ *J. Am. Chem. Soc.*, **33**, 564 (1911).

¹ *J. Am. Chem. Soc.*, **30**, 1295 (1908).

² *J. Biol. Chem.*, **8**, 391 (1910).

³ *Ibid.*, **8**, 392 (1910).

⁴ *Ibid.*, **8**, 383 (1910).

⁵ *Ibid.*, **8**, 382 (1910).

⁶ *Ibid.*, **8**, 389 (1910).

⁷ *Sci.*, **33**, 340 (1911).

⁸ T. F. Hunt, Penn. St. Coll., *Ann. Rpt.*, **11**, 1907-'08, pp. 68-93.

⁹ *Bull.* **107**, revised, Bur. Chem., U. S. Dept. Agr.

¹⁰ Schreiner and Failyer, *Bull.* **31**, p. 31, Bur. Soils, U. S. Dept. Agr.

of ammonia and nitrate that is commonly recognized as available to plants; the remaining nitrogen, or about 98 per cent. of the nitrogen in these soils, is of an organic nature in which condition the nitrogen is not considered to be directly available to plants.

TABLE II.—AMOUNTS OF ORGANIC AND INORGANIC NITROGEN IN THE SOILS STUDIED.

	Parts per million of oven-dried soil.			Per cent. of total N in soil.			
	Total N.	Ammonia N.	Nitric N.	Organic N.	Ammonia N.	Nitric N.	Organic N.
20.	1317.5	28.4	1.88	1287.2	2.15	0.143	97.707
21.	1240.0	25.6	2.06	1213.4	2.06	0.161	97.779
22.	1280.0	20.6	1.88	1257.5	1.61	0.145	98.245
23.	1052.5	16.9	1.74	1033.9	1.61	0.165	98.225
24.	1000.0	16.4	2.30	981.7	1.64	0.230	98.020

In order to determine, in a general way, the manner in which this organic nitrogen is combined in the organic matter of the soil, the method of Hausmann,¹ as modified by Osborne and Harris,² was used. This method which was first applied to the soil by Shorey³ is, in short, as follows: The soil is boiled with dilute acid and the acid solution evaporated and the excess of acid removed. The nitrogen present as ammonia is determined by boiling with an excess of magnesia; the nitrogen in the magnesia precipitate, termed "humin" nitrogen, is determined by the Kjeldahl method; the dibasic nitrogen in the filtrate is separated by precipitation with phosphotungstic acid and determined by the Kjeldahl method; the monobasic nitrogen is determined by difference from the total nitrogen determined on a separate portion of the solution. In this case 100 grams of soil were boiled with 500 cc. of hydrochloric acid, sp. gr. 1.115, for three hours in a flask supplied with a reflux condenser. The solution was filtered and the filter washed with distilled water, the filtrate evaporated on the water bath to remove the excess of acid and then made up with distilled water to a volume of 500 cc. Aliquot portions of this solution were taken for analysis.

In order to study the changes in the nitrogen compounds under the influence of moist heat, the soils were treated as follows: 40 grams of soil were heated at the desired pressure with 200 cc. of distilled water for one hour. The solutions were filtered, the soil washed with distilled water, and made up to a volume of 200 cc. and the ammonia nitrogen and the total nitrogen in solution determined in aliquot portions. For the determination of the nitrogen remaining in the soil, the entire 40 grams of soil were used.

Ammonia Nitrogen.—In consideration of the dissociation products, ammonia nitrogen comes first. Nasse,⁴ as well as later investigators, agree that after the dissociation of the protein molecule, either by acids or by heat, ammonia is always present in the dissociation products. It may be stated that although the amount of ammonia obtained in the dissociation products depends on the concentration of the acid and the length of heating, that the known final cleavage products of protein do not give off ammonia by such treatment. The figures given here for ammonia

nitrogen represent the actual amount of nitrogen in the ammonia obtained by dissociation and do not include the ammonia nitrogen already present in the soil.

TABLE III.—PER CENT. OF NITROGEN SPLIT OFF AS AMMONIA NITROGEN AND PER CENT. OF NITROGEN RENDERED SOLUBLE BY STEAM DIGESTION AT 2, 4, 6, 8, and 10 ATMOSPHERES PRESSURE. RESULTS EXPRESSED IN TERMS OF TOTAL N.

Plat. No.	Ammonia nitrogen.					Soluble nitrogen.					Nitrogen insoluble at ten atmospheres pressure.
	2.	4.	6.	8.	10.	2.	4.	6.	8.	10.	
20.	0.97	5.87	7.71	10.68	11.80	14.47	21.41	23.50	34.21	44.44	55.56
21.	2.31	5.62	9.85	10.97	14.45	13.67	20.01	23.82	28.30	39.09	60.91
22.	3.80	5.42	5.73	6.88	11.59	12.08	18.61	19.72	25.08	38.33	61.67
23.	3.12	3.12	3.12	3.78	7.83	10.42	13.67	16.10	22.86	37.49	62.51
24.	3.32	6.11	11.08	13.18	15.64	8.55	19.75	21.09	22.55	46.77	53.23

In Table III are given the data obtained by the digestion of the five soils under steam pressures of 2, 4, 6, 8 and 10 atmospheres and in Table IV, the data obtained by the digestion of the soils with hydrochloric acid in the manner already described. It will be seen from Table IV that the three plats, 20, 21 and 22, which have received organic fertilizers give the largest amount of ammonia on dissociation, the amount being highest in the plat which has received manure alone (20) and lowest in the check plat (24). In the pressure digestion of the soils, Table III, the majority of the soils under increased pressure show a proportional increase in the amount of ammonia nitrogen formed, as might be expected. However, in the case of the limed plat (23), the amount of ammonia formed at 2, 4 and 6 atmospheres is the same and only a small increase is obtained at 8 and 10 atmospheres. Soil 22, the other limed plat, shows a more gradual increase in ammonia, but the increase is much smaller than in the case of soils 20 and 21 which

TABLE IV.—ANALYTICAL CLASSIFICATION OF NITROGEN IN DECOMPOSITION PRODUCTS FORMED BY THE DIGESTION OF THE SOILS WITH HYDROCHLORIC ACID.

Plat. No.	Per cent of total nitrogen in soil.						Soluble "humin" N.	Total "humin" N.
	N insoluble in acid.	N soluble in acid.	Ammonia N.	Diamino acid N.	Mono-amino acid N.	Total "humin" N.		
20.	26.29	73.71	21.64	12.97	8.63	28.32	54.61	
21.	28.28	71.72	19.98	5.82	29.04	14.46	42.74	
22.	28.02	71.98	18.39	9.04	17.48	25.36	53.38	
23.	29.09	70.91	16.32	8.21	12.80	31.77	60.86	
24.	29.04	70.60	16.05	8.82	17.80	26.39	55.79	

have received organic fertilizers without lime and 24, which has received nothing. This indicates that the nitrogenous organic matter of the two limed plats is of somewhat different nature than that of the other plats and that the nitrogenous compounds have been made more resistant to decomposition by such treatment. In this connection it will also be noticed that although soils 22 and 23 show only a small increase in the amounts of ammonia formed under increasing pressure that the amounts of organic nitrogenous matter going into solution at the different pressures shows an increase comparable to that of the other soils, although the amount is not so great as in the cases of the soils not limed.

¹ Loc. cit.

² Pfünger's Arch. f. d. ges. Physiol., 6, 598 (1872); 7, 139 (1873); 8, 381 (1874).

"Humin" Nitrogen.—The compounds precipitated by the excess of magnesia from the acid solution of the soils are for the most part the so-called humin substances or melanoidins. The term "humin" was first used by Berzelius¹ in describing certain dark-colored constituents of mold. Mulder showed that on boiling protein matter with strong acid, that brown or black particles, which resemble the dark bodies of putrefying matter, separate. These bodies are also formed from many other organic compounds, including carbohydrates. However, they are uniformly high in carbon and low in hydrogen and nitrogen; they are generally insoluble in water and in acids; in alkaline solutions they are somewhat soluble and are precipitated from them by acids; they do not give any particular reactions and their decomposition products are not well defined. Samuely² holds that the indole, pyrrol, pyridine, and tyrosine groups of the albumin molecule contribute to the formation of these compounds. In the magnesia precipitate mentioned above there would also appear other compounds containing the pyridine ring, such as picoline carboxylic acid, first isolated from an Hawaiian soil by Shorey³ and later from other soils by Schreiner and Shorey.⁴ They conclude that such a compound might possibly arise in the soil as a secondary decomposition product of the protein molecule.

It is generally considered that when the nitrogen is combined in the ring, as in pyridine compounds, that it is unavailable, and may even be harmful to plants. It would seem probable that a large part, if not nearly all of the nitrogen classed here as "humin" nitrogen, is combined in such a way as to be unavailable to plants. Table IV shows that there is over 25 per cent. of "humin" nitrogen soluble in acid from four of these soils. Soil 21 is much lower in soluble humin nitrogen than the other soils, showing only about half as much. Since the nitrogen not soluble in acid may also be considered to be "humin" nitrogen, the total amount of nitrogen in such combination is, in four soils, over 53 per cent., while in soil 21, which has received dried blood, it is only 43 per cent.

Amino Acid Nitrogen.—The two classes of amino acids have been thoroughly studied, and their nature and composition is fairly well understood. The nitrogen is in a form from which it can be readily changed into ammonia by various agents. The amino acids are resistant to the action of acids and alkalies, but the amino group may be removed by the action of enzymes and bacteria, common both to the plant and the animal. In regard to the action of bacteria on amino acids, Czapek⁵ and Emmerling⁶ have shown that the α -amino acids are excellent nutritive materials. The amino acids are acted on by bacteria in two different ways: 1. The amino acids are converted into simple acids with the elimination of ammonia. 2. Carbon dioxide is split off,

leading, as Emmerling⁶ has shown, to the formation of Brieger's diamines, thus, lysine is converted into cadaverine. As a rule, the process does not stop here and the amino group is finally changed into ammonia.

That plants may use amino acids directly in their building process does not seem at all improbable. Different amino acids are present in the germinating plant seed and are used by young plants in their growth. Lefevre² has shown that in the absence of carbon dioxide plants are able to use certain amino compounds as a source of their carbon. He states that this transfer was not simply osmotic, but that these compounds were taken up by the plant roots. Work with nitrogenous compounds of this nature in water culture work in these laboratories indicates quite strongly that plants are able to use amino compounds in their building process. It would seem then that either directly or through the agency of enzymes, bacteria, etc., amino acids become available to plant use.

These soils differ rather widely in the amounts of diamino and monoamino acids which they contain, shown in Table IV, but there seems to be no agreement between the amino acid nitrogen formed and the plat treatment. However, the amino acid nitrogen as a whole represents 22 to 34 per cent. of the total nitrogen in the decomposition products of the soils.

These five samples of soil are really the same soil under long-continued treatment of different kinds. It is not improbable that work on widely different soils will show even much larger variations than those here noted. The work shows, however, that even in such cases there is a difference in the nitrogenous compounds in the soil and that different decomposition of the nitrogenous matter has and probably will continue to take place under the different conditions imposed upon the soils in the field.

BUREAU OF SOILS,
WASHINGTON, D. C.

[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

AN IMPROVEMENT IN THE METHOD FOR ESTIMATING HUMUS IN SOILS.³

BY J. B. RATHER.

Received May 3, 1911.

The term "humus" in this article is used to signify the ammonia-soluble organic matter of the soil, the *materie noire* of Grandeau.⁴

The Huston and McBride⁵ modification of the Grandeau method is the present one of the Association of Official Agricultural Chemists. The chief difficulty with this method is that with some soils considerable clay is brought into suspension by the ammonia. Most of this clay cannot be removed by filtration, and upon ignition it loses water and thereby increases the quantity of organic matter which ap-

¹ Poggendorff's *Ann.*, **44**, 375 (1838).

² Hofmeister's *Beiträge*, **2**, 355 (1902).

³ Hawaii Agr. Expt. Sta., *Ann. Rpt.*, **1906**, 55.

⁴ *Bull.* **53**, p. 32, Bur. Soils, U. S. Dept. Agr.

⁵ Hofmeister's *Beiträge*, **1**, 538 (1902); **3**, 47 (1902).

⁶ *Ber.*, **35**, II, 2289 (1902).

¹ *Z. physiol. Chem.*, **29**, 334 (1900).

² *Rev. Gen. Bot.*, **18**, 145, 205, 258, 302 (1906).

³ Full details of this work will be published in *Bulletin 139* of the Texas Experiment Station.

⁴ *Compt. rend.*, **1872**, p. 988.

⁵ *Bulls.* **37** and **107** (Revised), Bureau of Chem., U. S. D. A.

parently is present. With some soils the error is so large that it is several times greater than the amount of organic matter actually present. This fault with the method has been recognized for some time and several modifications have been suggested to remedy it. The most promising of these appears to be that of Mooers and Hampton.¹ Their modification consists in evaporating the solution to dryness on a water bath and heating on the water bath for several hours. The humus is taken up with 4 per cent. ammonia and filtered. The process is repeated and the filtrate evaporated, the residue dried, weighed, and ignited as usual.

The Mooers and Hampton method has been used in this laboratory, and although a considerable amount of clay was removed, further improvement seemed desirable.

The length of time necessary to complete an analysis, when heavy clay soils are used, makes the method very long, if evaporation and solution are repeated a sufficient number of times to give a clear solution.

It is well known that salts can coagulate clay, and throw it out of suspension. Fraps and Hamner² used non-volatile salts to precipitate the clay but call attention to the fact that the salt used might be decomposed or otherwise lost on ignition. It occurred to us that a salt which volatilized or decomposed below 100° C. would overcome this difficulty. Ammonium carbonate decomposes at 85° C., and was accordingly tested for this purpose.

EXPERIMENTAL.

The methods described below were compared on twelve soils, some high and some low in humus. The solutions were prepared by washing the soils with one per cent. hydrochloric acid to remove lime, with water to remove the acid, digestion with 4 per cent. ammonia and filtration, as prescribed in the Official Method. All comparisons were made on the same solutions.

1. Humus was determined in 100 cc. by direct evaporation (Official method). The residue was dried 3 hours at 100° C., weighed, ignited and washed again.

2. One hundred cubic centimeters were evaporated to dryness on a steam bath, baked two hours, the humus redissolved in 4 per cent. ammonia and decanted from the clay. The process was repeated, the ammonia solution filtered, and the analysis completed as in the official method (1) (Mooers and Hampton method).

3. To 130 cc. of the humus solution in a glass-stoppered cylinder was added 0.650 gram (5 grams per liter) ammonium carbonate. The salt was allowed to dissolve and the solution shaken. The clay precipitate was allowed to settle over night, the clear, supernatant liquid decanted through a filter and 100 cc. evaporated, and the determination completed as in the official method. Numerous tests showed that 3 hours was a sufficient time to dry the residues. A test of the ammonium carbonate used showed that it left no residue in the above process.

RESULTS OF THE WORK.

The results are shown in the following table:

PERCENTAGE OF HUMUS AND HUMUS ASH ESTIMATED BY DIFFERENT METHODS.

Laboratory number.	Direct evaporation (1).		Evaporation and solution (2).		Precipitation of clay with ammonium carbonate (3).	
	Humus.	Ash.	Humus.	Ash.	Humus.	Ash.
114 Travis gravelly loam.....	3.35	19.43	0.78	0.95	0.58	0.21
823 Orangeburg fine sandy loam, subsoil.....	5.00	33.45	0.86	0.51	0.78	0.19
829 Houston loam.....	1.85	4.50	1.54	0.72	1.33	0.27
830 Laredo gravelly loam.....	1.70	4.81	1.11	1.18	0.90	0.28
896 Norfolk fine sandy loam...	1.28	0.66	1.32	0.69	1.20	0.57
978 Lufkin clay.....	2.15	11.00	1.29	1.97	0.95	0.47
982 Cameron clay, subsoil.....	1.75	4.40	1.42	1.54	1.08	0.56
993 Orangeburg clay.....	0.86	3.97	0.58	0.35	0.45	0.37
947 Soil from alfalfa field, N. Dakota.....	6.20	13.09	5.77	3.94	5.07	0.78
941 Houston loam.....	3.14	11.95	1.25	0.55	1.07	0.20
1203 Houston clay, subsoil.....	2.18	9.51	1.00	1.53	0.83	0.45
949 Soil from an old field, Edge-ly, North Dakota.....	3.81	5.67	3.40	2.53	3.06	1.03
Average.....	2.77	10.20	1.69	1.37	1.44	0.45
10 per cent. correction for water in ash.....	1.75		1.55		1.39	

The amount of humus "ash" by the official method (1) varied from 3.97 per cent. (soil 993) to 33.45 per cent. (soil 823) and averaged 10.20 per cent.

The humus by the Mooers and Hampton method (2) averaged two-thirds as much as by the official method. The difference in some cases was very great. Humus in soil 823 by the official method was 5.00 per cent.; by the Mooers and Hampton method it was 0.86 per cent. The "ash" by the Mooers and Hampton method varied from 0.35 per cent. (soil 993) to 3.94 per cent. (soil 947), and averaged 1.37 per cent. This is about one-seventh as much as the average for ash by the official method.

The humus by the ammonium carbonate method (3) was lower in all cases than by the Mooers and Hampton method (2) and the ash averaged one-third as much as the ash by the latter method (2). The average for humus by the ammonium carbonate method was 1.44 per cent. and the average for ash was 0.45 per cent. This method gave very low results for ash with soils that gave a large amount of clay into suspension. With soil 823 the ash was 33.45 per cent. of the official (1) method; it was 0.51 per cent. by the Mooers and Hampton (2) method, and only 0.19 per cent. by the ammonium carbonate (3) method. With soil 114 the results for ash by methods 1, 2 and 3 are, respectively, 19.43, 0.95 and 0.21 per cent. With soil 947 the results for ash are 13.09, 3.94 and 0.78 per cent. An examination of the table shows similar differences with other soils.

When ten per cent. of the ash² is subtracted from the humus results, the difference between the results by the different methods are not so great. However, this correction is purely arbitrary and represent averages. Fraps and Hamner examined a large number of soils and found that the amount of water in the clay which is held in suspension by the ammonia varied from 8 to 20 per cent. A correction, therefore, is of little value.

The above results show that the official method is

¹ J. Am. Chem. Soc., 30, 800 (1908).

² Texas Experiment Station, Bull. 129.

¹ Peter and Averitt, Kentucky Experiment Station, Bull. 126, p. 63.

entirely misleading with some soils and that the Mooers and Hampton method does not remove all the suspended clay. It is possible that continued evaporation and solution would finally remove the clay from the soils we have used, but the amount of time required renders this process impracticable. During evaporation the ammonia is liable to absorb acid fumes from the laboratory and the continued baking is liable to oxidize or decompose some of the constituents of the humus.

The advantages of the method proposed by us are simplicity, speed, and the production of perfectly clear solutions.

Proposed Modification of the Official Method.—On the basis of the work just described the following modification of the official method is proposed:

Prepare the humus solution as described in the official method, and dissolve 0.65 gram ammonium carbonate in 130 cc. of the solution. Allow to stand over night in a glass-stoppered cylinder to allow the clay to settle and decant the clear supernatant liquid through a dry filter into a dry flask. Evaporate 100 cc. of the filtrate in a tared platinum dish, dry for three hours at 100°, weigh, ignite, and weigh again. Record loss on ignition as humus.

SUMMARY AND CONCLUSIONS.

1. Clay in humus solutions may be precipitated by ammonium carbonate and the precipitant disappears on evaporating the solution and drying the residue.
2. Evaporation and solution does not remove the clay completely from humus solutions.
3. Precipitation of the clay with ammonium carbonate is more nearly complete than by evaporation and solution and is a much shorter method.

THE DETERMINATION OF DUST IN BLAST-FURNACE GAS.

By WILLIAM BRADY AND L. A. TOUZALIN.

The comparatively recent introduction of gas engines for power development from blast-furnace gas, and the general realization of modern blast-furnace operators of the desirability of more thorough cleansing for gas used in stoves and boilers, has brought the iron and steel chemist face to face with the rather perplexing determination of dust in a stream of constantly flowing gas.

The writers have given this question considerable attention, and during the past five years various forms of apparatus have been constructed, many experiments have been made, and every conceivable filtering medium has been tried. It was early determined that, with a curved sampling pipe facing the flow of gas, and an extremely porous filter, fairly satisfactory comparative results could be obtained, where the gas contained less than 1.5 grains per cubic foot, by allowing the gas to flow through the filter and then through a wet test meter into the atmosphere. The static pressure of the gas alone was utilized to cause such flow, and the test was allowed to take care of itself for periods varying from eight

to twelve hours. Such tests have been run day and night for the past two years to determine the efficiency of wet scrubbers and Theisen washers. The grains of dust per cu. ft. at the entrance and exit, of any cleaning device, obtained in this way, while not ultimately correct, are comparative where the gas is not too dirty, and serve to show what the cleaning device is doing.

During the past year, however, there has been an increasing demand for some method of making dust determinations in dirty gas, which would give absolutely correct ultimate results. Tests run near the blast furnace, where the dust per cu. ft. runs higher than 1.5 grains, demonstrated that under such conditions the results obtained by merely allowing the gas to pass through the filter and deposit its dust were absolutely worthless. After encountering innumerable difficulties due to the irregularities of blast-furnace conditions the form of apparatus and method of operating to be described have been worked out, and the results appear, theoretically and practically, to be correct ultimate figures. By means of this apparatus and method of operating the same the dust may be determined in any blast-furnace gas and at any stage in its passage from the furnace to the stoves, boilers or cleaners. By means of two sets of such apparatus the efficiency of any cleaning system may be accurately determined. The results of many tests have shown that very slight changes in the construction of a dry gas cleaner may have a wonderful effect on the efficiency of the same. The value of such efficiency dust tests may, therefore, readily be appreciated.

Before the apparatus was constructed the experience of five years of preliminary work had made it clear that in working with dirty gas several important principles must be observed. These principles may be enumerated as follows:

1. In sampling gas containing solids in suspension the sample shall be withdrawn from that region of the main in which the mean velocity of the gas is found to exist.
2. In withdrawing said sample, means must be employed to change the direction of flow gradually and to cause the flow in the entrance end of the sampling pipe to be at the same velocity as the passing stream of gas.
3. Where possible, samples shall be taken from a vertical main and at least 15 feet from any bend or obstruction.
4. The gas must be filtered above 212° F. and cooled below its dew point before being delivered to the wet test meter.

In regard to Principle No. 2, it had been considered an important point to have equal velocities in the main and sampling pipe, several years before the correctness of the principle could be proved in practice. Within the last few months, the importance of observing this fundamental principle of dust determinations has been absolutely proved by tests run on gas flowing through a supply pipe to a stove. The gas was traveling at an average velocity

of 44 ft. per second. Apparatus No. 1 was inserted in the pipe and gas was withdrawn at a velocity, in the sampling pipe, of about 43 to 45 feet per second. Simultaneously, Apparatus No. 2 was inserted a few inches at the side of No. 1 and at such a point that both entrance ends of the sampling pipes were within 2 inches of each other. The gas was withdrawn through the sampling pipe of Apparatus No. 2 at about 21 to 23 feet per second. After about ten double tests had been run in this way the velocities were reversed, *i. e.*, Apparatus No. 1 was run at 21 to 23 feet per second and Apparatus No. 2 was increased to from 43 to 45 feet per second. In every test of the total run the apparatus sampling at the slower velocity showed much higher dust per cu. ft. of gas. In fact the average increase in grains of dust per cu. ft. due to slow sampling, was over 44 per cent. This test demonstrated that where a retardation occurs in the sampling pipe, the distortion of flow around the entrance end of the pipe causes an undue proportion of dust to lodge in the sampling pipe and be

velocity when working with gas of 1.5 grains, or more, of dust per cu. ft. There is undoubtedly an error made in sampling even cleaner gas at an incorrect velocity but probably not so great an error. There is so little known in regard to dust in gas during the various phases of its passage from the furnace to stoves, boilers and cleaners, that a mass of work must be done and many experiments be made before the influence of velocity of sampling can be definitely known with gas of various degrees of cleanliness.

To determine dust by the Velocity Method, if we may call it such, the following are the conditions which must be known and the means for arriving at the same.

1. *Dew Point of the Gas.*—This is obtained before starting the dust test by means of the special psychrometer shown in Fig. 1, which is really an aluminium casting of 2 1/2 inches diameter arranged for supporting a dry and wet bulb thermometer in a stream of gas flowing from the main into the atmosphere. By means of a gate valve the flow of gas through

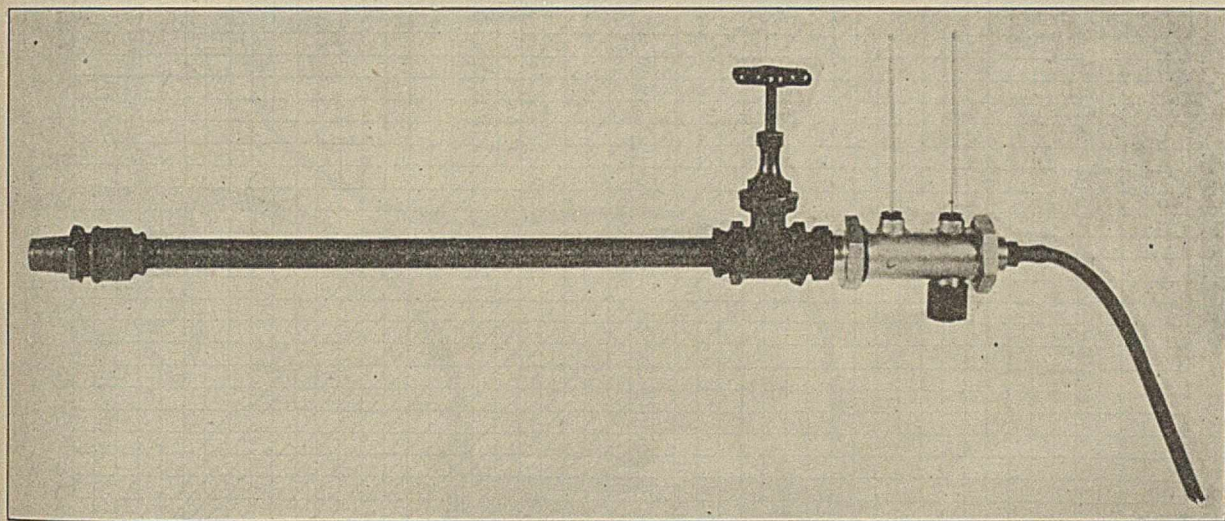


Fig. 1.—Special psychrometer used for determining the dew point of blast furnace gas.

carried over into the filter. This is exactly as we would expect since, in a section of gas and dust mixture equal to the area of the sampling pipe, the dust, having greater inertia than the gas, would naturally be more difficult to distort, and instead of flowing around the open end of the sampling pipe would lodge inside of it and be carried over into the filter. On the other hand, if the flow of gas in the sampling pipe exceeds that in the main, there will be a flow of gas from a zone outside the section equal to the area of the sampling pipe, and an undue proportion of gas will be distorted from its path and drawn into the sampling pipe. Hence, in case of excessive velocity in sampling, low results may be expected. After the above experiments had been completed, both sets of apparatus were run at the same correct velocity of 43 to 45 feet per second, and in all cases the results checked very closely—within a few hundredths of a grain.

These tests settle once for all the question of sampling

the instrument is regulated so that the temperature of the gas is reduced to a point between 130° and 140° F. Dry and wet bulb readings are then taken for half an hour or more. By referring to Psychrometric Tables, the dew points are obtained and the average dew point for the period is accepted for use in the formula used in running the test. For gas from furnaces on Bessemer burden the average dew point is about 118° F.

2. *Weight of One Cubic Foot of the Gas at Main Conditions.*—From average analyses of the gas in question, the weight of one cu. ft. of dry gas at standard conditions of 62° F. and 30" Hg is calculated, using the following weights, as recently given by the Bureau of Standards, Washington, D. C.

CO ₂	0.11660 lb. per cu. ft.
CO.....	0.07375 lb. per cu. ft.
H.....	0.005302 lb. per cu. ft.
CH ₄	0.04228 lb. per cu. ft.
N.....	0.07377 lb. per cu. ft.

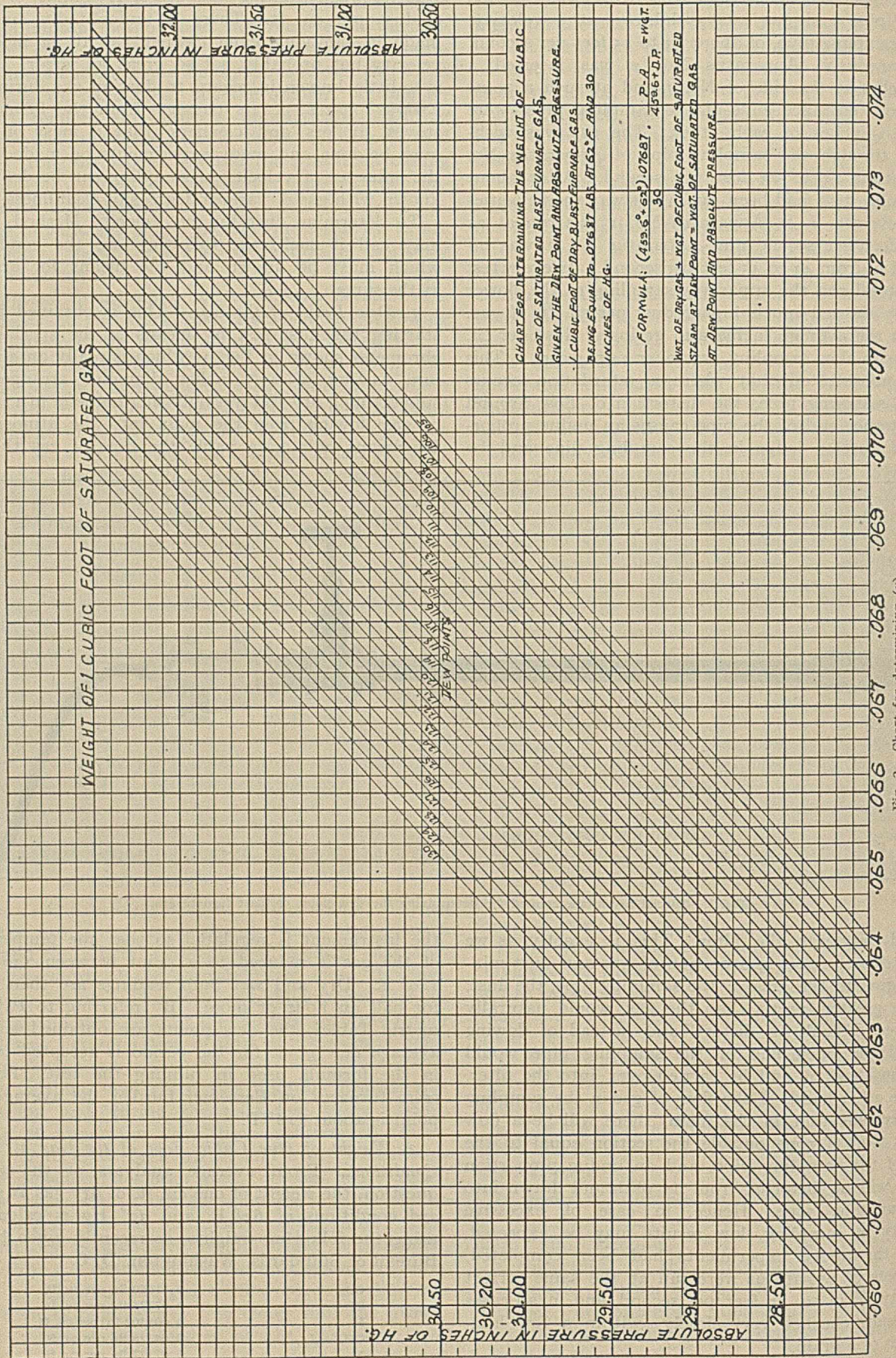


Fig. 2.—Chart for determining (5).

The average analysis, by volume, of blast-furnace gas from a furnace on Bessemer burden is as follows:

CO ₂	13.0% by vol. dry gas.
CO.....	26.1
H.....	3.5
CH ₄	0.2
N.....	57.2

Thus one cu. ft. of blast-furnace gas at 62° F. and 30" Hg weighs 0.07687 pound. These figures are the average of the results of over 4000 daily analyses of 24-hour cumulative samples.

Knowing the absolute pressure of the gas at main conditions, and having determined the dew point, the weight of one cu. ft. of saturated gas at this dew point temperature is determined from the chart, shown in Fig. 2, which gives the combined weight of dry gas, calculated to the desired temperature and pressure, and the aqueous vapor, as given in Marks and Davis' Steam Tables, in one cu. ft. of

developed from the well known velocity formula $V = \sqrt{2gh}$ as follows:

If: V equals velocity, in feet per second.

g equals gravity, equals 32.16.

h equals height of a column of gas in question one foot square equal to the velocity head.

h' equals equivalent velocity head in inches of water.

p equals equivalent velocity head in lbs. per sq. ft.

d equals weight of one cu. ft. of the gas in question at main conditions.

$$\text{Then: } h = p/d \quad (1)$$

And since one cu. ft. of water weighs 62.3 pounds

$$p = h' \cdot 62.3/12 \quad (2)$$

$$V = \sqrt{\frac{64 \cdot 32 \cdot h' \cdot 62.3/12}{d}} \quad (3)$$

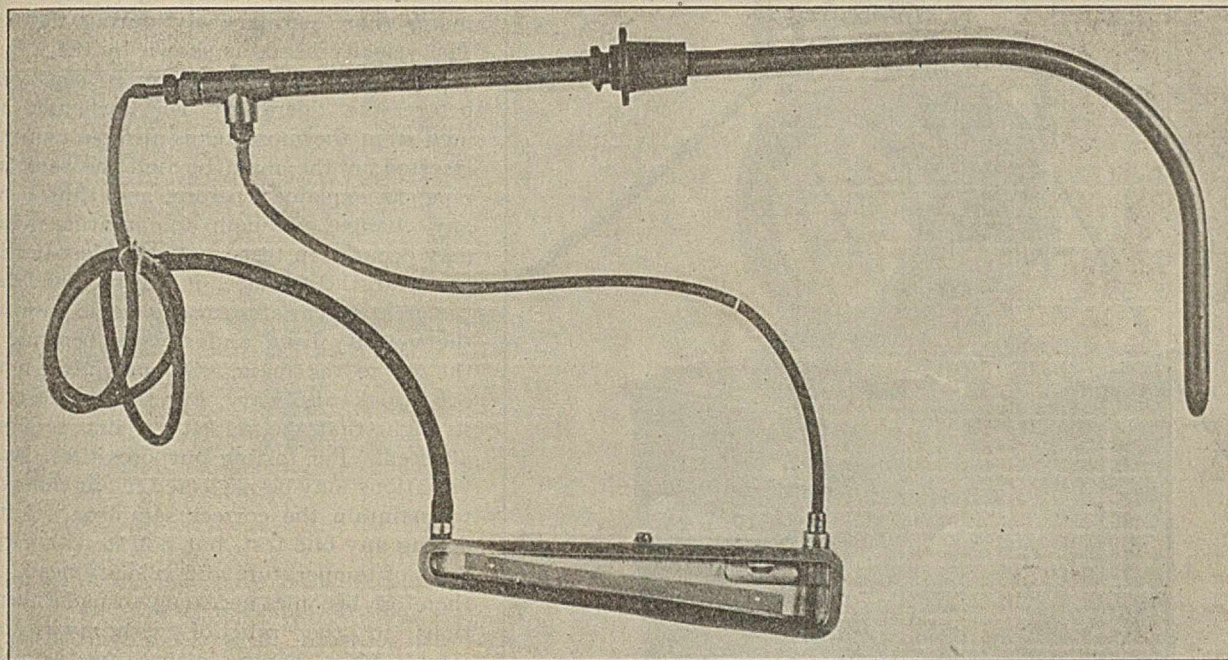


Fig. 3.—Pitot tube connected with Ellison gage.

saturated gas at any desired pressure and dew point. This figure is then converted to the new weight at the main temperature, calculating as though the saturated gas were a perfect gas.

3. *Temperature of the Gas in the Main.*—This is obtained by a mercury thermometer with an 18-inch stem, which is inserted into the main just beyond the point where the dust sample is taken.

4. *Pressure of the Gas in the Main.*—This is determined by means of a mercury column, graduated in inches.

5. *Velocity of the Gas in the Main.*—Knowing the weight of one cu. ft. of gas, at main conditions, all that is needed to determine velocity is the velocity head expressed in inches of water. This is obtained by a properly designed Pitot tube, shown in Fig. 3, and an Ellison differential gage. The formula is

$$V = \sqrt{\frac{334 h'}{d}} \quad (4)$$

6. *Temperature of the Gas at the Meter.*—This is obtained by means of an ordinary chemical mercury thermometer inserted at the proper place on the meter (see Fig. 4).

7. *Pressure of the Gas at the Meter.*—This is obtained by means of a mercury column attached to the meter (see Fig. 4).

8. *Time in Seconds Required to Meter 0.1 Cubic Foot at Meter Conditions.*—Ordinary wet test meters are so graduated that the large indicator makes one complete revolution for each 0.1 cu. ft. An ordinary stop watch, graduated in fifths of a second, is used to obtain the time required for the indicator to make one revolution.

9. *Aqueous Pressure at the Temperature of the Dew Point and of the Gas at the Meter.*—All aqueous pressures used are taken from "Steam Tables and Diagrams," by Marks and Davis.

10. *Total Grains of Dust Collected.*—The filter used is the Brady Gas Filter, shown in Fig. 5. In this apparatus the dust is collected in a Soxhlet extraction shell of 33 by 93 mm., supported in a horizontal

seconds time, makes this a convenient apparatus for dust determinations.

11. *Total Volume of Gas Metered.*—This is determined by a Junker's improved wet test meter graduated in cu. ft. The greatest speed at which this meter can correctly register is about 0.1 cu. ft. per 9 to 10 seconds. This fact must be borne in mind when selecting the size of the sampling pipe to be used to obtain the desired velocity.

12. *Duplication of Main Velocity in Sampling Pipe.*—Having described the requisites for a correct dust test and means for procuring the same, it will next be in order to briefly describe the method of obtaining the correct velocity in the sampling pipe—or in other words, of duplicating the main velocity. The method for obtaining the latter has already been given above. The Pitot tube mentioned, shown in Fig. 3, is inserted at the side of the sampling pipe and remains there permanently during the test. The velocity head, as shown by the Ellison gage, see Fig. 3, therefore, is constantly before the operator. The armoured 18-inch stem thermometer is also permanently inserted in the main beyond the sampling pipe, as explained before, and thus shows any changes of main temperature which may occur. In tests made on blast-furnace gas near the furnace, it will be found that the greatest variables to be dealt with are the velocity head and the temperature of the gas in the main. Of course, the other conditions also vary, but they are usually so slight that the velocity is not seriously affected. For testing purposes these latter variations may be neglected in our endeavor to maintain the correct sampling velocity during any one test, but not so with variations of temperature and velocity head. It therefore becomes necessary to make alterations in the rate of withdrawing our sample when changes in these two variables occur.

The expressions and calculations used in the mathematical computations for obtaining proper velocities are as follows:

V_m equals volume of gas at meter conditions metered in time t .

V_p equals equivalent volume of gas at main conditions.

V_1 equals equivalent volume of gas at dew point conditions.

T_1 equals absolute temperature of the dew point of the gas.

T_p equals absolute temperature of the gas in the main.

T_m equals absolute temperature of the gas at the meter.

P_p equals absolute pressure of the gas in the main.

P_m equals absolute pressure of the gas at the meter.

A_1 equals pressure of aqueous vapor at T_1 .

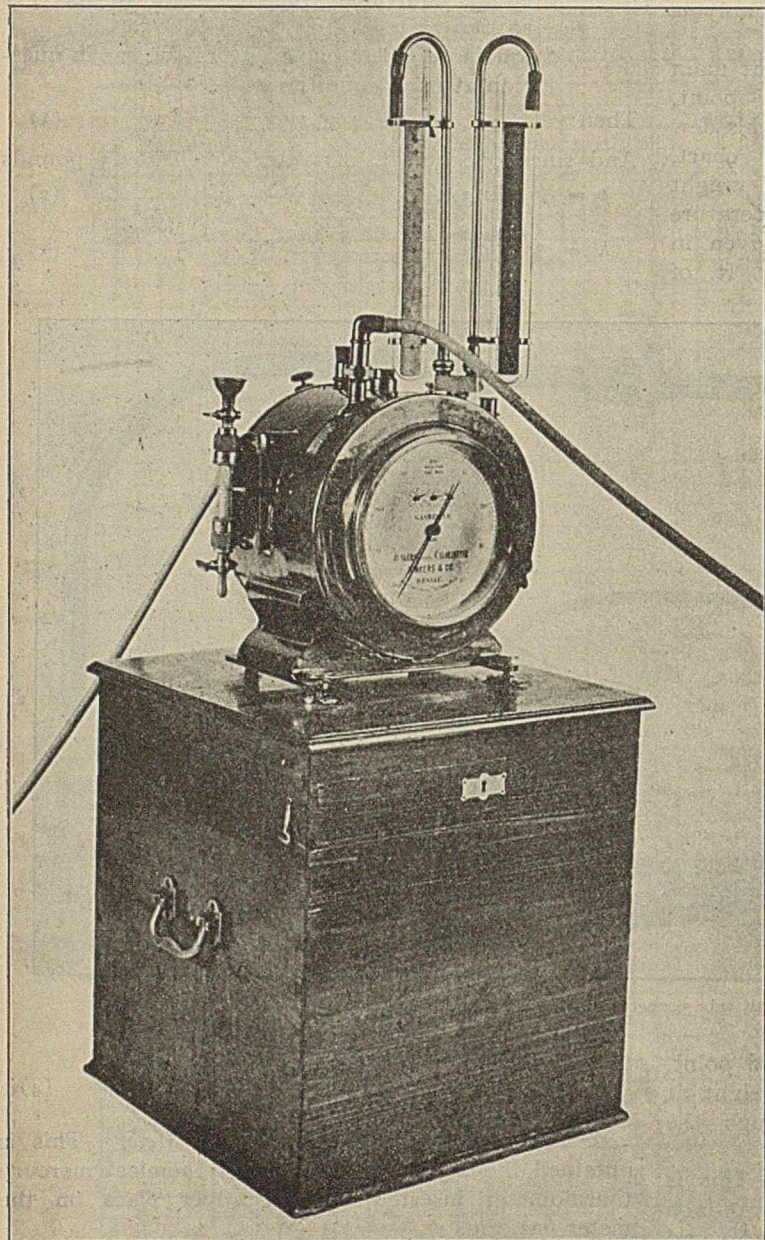


Fig. 4.—Wet test meter and attachments.

position by having its open end clamped between two tapering cylindrical faces. The gas flows through the paper shell into a surrounding metallic shell, there being a space of about $\frac{3}{16}$ of an inch between the outer surface of the former and the inner surface of the latter. The wonderful porosity of this filter and the convenience of being able to easily withdraw the used filter and substitute a new one in a few

A_m equals pressure of aqueous vapor at T_m .
 t equals time in seconds required to meter V_m .
 a equals cross sectional area of sampling pipe in sq. ft.
 v_p equals velocity of gas in main in feet per second, therefore the velocity desired in the sampling pipe. Since the gas is cooled below its dew point before being delivered to the meter it will reach the latter in a saturated condition. We wish to determine what the volume V_m will be at actual main conditions in terms of V_1 . This can best be shown in considering the operation in two steps: first, obtain the expression for the volume at dew point conditions; second, convert the volume at dew point conditions to actual main conditions. We know that in a cu. ft. of saturated gas the dry gas present will occupy the same volume as the saturated gas but the pressure will be different. We may, therefore, consider that V_m is the volume of either dry or saturated gas at the meter. Likewise, V_1 may be considered as being the equivalent volume of either dry gas or saturated gas at the

$$t = \frac{V_m}{a \cdot v_p} \cdot \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \tag{9}$$

If the velocity in the main and in the sample pipe are to be equal then $V = v_p$.

Substituting the value of $V = \sqrt{\frac{334 h'}{d}}$ for v_p in formula (9), we have

$$t = \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \cdot \frac{V_m}{a \cdot \sqrt{\frac{334 h'}{d}}} \tag{10}$$

If we designate the weight of one cu. ft. of the saturated gas at the dew point and main pressure, as shown on the chart (see Fig. 2) as y , then

$$d = y \cdot \frac{T_1}{T_p} \tag{11}$$

Substituting this value of d in (10) we have

$$t = \frac{(P_m - A_m) \cdot V_m \cdot T_p}{(P_p - A_1) \cdot a \cdot T_m} \cdot \sqrt{\frac{y \cdot T_1}{334 \cdot h' \cdot T_p}} \tag{12}$$

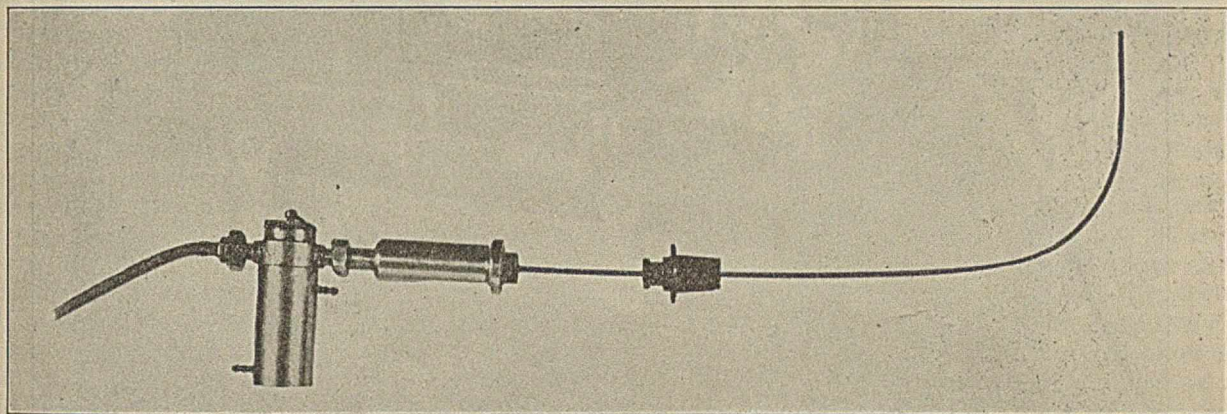


Fig. 5.—Sampling pipe, Brady filter and condenser.

dew point. Considering both volumes as being of dry gas, for the time being, we may apply the gas laws to convert V_m to V_1 , knowing the temperature T_m and T_1 and by subtracting the vapor pressures as given by the tables from the absolute pressures P_m and P_p .

$$V_1 = V_m \cdot \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_1}{T_m} \tag{5}$$

Having now the volume at the dew point we need only convert it to its new volume at T_p .

Thus we have

$$V_p = V_1 \cdot \frac{T_p}{T_1} = V_m \cdot \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \tag{6}$$

The volume V_p , being the volume of gas which flows through a in t seconds, then

$$V_p = v_p \cdot a \cdot t \tag{7}$$

From (6) and (7)

$$v_p \cdot a \cdot t = V_m \cdot \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \tag{8}$$

or

or

$$t = \sqrt{\frac{y \cdot T_1}{334}} \cdot \frac{V_m (P_m - A_m)}{T_m \cdot a} \cdot \frac{1}{P_p - A_1} \cdot \sqrt{\frac{T_p}{h'}} \tag{13}$$

This arrangement is most convenient, since for any test the above two factors on the right side of the equation may be considered as constant, and the third factor only will vary. This last factor is determined with the slide rule as often as changes in conditions warrant. The result of the latter calculation is then multiplied by the already obtained product of the first two factors. The final figure thus obtained will be the time in seconds which should elapse while the indicator on the meter is making one revolution, in order to insure the same velocity in the sampling pipe as in the main.

The actual method of running a dust test is as follows: Having selected the most advantageous point at which to withdraw the sample, four holes are drilled in the main in the following relative positions: The sample hole should be in such a position that the sampling pipe can be easily inserted and withdrawn

from the main at will, and should be tapped for a $1\frac{1}{2}$ -inch pipe thread. At about the same level, assuming that the main is vertical, another $1\frac{1}{2}$ -inch hole is tapped for the Pitot tube. Beyond these holes, relative to the flow of gas, a 1-inch hole is tapped for the large armoured thermometer, and several inches at one side of this 1-inch hole, a short length or nipple of $\frac{1}{8}$ -inch pipe is inserted to receive the rubber tube connecting with the mercury column which is used to show the static pressure of the gas. Brass collars, having an inner tapering surface, ground to fit similarly tapering plugs, are screwed in the $1\frac{1}{2}$ -inch holes. All parts of the apparatus inserted in the main at any time during the test are fitted

accurate readings with this apparatus, a velocity of at least 15 feet per second should be maintained while making dry and wet bulb readings. The Pitot tube is connected to an Ellison 2-inch differential draught gage by means of suitable tubing. In practice it is advisable to insert a three-way stopcock in each tube so that by turning both cocks simultaneously one-half turn, the gas pressure is shut off and each end of the gage subjected to atmospheric pressure only. The oil in the gage tube can then be made to register zero to start with. This also gives excellent means of checking up the gage at any time during the test. The main is then explored to find the zone of average velocity, and the sampling pipe is later

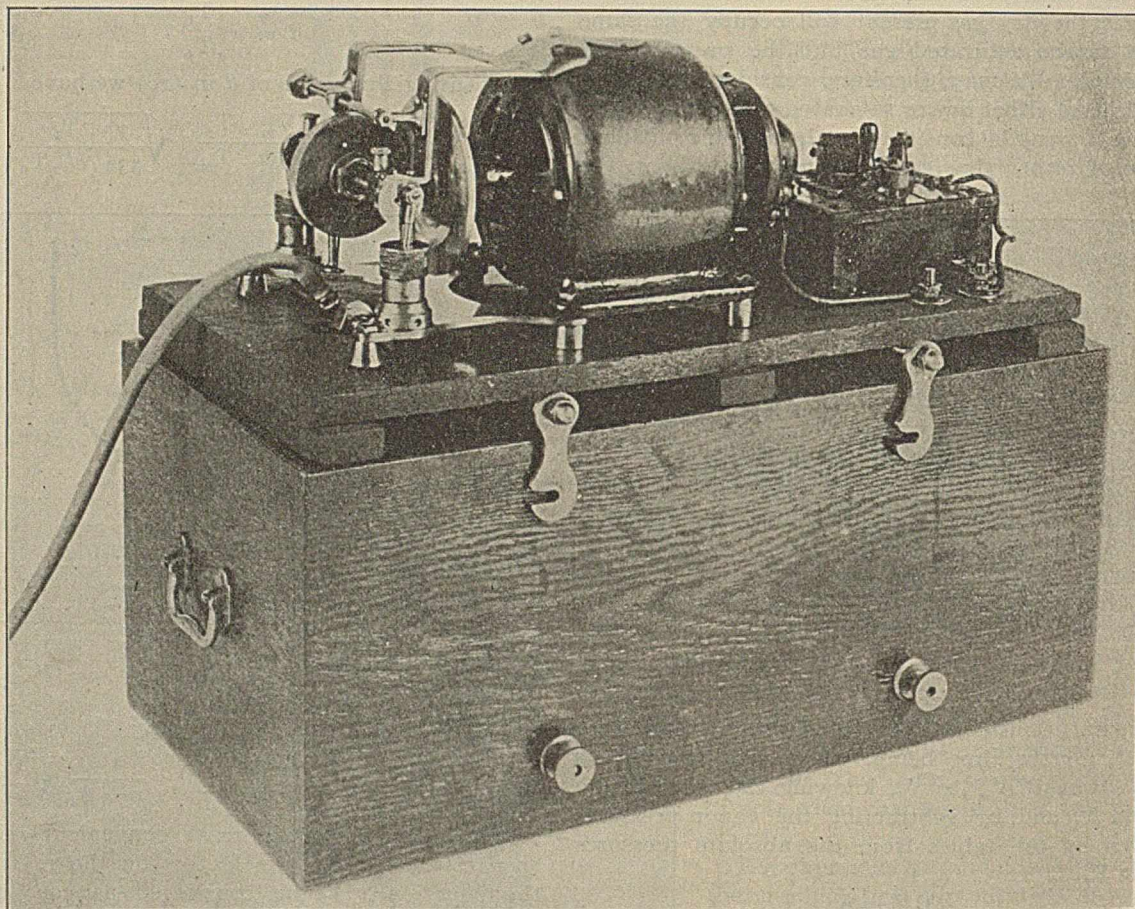


Fig. 6.—Suction pump connected to $\frac{1}{4}$ H. P. motor.

with the above-mentioned tapering plugs which fit these collars and thus allow the insertion and withdrawal of such apparatus without making any threaded connections. A solid tapering stopper is used to plug the hole when there is no test being run. The special psychrometer is next inserted in one of these $1\frac{1}{2}$ -inch collars and the Pitot tube in the other.

It is sometimes necessary to insert a length of $1\frac{1}{2}$ -inch pipe between the tapering plug and the psychrometer to facilitate cooling the gas down to the proper temperature without too much loss of velocity. It may be here stated that to obtain

adjusted to sample at this same distance within the main. The armoured 18-inch stem thermometer is next screwed in place and connection is made by rubber tubing between the small $\frac{1}{8}$ -inch nipple and the mercury column on the meter used to register static pressure. Readings are then taken periodically for 30 minutes or more, of the velocity head, dry and wet bulb temperatures, main temperature, and static pressure. By means of the Psychrometric Tables the average dew point is determined from the dry and wet bulb readings. The average data obtained from all these readings can then be used to determine the average velocity in the main by use of

the velocity formula given above. Having determined the velocity at which the gas flows in the main, and, therefore, the velocity at which the gas must flow in the sampling pipe, we are now in a position to determine what size sampling pipe will be the most convenient to use. If the operator has had some experience, this can readily be decided from past experiments, but, if it is desired to mathematically determine the correct pipe to be used, equation (9) may be solved for a . By substituting atmospheric pressure and temperature for the meter conditions in the formula to determine t (see Formula 9), an approximate time for metering 0.1 cu. ft. is obtained. It must be understood, of course, that only an approximate figure is desired at first, since, as soon as the test starts, the necessary data will be obtained for calculating a more accurate result. In all of these calculations, a 10-inch slide rule is used and the result is accurate enough for the desired purpose.

A previously dried and weighed Soxhlet shell is next inserted in the Brady filter, which is then attached to the sampling pipe decided upon, and the aluminium condenser is connected to the exit end of the filter. A rubber tube of $\frac{3}{8}$ -inch diameter is used to connect the exit end of the condenser to the meter and another similar tube connects the exit end of the meter to the suction pump, shown in Fig. 6. In case the static pressure of the gas is sufficiently high it may be unnecessary to use the pump, in which case a screw cock placed on the tubing from the exit end of the meter serves to regulate the flow of gas through the sampling pipe. The apparatus being connected and ready for the test, an aluminium cap is slipped over the entrance end of the sampling pipe, the hole in the main is opened, and the pipe inserted in position, thus sealed, in order to warm up and prevent a deposition of moisture from tending to clog up the pipe on starting the test. At the same time the electric heater, which consists of a tin box containing two 16 c. p. electric bulbs, is placed in position surrounding the Brady filter and the reading of the meter is recorded. When both the sampling pipe and the filter have become heated, the apparatus is quickly withdrawn from the main, the aluminium cap promptly removed, and the pipe again inserted ready to take gas. As soon as possible after inserting the end of the sampling pipe in the main, the operator throws the switch which starts the pump, causing the sample to be drawn through the apparatus. By means of a wire suspended from above, or a stick supported on the floor, the apparatus is braced to keep it in a horizontal position. The operator at once begins to record the various readings such as meter pressure and temperature, main pressure and temperature, velocity head, static pressure and time required to meter 0.1 cu. ft. With this data and the figures from the aqueous pressure table he is able to obtain the correct value for t by means of the formula given, which is already partly calculated as previously described. From now on, readings are recorded regularly at specified intervals and quick calculations continuously made with the

slide rule to insure running the test at the correct velocity. At the end of the test the sampling pipe is withdrawn, the filter shell removed and a new one inserted for the next test. The meter is read and the difference between this and the previous reading gives the volume of gas metered. The shell containing the dust is dried for one hour and again weighed in a weighing bottle. The difference between this weight and the weight of the empty shell gives the total weight of dust collected. The average velocity of the main for the entire period is carefully figured together with the average velocity through the sampling pipe, and results are not accepted if a variation of over 5 feet per second was obtained between the two. The pump used is a friction-driven suction pump attached to a $\frac{1}{4}$ h. p. motor, and by means of a knurled wheel the speed of the pump may be regulated at will to obtain the desired velocity of sampling. The period of ordinary tests varies from 30 minutes to one hour and the size of the sample taken varies from 10 to 25 cu. ft., figured to standard conditions of 62° F. and 30 inches Hg. The size of sampling pipe most suitable to ordinary blast-furnace conditions is $\frac{3}{16}$ -inch inside diameter.

If the proper sampling pipe has been chosen, apparently considerable variations in conditions have a very slight effect on the rate of correct metering. While the above description of manipulations may give the idea that the method of running the test is difficult and complicated, it must be borne in mind that it is impossible and entirely unnecessary to make such delicate adjustments that the velocity in the sampling pipe will exactly duplicate the main velocity. It has been proved by our tests that a velocity in the sampling pipe within two or three feet per second of the main velocity is all that is necessary. Again, with practice it is surprising how expert the operator will become in judging what change in speed of sampling, or running the pump, is necessary for given changes in conditions. He is able to adjust his speed by judgment and then check up with the slide rule with surprising success. In about 100 tests run under quite a range of blast-furnace conditions our records show that the average velocity of the gas through the sampling pipe is within one or two feet per second of the main velocity.

SUMMARY.

1. Dust tests made in a continuously flowing stream of gas, where the dust per cu. ft. runs higher than 1.5 grains, are valueless unless the gas has been withdrawn from the main within two or three feet per second of the main velocity. It is possible that this statement may also apply for gas where the dust per cu. ft. is less than 1.5 grains, especially if ultimate results are desired.

2. Where the velocity of the gas in the sampling pipe is less than the velocity of the main the results obtained are high. Conversely when the velocity of sampling is too great, low results are obtained.

3. In all cases where it is desired to determine dust in gas the sample should be withdrawn through

a sampling pipe curved with a radius of 12 inches and facing the flow of gas.

4. The sample must be withdrawn where possible from a vertical pipe, or as near vertical as practicable and the sampling pipe should be inserted to such a degree

that the open end is in that region of the main where the mean velocity has been found to exist.

CHEMICAL LABORATORY,
ILLINOIS STEEL CO., SOUTH WORKS,
SO. CHICAGO, ILLINOIS.

PLANTS AND MACHINERY

A NEW ACCELERATED TEST FOR PAINTS,

By H. K. BENSON AND CARL POLLOCK.

Received July 20, 1911.

The ease with which iron corrodes when subjected to the action of electrolysis suggested the experimental work undertaken for the purpose of developing an accelerated test for the efficiency of paint used on metallic surfaces. When iron is coated with a protective paint, no corrosion takes place as long as moisture and air can be excluded. Whatever the real mechanism of corrosion may be, it is recognized that a paint must protect the metal surface by insulating or excluding it from the activity of air and moisture. Any means, therefore, that may show the resistance of paint materials to the breaking down of the coating film may be used to measure the comparative value of such films with regard to their permanency or endurance under actual and less active conditions.

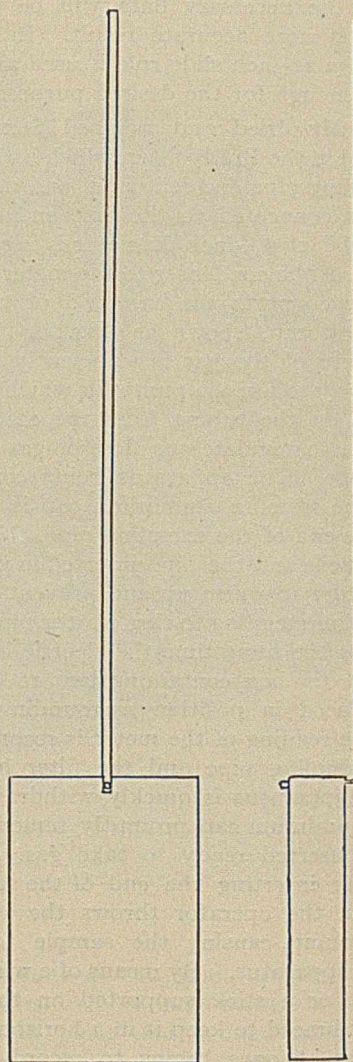
The apparatus used in obtaining the data given in the tables below consists of a simple electrolytic cell containing a normal salt solution for the electrolyte. The anode was a piece of clean steel coated with the paint to be tested. The cathode was platinum and the electrodes were placed four inches apart. Eight volts of direct current were used. A milliammeter was connected in the circuit to indicate the current flowing. Ammeter readings were taken as shown in Table III and from these readings and the constant voltage, the wattage was computed.

The painted electrodes used were made of pieces of steel about 1.4" long, 1.0" wide by 0.3" thick. A piece of copper wire about six inches long was fixed into one end of this steel rectangle by first cutting across the end with a hack saw a notch about an eighth of an inch deep and then wedging the wire into it. The diameter of the wire should be a little greater than the width of the saw kerf. The wire was then bent upwards as shown in the accompanying sketch.

The electrodes thus made were given two coats of paint, about a week being allowed for the first coat to dry. When the second coat was apparently dry, the electrodes were placed in an oven and kept at 45° C. for 12 hours. In order to facilitate rapid and uniform drying, it was found advantageous to round the edges of the electrode. (All the tests given in Table III except red lead (a) and aniline pitch dip were made with square cornered electrodes.) The electrodes were all of the same area and immersed in the solution to the same depth. The results are given in Table III.

For the purpose of this experiment, the insulating efficiency of the paints tested is taken as inversely

proportional to the wattage at the end of six hours. With a constant voltage, the efficiency is also inversely proportional to the average conductivity for the first six hours. While in general the experiments were conducted for 24 hours, in some cases the paints broke



*Sketch of Electrode.
Natural Scale*

down so completely before that time that the test was discontinued. For this and the additional reason that, in most cases, a nearly constant current had been reached by the end of six hours, that period was made the basis of comparison.

TABLE I.—PASSIVITY. BUBBLING TEST.

Pigment or base of	Weight. Steel Lost. Gram.	Pro- portional		Relative inhibitive value.
		area of steel.	Wt. lost per unit area.	
1. Aluminum paint....	0.0562	0.938	0.0598	1.000
2. Tar cement paint...	0.0780	0.939	0.0832	0.718
3. Asphaltum paint....	0.1000	1.000	0.1000	0.598
4. Red lead.....	0.1390	0.921	0.1510	0.396
5. Pitch paint.....	0.203	1.032	0.1970	0.302
6. Acheson graphite....	0.222	0.912	0.2160	0.277
7. R. I. W. paint.....	0.279	1.000	0.2790	0.214
8. P. & B. paint.....	0.298	0.912	0.3270	0.185
9. Slate lacquer.....	0.355	0.982	0.3650	0.165
10. Cement paint.....	0.4441	0.904	0.491	0.122

TABLE II.—PASSIVITY. DAMP FILM TEST.

Order of efficiency.	Pigment or residue.
1.....	Red lead
2.....	P. & B. paint
3.....	Aluminum paint
4.....	Asphaltum paint
5.....	Tar and cement paint
6.....	Acheson graphite
7.....	Slate lacquer

other of an insulation type like the one above described, are necessary to determine the efficiency of a paint. By carefully standardizing these tests it should be possible to compute the value of a paint in relation to some commonly accepted unit.

By way of illustration, we may use red lead for one example and aniline pitch paint for the other. The problem is to ascertain the relative efficiency of these two paints. Let "I" equal the inhibitive value of a paint and "R" the resistant or insulating value of the same paint, then "V" the total value of the paint equals "RI." (An absolute standard to which to refer the inhibitive and insulating values of a paint must, of course, be eventually chosen.) In the case of red lead

$$V = 0.282 \times 0.396 = 0.112$$

and for aniline pitch paint

$$V = 0.473 \times 0.302 = 0.145,$$

TABLE III.—INSULATION TESTS.

Paint used.	No. of coats.	Voltage.	Amperage at end of						Wattage at end of						Efficiency R. I. W. = 1.	
			0 min.	10 min.	30 min.	1 hr.	2 hrs.	6 hrs.	24 hrs.	0 min.	30 min.	1 hr.	2 hrs.	6 hrs.		24 hrs.
1. R. I. W. paint.....	2	8.0	0.002	0.005	0.008	0.010	0.013	0.012	0.040	0.0006	0.0028	0.0073	0.0193	0.0693	0.5273	1.00
2. Pitch in aniline.....	2	8.0	0.002	0.005	0.010	0.015	0.020	0.040	0.040	0.0006	0.0031	0.0091	0.0266	0.1466	0.8666	0.473
3. Red lead (a).....	2	8.0	0.000	0.003	0.008	0.015	0.020	0.090	0.115	0.00025	0.0021	0.0081	0.0256	0.2456	2.095	0.282
4. Red lead (b).....	2	8.0	0.000	0.003	0.010	0.028	0.045	0.090	0.115	0.0002	0.0024	0.0115	0.0480	0.3180	2.168	0.218
5. Cement paint.....	3	8.0	0.025	0.032	0.042	0.054	0.065	0.070	0.060	0.0048	0.0171	0.0411	0.1056	0.3756	1.545	0.185
6. Acheson's graphite....	2	8.0	0.055	0.058	0.066	0.075	0.088	0.100	0.100	0.0094	0.0300	0.0652	0.1467	0.5227	2.323	0.1315
7. P. & B. paint.....	2	8.0	0.020	0.100	..	0.130	0.130	0.130	..	0.005	..	0.101	0.231	0.751	..	0.0923
8. Asphaltum paint.....	2	8.0	0.025	0.100	0.15	0.120	0.130	0.140	..	0.0104	0.0463	0.1048	0.2298	0.7698	..	0.0900
9. White shellac.....	2	8.0	0.000	0.100	0.150	0.180	0.200	0.200	..	0.00	0.0500	0.1325	0.3225	1.1225	..	0.0615
10. Slate lacquer.....	2	8.0	0.010	0.120	0.155	0.180	0.210	0.210	0.195	0.0126	0.0584	0.1419	0.3369	1.1569	4.8019	0.060
11. Aluminum paint.....	2	8.0	0.085	0.155	0.185	0.0183	0.0749
12. Dull black var-lac.....	2	8.0	0.120	0.150	0.180	0.0225	0.0775
Pitch dip ¹	very thick	8.0	0.002	0.0025	0.0025	0.0020	0.0010	0.000	0.000	0.0002	0.0085	0.0095	0.0110	0.0130	0.0130	5.33

¹ Not comparable with others.

Efficiency = K/W₆. Assuming efficiency of R. I. W. = 1. Then K = 0.0693. Wattage at end of 6 hrs. = W₆.

COMPARISON TESTS.

In order to obtain other means for comparison, the same paints were tested by the accelerated tests described by Cushman.² Table I gives numerical values from the bubbling test while Table II gives the relative efficiency of the paints as determined by the damp film test.

A number of the paints were tested by Magnusson³ and Smith,² in attempting to find means to prevent the corrosion of iron in concrete. While in these experiments, the conditions were different, the results in the main tend to confirm the same order of relative efficiency.

INTERPRETATION OF RESULTS.

To obtain a comparative rating, the efficiency of some one paint was taken at unity and all others calculated on that basis. It is the opinion of the writers that two accelerated tests, one of the inhibitive character described by Cushman³ and the

comparative results which are consistent with service tests of a limited character.

LABORATORY OF INDUSTRIAL CHEMISTRY,
UNIVERSITY OF WASHINGTON.

A THERMOSTAT FOR MODERATE TEMPERATURES.

By A. M. BUSWELL AND RALPH H. MCKEE.

Received August 7, 1911.

The ordinary thermoregulator consisting of a mercury interrupter and relay, operated at low voltage, for turning on and off the heating system (electricity or gas), has given satisfaction. The other simpler type of thermoregulator, depending on the effect of temperature on a gas or a liquid, placed in a vessel whose only outlet is a J shaped tube filled with mercury and having platinum wires piercing each arm to serve as binding posts for the electrical connections, is, in the forms previously used,¹ for a short time fairly satisfactory where a range of several degrees is allowable. But when it is desired to keep an in-

¹ Bull. 35, Office of Public Roads, U. S. Department of Agriculture.

² A. I. E. E. Proceedings, 30, 939 (May, 1911).

³ Loc. cit.

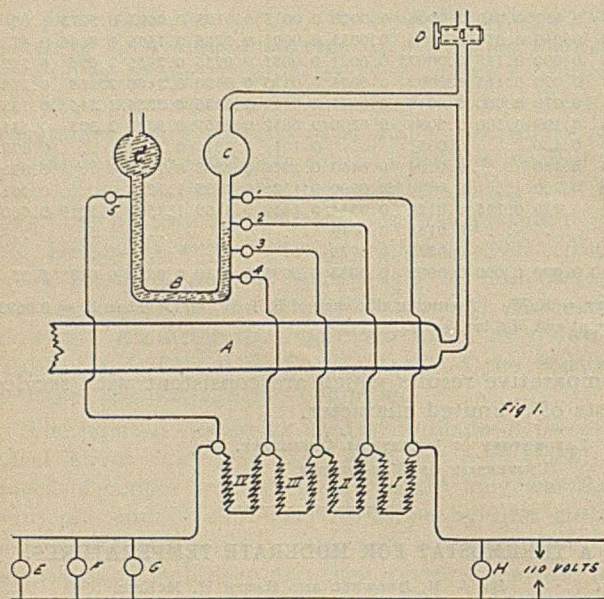
¹ Summerville, Elec. World, 57, 112 (1911); cf. bibliography given by Geer, J. Phys. Chem., 6, 101 (1902).

incubator constant to well within one degree the following difficulties arise.

1. When air is the expanding substance, the variation in atmospheric pressure, say 1.5 cm., will cause a change in volume of the gas of one in 50, whereas at 37° C., one degree will cause a variation of only one in 310; and the arcing, if the interrupter is used across a 110 volt circuit, volatilizes and oxidizes the mercury.

2. When toluene or ethyl alcohol is the expanding substance, the arcing cracks the liquid, giving carbon and a gas in the case of toluene and a permanent gas (hydrogen?) in the case of alcohol. The production of gas in either case is so great when 110 volts are used that the mercury is forced back and prevented from closing the circuit at the desired temperature.

The fact that there is a critical arcing voltage, varying with the composition of the electrodes, below which no arc can be formed, suggested that by cutting down the voltage across which the interrupter operated the production of gas might be eliminated. Experiment soon showed that with platinum and mercury electrodes operating across 20 volts or less, there was no arcing effect and practically no gas was formed by the spark at the make and break.



A thermostat (bacteria incubator) for water analysis, to be kept at 37° by a thermoregulator operated on this principle, was made, using a wooden box 14" × 18" × 24". Incandescent lights for heating were arranged at the bottom and a sheet iron plate was placed above them to give uniform distribution of heat and to shade the cultures.

The thermoregulator as shown in Fig 1 is easy of construction. A is a glass tube one centimeter in diameter, holding about 150 cc. of absolute alcohol. B is a capillary tube (inner diameter about 1.2 mm.) extending between the reservoirs C and C'. Mercury fills B and C'. A is connected to C and D by ordinary 6 mm. glass tubing. D is a stopcock for filling the apparatus. Nos. 1, 2, 3, 4 and 5 are platinum wires

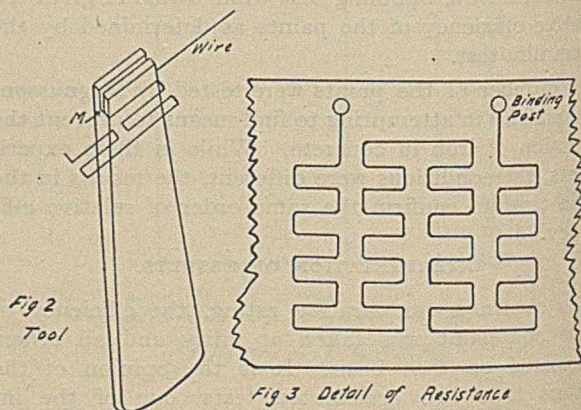
which pierce the capillary tube B and are connected by wires to the "Nichrome" resistances I, II, III and IV. The latter are mounted on an asbestos board placed with the lights beneath the iron plate, and are so constructed that the drop in pressure across each is 20 volts. Lights E, F and G (one 8 c. p. and two 4 c. p. lights) are arranged in series with the mercury, and with an eight candle power light H, connected to burn at full heat continuously, give somewhat more than enough heat to keep the temperature at 37° C.

The apparatus is so adjusted by the stopcock D that at 37° the mercury just makes contact with wire No. 2. The circuit then contains resistance I and the mercury in series with the lights E, F and G. If the temperature rises slightly the mercury is forced down, the contact at 2 is broken, and resistance II is thrown into the circuit. If it continues to rise, III and IV are thrown in in like manner. If the temperature drops, the mercury rises cutting out the resistances and brings the lights up to full heat.

Without attention the incubator kept within half a degree of 37° for two months. Reservoir C is large enough so that if the current is cut off for any reason, mercury will not be drawn over into A, and C' contains enough mercury so that under the same conditions the left arm of B will never be emptied below 5. On turning on the current the incubator comes up to temperature without attention.

The number of ohms for the resistances were determined by the formula $r = \frac{Re}{L - e}$, where r is the resistance desired, R the resistance already in circuit, e the drop in voltage desired (20 volts in this case), and L the line voltage. In our case where the resistance of E, F and G was 110 ohms, resistance I was 24.4 ohms, II 29.9 ohms, III 37.0 ohms and IV 45.5 ohms. These resistances were made of No. 32 Nichrome wire, two ohms resistance per foot.

A convenient tool for making the resistance plates is shown in Fig. 2, in which M is a slit sawed in the



end through which the wire runs. The lower end is flattened so that the tool may be held easily between the thumb and fingers. It works equally well with ribbon or wire. The plates are as compact as those

of the same resistance wound in the old way on brads driven in a board, and not more than one-third the time is required for winding. The network may be conveniently stayed by the use of a little asbestos cement.

The glassblowing and bending is all of a simple character and can easily be done in three or four hours; and the winding of resistances and making connections should require no longer time.

UNIVERSITY OF MAINE,
ORONO.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE OKLAHOMA AGRICULTURAL EXPERIMENT STATION.]

A NEW FORM OF EXTRACTION APPARATUS.

By C. K. FRANCIS.
Received July 15, 1911.

The apparatus¹ (Fig. 1) consists of a modified condenser, A, and an improved flask, B, together with an extraction tube, C. There are no ground joints, the one seal necessary being made with mercury. No support is required for the flask.

The condenser used in the apparatus shown is of the Hopkins type, provided with a special extraction chamber, EC, and a dropping tube, DT.² The lower part of the extraction chamber is partially constricted on opposite sides about 10 mm. above the bottom. The two constrictions are so made (Fig. 2, IN) that each extends nearly one-half the circumference of the tube without meeting on either side. This arrangement leaves the internal diameter, 3 cm., unchanged in two diametrically opposite places and reduced to about 2.7 cm. for the remainder of the circumference.

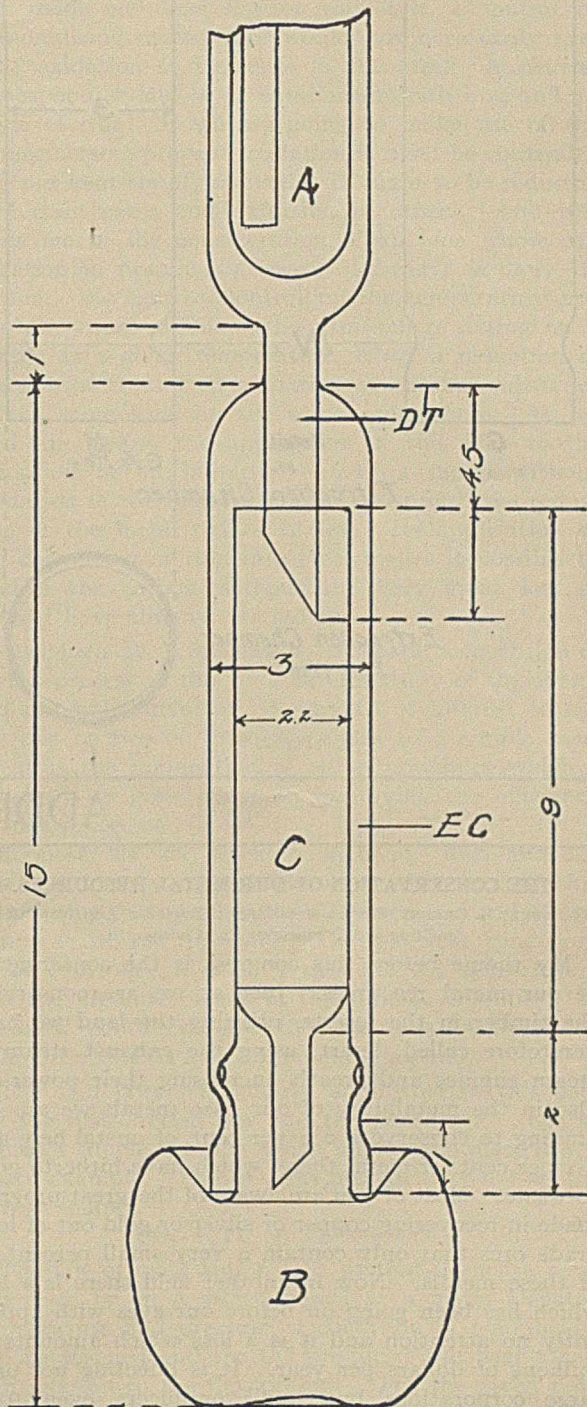
The modifications of the Knorr flask are two knob-like perforated projections (Fig. 3, PP) on opposite sides of the neck and about 15 mm. above the base of the shoulder. These projections are so placed that they fit into the extraction chamber where the internal diameter is greatest. The holes (Fig. 3, HO) in the neck of the flask are about 3 mm. in diameter. These permit ample passage for vapor and return for the liquid which would otherwise collect around the neck of the flask.

The extraction tube (Fig. 1, C) is 9 cm. long, 2.2 cm. external diameter and has a stem about 2 cm. long. It may be packed with cotton, asbestos, etc., together with the sample, and supported on the flask as shown in Fig. 1. A spiral spring of copper wire laid cross-wise and pushed down on the charge prevents the contents from being forced out of the tube by expansion of vapor. The regular paper shells may be used in place of glass tubes if supported on very small funnels.

The flask may be locked into the condenser by inserting the neck into the extraction chamber and giving the flask a quarter turn. This system fixes the flask securely and it cannot be accidentally pulled over or disturbed in any way. No support for the flask is necessary; this is especially convenient when heating with electricity or with warm water.

¹ A modification of a piece of apparatus designed by G. L. Holter and which has been in use in this laboratory for several years.
² Any of the ordinary condensers may be modified in the same way.

The temperature may be lowered by raising the apparatus above the source of heat. Electric lights, encased in compartments made of asbestos board, are used in this laboratory for heating the extraction flasks, but the apparatus described may be



Complete Apparatus.

Fig. 1.

found convenient where there is waste steam or warm water available.

The arrangement is economical in the use of solvents; 30 cc. of ether are ample for the usual fat extractions.

The position of the holes in the neck of the flask prevents any appreciable amount of condensed vapors

from collecting outside of the flask. The apparatus is especially applicable to alkaloidal and fat ex-

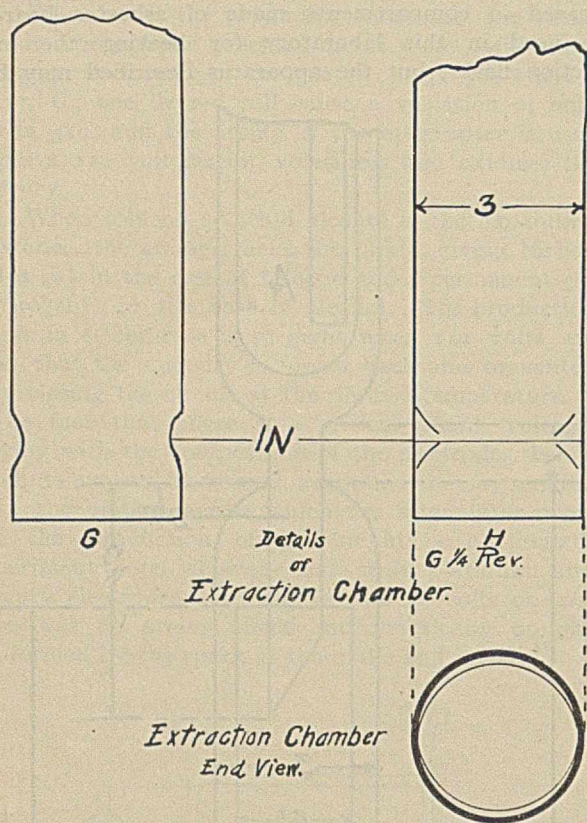


Fig. 2.

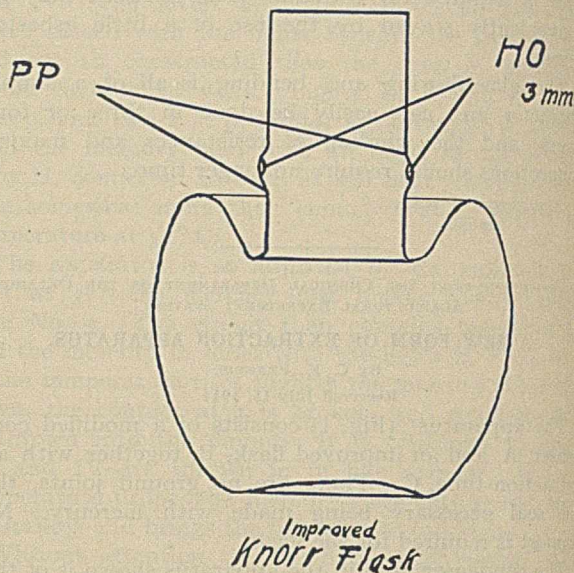


Fig. 3.

tractions. The cost is much less than that of the older forms of extraction apparatus.

E. H. Sargent & Co., Chicago, Ill., have recently made a large number of these special condensers and flasks for this laboratory.

STILLWATER, OKLA.

ADDRESSES.

THE CONSERVATION OF OUR METAL RESOURCES.¹

By ALBERT E. GREENE, Electro-Metallurgical Engineer, American Electric Smelting and Engineering Co., Chicago, Ill.

My theme before this congress is the conservation of our metal resources. Just as we are conserving the timber in the forests, utilizing the land we have heretofore called desert, using the exhaust steam of steam engines and greatly increasing their power, so also in the metallurgy of our base metals we are beginning to conserve a 0.1 per cent. of metal here and a 1 per cent. of metal there, which have hitherto gone to waste. Most of you are aware of the great progress made in recovering copper or silver or gold out of low-grade ores that only contain a very small percentage of these metals. Now in another field there is a loss which has been going on before our eyes with apparently no attention and it is a loss which amounts to millions of dollars per year. It is affecting not only large corporations but small producers even to a greater extent. The loss to which I refer is the loss of metal in the processes of making steel and other metals from ores.

In the production of the 20 million tons of steel per annum in this country there is a loss of metal by oxidation during the conversion process which proba-

bly aggregates one million tons. Most of this metal is lost in the slag and some of it can be reduced again by smelting the slag in the blast furnace, but in the Bessemer process a large part is blown out of the vessel in fine dust which is difficult to collect. The loss of metal by oxidation in the Bessemer process alone probably aggregates over 500,000 tons per year.

Another significant fact is that a very considerable part of the metal lost by oxidation consists of elements which are more valuable than iron—such as manganese and silicon. Those elements are usually required by specification in the finished steel, and although the iron ore usually contains enough of them, and the blast-furnace process usually reduces them into the iron in sufficient quantity to meet specifications without any additions, yet in the Bessemer and open-hearth processes they are almost invariably oxidized again and practically lost. When one remembers these facts and what it costs to reduce these metals into the iron and that after they are oxidized out they have to be replaced by expensive alloy additions to the steel, it seems as though this were an excellent opportunity to apply conservation theories to advantage.

My object in this paper is to point out how such losses as these can be and are beginning to be dimin-

¹ Presented before the Congress of Technology at the Massachusetts Institute of Technology, Boston, April, 1911.

ished, and another object is to show how the application of physical and chemical principles to those problems is one of the greatest aids we have in accomplishing this end. If I can do this I shall feel that, in some small way at least, I shall have served my Alma Mater, to whom I feel very greatly indebted.

It has been my privilege to have followed one of the newer fields of development influencing the conservation of our metal. This is the field of high-temperature chemistry which the advent of the electric furnace has opened up. It has been said by prominent steel men that in the next ten years the greatest developments in that industry will be those affecting increased metallurgical efficiency. I venture to say that in this one industry by the application of electricity together with improved chemical processes there will result a saving of metal which will amount to hundreds of thousands of tons per annum.

I wish to try to show how the electric furnace can influence conservation in such a way. It is not simply because the electric furnace provides a means of getting extremely high temperature but rather because by means of electrically developed heat we can simultaneously control the temperature and the chemical reactions wholly independently of one another. This is a most important fact and it opens up a whole new field of chemistry especially where the gaseous treatment of metal is involved.

For sake of comparison, let us consider the methods of heating now in use. Almost invariably heat is obtained by the combustion of fuel. The fuel is usually burned in the same chamber with the material heated so that gaseous products of combustion come in contact with the material. These products of combustion are themselves of an oxidizing nature since they always contain oxygen and, furthermore, to obtain high temperatures efficiently, it is necessary to burn the fuel with excess of oxygen which makes the atmosphere still more oxidizing. Thus we see that as a general thing high temperatures are obtained only under more or less oxidizing conditions, whether such conditions be desired or not. For example, where steel scrap is melted in an open-hearth furnace the steel takes up more or less oxygen in some form or other and the melted steel must be deoxidized by use of silicon and aluminum or other agents. Here much metal could be saved if the atmosphere could be controlled. In another example, such as the open-hearth process, where pig iron is being converted into steel, the oxidizing atmosphere aids in oxidizing the carbon, but the trouble is that it oxidizes the metal too, and this is the important cause of the great loss of metal referred to above. Even though the atmosphere may be modified slightly by allowing the gas to enter the furnace chamber next the charge and beneath the air, yet this does not prevent the loss by oxidation. And so we are practically driven to use the electric furnace if we desire to control temperature and atmosphere independently of one another.

Let us now see what can be accomplished by means of such independent control of temperature and gases

and let us consider in this connection the meaning and use of the term "neutral atmosphere."

One often hears of maintaining a neutral or a non-oxidizing atmosphere in an electric furnace to prevent oxidation. If we have a bath of steel and an iron oxide and lime slag on top of it, a neutral or non-oxidizing atmosphere would not necessarily prevent oxidation of elements in the steel. A neutral atmosphere would be in equilibrium with iron and an oxide of iron. If we are going to make use of the atmosphere to prevent oxidation it must be controlled and not kept simply neutral. It ought to be reducing in certain cases and oxidizing in others. And this leads me to the consideration of an idea whose application in practical processes I believe is new. It is this: We can, by controlling the temperature and also the composition of the atmosphere acting on a charge at a given temperature, effect a reduction of one substance and an oxidation of another substance at the same time by the same atmosphere. As far as I am aware, the application of this idea to the oxidation of an impurity out of a metal without oxidation of the metal itself and even with the reduction of the metal oxides is new. Its application to the conversion of iron into steel makes it possible to oxidize the carbon without the very great loss of metal I have already referred to.

Inasmuch as I was led to a clearer conception of such a process as this by a careful study of the chemical principles involved, it may be of interest to apply one or two of these principles to a simple case, for it is the application of these principles which I believe is of great value in improving the efficiency of such processes.

Suppose we are working with pig iron and can react on it in a furnace chamber with an oxidizing or reducing gas or mixtures of those gases and at any temperature and pressure. The physical conditions to be controlled in such a case are the temperature and the pressure of gas in the furnace chamber; the chemical conditions are the reactions between the different elements and compounds present.

The two laws particularly applicable in this case are the mass action law and the phase rule. Let us choose a simple reaction which might take place in the above example. The CO₂ gas present may act on the iron as follows:



The law of mass action tells us that if such a reaction goes on in a closed vessel at a given elevated temperature and pressure, a condition of equilibrium will be reached and the CO produced will bear a certain relation to the CO₂ present. For the given temperature and pressure the ratio of the amount of CO and CO₂ will have a particular value. The mass action law also tells us that if we force more CO₂ into the closed vessel the oxidation will proceed further, and if CO is forced into the space the oxidized iron will be reduced.

Now suppose we replace the mixture in the vessel by a mixture of CO and CO₂, in which the CO is in

excess of the amount present under the equilibrium conditions just referred to; the result will be that some iron oxide will be reduced and CO_2 formed, and equilibrium will tend to be restored but the amount of solid or liquid iron oxide remaining will be less than at the start. We can make this replacement continuous, so that the gas in the chamber is always reducing toward iron oxide and we therefore have a means of carrying the reduction of iron oxide to completion and preventing the further oxidation of iron, it being remembered that the amount of solid FeO present does not influence the equilibrium. And, furthermore, this can be done with a gas containing the oxidizing agent CO_2 . By keeping enough CO_2 present it is possible to oxidize carbon without oxidizing iron, since carbon oxidizes more easily than iron at high temperatures.

With respect to temperature and what the control of it enables us to do, the phase rule tells us among other things what the effect of temperature will be on the equilibrium we have just considered. It tells us that the tendency of oxygen to separate from iron oxide has a certain definite value for every temperature. Increasing the temperature increases the tendency to separate or dissociate. This tendency is called the dissociation pressure of oxygen for the particular oxide and it has been measured for a few compounds. For our purposes, at present at least, we can and must get along without knowing what these actual pressures are, because they have not, except in a few cases, been determined; it serves our purpose, however, if we know what ratios of reducing gas to oxidizing gas will prevent the undesired oxidation for given temperatures. Thus we need only to know, first, what ratio for CO is needed with a given per cent. of CO_2 in a gas in order to prevent oxidation of iron at a given temperature, and second, how this ratio changes with the temperature.

The phase rule tells us the same thing about other elements, for example silicon, manganese, carbon, phosphorus, etc., these being the ones with which we are concerned in steel processes, and we find that at a given temperature these different elements as a rule have different tendencies to oxidize. Since the temperature affects different elements differently, we find also that at certain temperatures two elements may have the same tendency to oxidize, and the so-called critical temperature of the Bessemer process when both silicon and carbon have an equal tendency to oxidize is one of these temperature points.

To sum up a few of these considerations, we have seen how, by continuously controlling the atmosphere acting on a given charge, we may carry out any particular reaction to completion or how we may prevent a given reaction for an indefinite time; how an atmosphere which is reducing to one metal at a given temperature may not be reducing, but may even be oxidizing to another element, and that the term "neutral" is indefinite unless something more is specified.

And, finally, I think you will see how the electric furnace, by reason of enabling us to control temperature and, at the same time, oxidize one element while

keeping another reduced, makes it possible to do what the present steel-making processes cannot do, that is, oxidize carbon without the tremendous loss of other elements I have already referred to. It enables us to oxidize carbon and not iron or manganese or silicon; it enables us to oxidize phosphorus without oxidizing iron or manganese; it enables us to separate iron from copper by oxidizing the iron without oxidizing the copper; and these are only a few of the things that the combination makes possible.

The important question is: Can such processes be carried out economically, can they compete with present processes? When we started to develop these processes we had first worked them out theoretically, and we too wondered if they would really work in practice. We carried out an extensive series of tests on a small scale, and as these tests proved that it was possible to accomplish the oxidation of one element without oxidizing others, we then designed and built larger furnaces to try this process on a practical scale. Our first practical furnace was of about 300 pounds capacity for making steel for castings. I have presented a paper before the American Electrochemical Society at New York, which goes into more detail in regard to this process, but it may be of interest to make a brief comparison with the converter process used by many small steel foundries for making high-grade steel.

In the converter process, molten low-phosphorus pig iron is poured into the converter and blown with a blast of air usually through tuyeres near the level of the metal, the air burning out the silicon, manganese, carbon and considerable iron. In those small converters, such as used in steel foundries, the loss is very high; it is often more than 18 per cent. of the weight of the molten pig iron started with. True, about 4.5 per cent., which goes to make up that 18 per cent., is carbon and silicon, which have to come out any way, but there remains a loss of 13 or more per cent., which is so much waste of metal. In a plant making only 20 tons of molten steel per day, the value of this 13 per cent. of steel (for it would be steel if saved) would at \$30.00 per ton amount to over \$2300.00 per year, and in this loss is included manganese and silicon, which have to be put back again by adding alloys, and their addition entails further losses. These alloys, usually ferro-manganese and ferro-silicon, serve two purposes: they partly combine with the oxides in the iron which have come from the air blown through the iron and separate out as slag, and part of them remains in the steel and raises the percentage of these elements enough to meet the specifications.

The process we have developed and which we are calling an electric converter process is carried out in an electric furnace instead of a Bessemer converter and the molten metal is blown with gas of regulated composition instead of with air. The vessel must be electrically heated because the reactions of the gas on the metal do not supply much heat, as the corresponding reactions in the Bessemer process do. We use a gas which may be obtained from a cupola, or a gas producer, or from a blast furnace. This gas would

contain 6 or 8 per cent. of carbon monoxide, CO, and 12 or 15 per cent. of carbon dioxide, CO₂. When blown into molten pig iron this gas does not oxidize iron or manganese, and as pig iron usually contains manganese in sufficient quantity to meet specifications, this process avoids replacing that element by expensive alloy additions. The metal is heated to about 1450° Centigrade and blown with this gas, and the carbon is taken out by it. The carbon is oxidized, but not the iron nor the manganese. There is a small loss of manganese by vaporization, but this is so small that after the carbon is out the percentage of manganese may even be larger than at the start.

In the small furnace which we have used to make various grades of steel, we have been able to convert pig iron into steel with a total conversion loss of only about 2.5 per cent. plus the weight of carbon burned, including metal spilled in handling and left in the furnace, and this compares with a total loss of 15 per cent. plus the carbon burned by the Bessemer process in small converters. This furnace was heated by induced electric currents in the metal. The process is now installed and under test in a two-ton furnace, and we believe that the developments we have made are a step toward the saving of that immense loss which is going on to-day.

One of the most interesting applications of the process has been in the production of manganese steel. As is well known, manganese steel containing about 12 per cent. manganese has very valuable properties of strength and resistance to wear, which render it very useful for such articles as railway crossings, rails, crusher-jaws, safes and many similar things. The scrap steel, such as heads and gates, etc., from castings made of manganese steel, contains a valuable amount of manganese, but in the melting up of manganese steel scrap in cupolas much of the manganese is lost and when the melted mixture of scrap and iron is blown in the converter, all the rest of the manganese not already lost is oxidized. This tendency of manganese to oxidize has made it practically impossible, at least from a commercial standpoint, to make low-carbon manganese steel, and the properties of such steel are almost unknown. By applying our process it has proved practical to melt manganese steel scrap into pig iron and then remove the carbon without practically any loss of manganese, and it has further proved practical to produce very low-carbon manganese steel in this way. The commercial saving resulting from the utilization of the manganese that has heretofore gone to waste is a most important consideration to the manufacturer, and this saving can be accomplished at a cost very much less than the value of the metal saved.

These examples of losses in steel processes are characteristic of similar losses in the metallurgy of various other metals; in the process of converting copper matte for removing the sulphur and the iron from the copper there is an oxidation of copper which totals up very high. Likewise in the metallurgy of lead there is a similar loss and in the case of many other metals. These losses can be prevented by the

use of electric heat for controlling temperature and simultaneously controlling the composition of the gaseous reagents.

The commercial practicability of such processes depends on many factors, but we believe that the losses which can be prevented will in a great many cases prove to much more than offset the cost of electric heating.

The field of chemistry opened by the electric furnace is a most fertile one from the standpoint of scientific research as well as on the practical side. We need exact knowledge about all the metals and elements concerned in high temperature metallurgy, such as the dissociation pressures of various metallic oxides and the variation of these pressures with the temperature. Such data will be of the greatest value to the manufacturer, so that there shall be an additional incentive to its collection of scientific workers. By means of such data and by the application of simple physical and chemical principles in practical processes I believe the chemist has in his power one of the greatest means to-day of aiding the cause of conservation of our metals.

THE WORK OF ENGINEERS IN THE GAS INDUSTRIES.

By FREDERICK P. ROYCE.

Received April 26, 1911.

The business of manufacturing and distributing gas is older than that of any other of the public utilities with the exception of that of distributing water.

Early in the nineteenth century companies were established and in active operation in England. Many of the companies still doing business in this country were organized and in operation prior to 1850. It was not until a much later date, however, that results due to the efforts of scientifically trained men were generally apparent.

The first dry distillation of coal producing gas for commercial purposes was accomplished in retorts made of iron placed in a horizontal position, the heat necessary being directly applied by furnaces placed underneath the retorts.

With the exception of the substitution in the retort of fire-brick material for cast iron, this type of retort, with slight modification, was used for many years and in some small plants is used to-day.

In the early days of the industry it was found that with little effort sufficient gas could be produced and sold at a high price for lighting purposes to furnish a satisfactory return on the capital invested.

At the time, little or no consideration had been given to the relations of the companies and the public, which are now properly regarded as of great importance.

It was not understood that to get the best results for all, these companies should be operated as regulated monopolies, and the earnings of the companies were not sufficiently large to invite general competition.

These gas companies then furnished all illumination not produced by lamps or candles.

Under such circumstances there was apparently

little incentive to the engineer to enter the business and apply a scientific knowledge to the reduction of the cost of the plant or of operating it.

As time went on these conditions changed, and in the early eighties a very strong competition was introduced through the development of the electric lighting companies, which for a time threatened to destroy the business of the gas companies and in some places actually did reduce it materially.

It was then absolutely necessary that the owners of these properties should devise means of reducing their operating cost and to do a much larger business at a smaller rate of profit.

This could only be done through the employment of trained engineers.

At that time coal gas was made almost exclusively and the largest element of cost in the production of the gas was in the carbonization of the coal. There has always been a saying to the effect that money was made or lost in the retort house, and it has been in the retort house that the greatest improvement has been effected.

As has been said, the retorts were then of the direct-fired type: the coal to be carbonized was placed in the retorts by hand and the coke was removed in the same way.

It was then considered good practice if 30,000 feet of gas could be made in a day by each man employed in the retort house. This hand-firing was slow, resulting in a serious waste of gas and loss of heat.

The first step toward improvement was the introduction of machinery to charge the retorts and remove the coke.

Notwithstanding the extremely difficult conditions under which this apparatus must be operated, it has been on the whole very successful. Numerous types of machinery have been built applicable to the smallest or the largest works.

At about the same time the regenerative setting of retort benches was designed and put in successful use.

In this a generator is made a part of the bench setting and used to produce carbon monoxide gas through partial combustion, using a limited amount of primary air. This monoxide gas is distributed as desired through the bench and brought in contact with secondary air which has been preheated by passing through flues adjacent to other flues through which the products of combustion are carried to the chimney. The carbon monoxide being fired as it combines with the secondary air produces a high heat which can be satisfactorily controlled, assuring a uniform temperature throughout the various retorts of the setting.

This type of bench was followed by the inclined retort setting. In this bench the retorts are set at an angle of approximately 31° from the horizontal, the charge being introduced from the top and distributed through the retort by gravity, the coke falling from the bottom mouthpiece as desired.

The principal advantage of this type of setting is in the avoidance of the use of expensive charging and drawing machinery.

The inclined setting was followed in a few years by the vertical type.

It is interesting to note that although experiments were made with vertical retorts in the very early days of the gas industry, it was not until three or four years ago that engineers in Germany were able to build and operate them successfully on a commercial scale.

The first successful installations of this sort were designed for intermittent charging and discharging. Little machinery was required to operate them and, due to the fact that the retort was completely filled with coal, a marked improvement was noted in the character of the by-products.

As the weight of the coal in the vertical retorts is supported principally by the lower mouthpiece rather than the retort itself, the mouthpiece being easily repaired as needed, there should be and apparently is an improvement in the life of the setting.

A more recent development in the vertical retort setting has been accomplished by the perfecting of charging and discharging apparatus, by means of which a continuous carbonization of the coal is effected.

A still further improvement in the carbonization of coal in large plants has been effected by the successful design and operation of the so-called coking chamber. This in reality is a development of the inclined retort, but instead of using a comparatively small retort which would contain a charge probably not to exceed one thousand pounds in weight, a large chamber designed to contain and carbonize six or seven tons is used. The bottom of this chamber is built at an angle similar to that of the inclined retort so that the coke slides freely from it when the mouthpiece, which is really the entire lower end of the chamber, is removed.

Through these developments the cost of labor has been greatly reduced, and whereas with the early benches there was a production of 30,000 cubic feet per man per day, with the coking chambers a production of 150,000 cubic feet per man has been made possible.

At the same time the yield of gas from a pound of coal measured by the product of its volume and candle power has been increased twenty-five per cent.

The amount of fuel required to carbonize the coal, an important item of cost, has been very greatly reduced.

The capacity of unit has been increased to such an extent that much less space is required to produce a given amount of gas, which results in a reduction of plant cost.

The quantity of certain by-products has been increased and the character of these by-products much improved. This has been particularly noteworthy in connection with the vertical type of setting.

The coke made in the vertical retorts and in the coking chambers is of much the same character as that made in the beehive oven. It is stronger and consequently a smaller percentage of it is in the comparatively worthless form of screenings or breeze.

A larger percentage of ammonia is recovered. The tar produced is better and comparatively free from lampblack and other impurities.

It is regrettable that most of the improvements noted in retort-house operation have been due to the efforts of foreign engineers. The charging and drawing machinery was first perfected in England. The inclined and vertical retort benches for intermittent carbonization were developed by German engineers, and the continuous system of carbonization with vertical retorts is due principally to the efforts of Englishmen.

To American engineers, however, there may be fairly attributed the development of the water-gas process.

The Lowe type of apparatus developed in this country is now the standard throughout the world where water gas is made. It is estimated that more than one-half of the total production in this country is of water gas.

This has been of great importance in connection with the production of coal gas.

The cost of the latter is directly dependent on the price received for residuals, and it is probable that if coal gas only were made in this country the increased supply of residuals would be in excess of the demand, so that the average price received for them would be reduced and consequently the cost of producing the coal gas would be increased.

It is now common practice in America to make both water gas and coal gas in the same works. The water gas can be made of any desired candle power and mixed with the coal gas, making it possible to furnish a commercial product of almost any quality desired.

The improvements in the art, however, have not been confined to the generating house.

The quality of the gas depends in great measure on the method used to clean and purify it. The importance of this may be seen when it is realized that the so-called impurities in the gas, which are harmful as a part of the gas, are themselves valuable by-products when removed.

To obtain the best results the temperature of the gas must be made to pass through wide ranges during the different steps of cleansing and purification. Engineers have determined the correct temperature for each stage and have devised apparatus by which these conditions can be controlled.

This work of the engineers has produced a great decrease in the cost of gas. Twenty years ago it was possible to reduce the price of gas to a point where it could be made to compete successfully with

coal and other fuels, thus greatly increasing the market for it and definitely establishing the stability of the industry.

Some companies which sold gas at as high a rate as \$4.00 per 1,000 cubic feet in 1870 are to-day able to produce and sell it at less than \$1.00 per 1,000 cubic feet and still make a fair return on the necessary investment. This great decrease is the result of the reduced cost of production and of the largely increased output that followed it.

Through the development of the Welsbach mantle it is now possible to get much more light with a given amount of gas than could ever be obtained with the open burner and at the same time to use gas of a low candle power, thus materially reducing its cost. This has helped to place the gas companies in a position where they can successfully compete with the electric companies for a large portion of the lighting business.

The field at the present time is a most excellent one for the engineer. There are still opportunities to improve the methods of carbonization of coal and the generation of water gas. The highest efficiencies in these departments have been by no means reached. The actual chemical reactions in the process of carbonization and the effect on them of various temperatures offers a subject for further profitable study.

There is opportunity to increase the quantity of residuals recovered and to improve their quality. There is also every reason to believe that the market for these residuals can be substantially increased.

A small percentage of saving in the cost of the product is quickly reflected in the year's earnings. A company selling 500,000,000 cubic feet per annum is one of medium size, and yet a reduction of one cent per 1,000 cubic feet in the cost of manufacture or of distributing the gas means a saving to that company of \$5,000.00 per annum.

It has been demonstrated that gas can be manufactured by a large plant and distributed by means of a high-pressure service to smaller communities many miles distant, where it can be sold at a price much less than that at which it could be manufactured and distributed locally. This is a development which is certain to be of future importance but calls for more engineering skill than it has received.

Gas is becoming used more freely for industrial purposes, and this field should have the most careful consideration.

The man who is best equipped to improve and develop the gas business should have the knowledge of chemical and mechanical engineering that can be obtained at the Institute, and for such a man there should be a successful future in this industry.

SCIENTIFIC SOCIETIES.

REPORT OF THE SUB-COMMITTEE ON GLYCERINE ANALYSIS.¹

By A. C. LANGMUIR, Chairman, A. M. COMEY, ROBT. E. DIVINE, S. S. EMERY, J. W. LOVELAND, W. H. LOW.

As a result of some wide discrepancies in the analy-

¹ A sub-committee of The Committee on Fats, Soaps and Glycerine

sis of a crude glycerine sent out to a number of chemists, Mr. B. T. Babbitt Hyde suggested the application of standard methods of analysis to this field.

of the Division of Industrial Chemists and Chemical Engineers. The report has received the approval of the Supervisory Committee on Standard Methods of Analysis, American Chemical Society.

Acting on this idea and extending its scope, Dr. W. F. Hillebrand, the chairman of the Committee on Uniformity in Technical Analysis, appointed early in 1908 a committee to investigate the methods used in testing fats, soap and glycerine, with a view to the development of standard methods of analysis.

The committee thus appointed, with W. D. Richardson as chairman, held its first meeting at New Haven on June 30, 1908. It was decided that the scope of the work be limited to the consideration of the analysis of such materials as are commonly bought and sold.

A number of sub-committees were appointed, among which was the Sub-Committee on Glycerine Analysis, consisting of the following gentlemen: A. C. Langmuir, Chairman, Robt. E. Divine and B. T. Babbitt Hyde. Mr. Hyde subsequently resigned in favor of Mr. Loveland. In 1909 three members were added to the committee, making its composition as follows:

A. C. Langmuir, Chairman, Supt. and Chemist, Marx & Rawolle, New York.

A. M. Comey, Director, Research Laboratory, Dupont Powder Co., Chester, Pa.

Robt. E. Divine, Glycerine Specialist, Detroit, Mich.

S. S. Emery, Chemist at the Louviers Plant of the Dupont Powder Co.

J. W. Loveland, Works Manager, B. T. Babbitt, Inc., New York.

W. H. Low, Chief Chemist, Cudahy Packing Co., So. Omaha, Neb.

In order that the glycerine trade might be informed of the work to be taken up and that we might learn the prevailing methods in use for the analysis of glycerine, a letter was drawn up and widely circulated among glycerine producers, refiners and chemists in the U. S., England and Europe. The letter was published in *THIS JOURNAL*, April, 1909, p. 268.

Two samples of crude glycerine and a prepared glycerine containing a known amount of anhydrous glycerine were then sent to a number of chemists for analysis, with a request that their method be returned with the report.

A meeting was held at Boston in Dec., 1909, to discuss the replies to the circular letter, the results of the analysis of the samples, and to outline the research work required. A full report of this meeting, together with a synopsis of the methods of glycerine analysis received, may be found in *THIS JOURNAL*, May, 1909, pp. 222-229.

A consideration of the methods turned in showed that the bichromate method was more commonly in use, but that there were apparently as many modifications as there were chemists using the process. The acetin method, although less frequently employed, was warmly recommended. It had suffered but little change from the original Benedikt and Cantor process.

The bichromate and acetin methods were the only ones referred to in our correspondence and we have not discovered that the acetone extraction, permanganate oxidation or determination as isopropyl iodide

are anywhere in general use in the analysis of crudes. Our committee has therefore confined its work to the examination of the two methods first named.

The bichromate method has in its various modifications traveled a long way from the original Hehner process and most of the changes made have diminished rather than improved the accuracy of the method. It will be shown that the effectiveness of different purifying agents in removing organic impurities varies greatly and yet there are in use: silver sulphate, copper sulphate, silver oxide, silver carbonate, silver acetate and basic lead acetate, either alone or in combination with some silver salt. The basic lead acetate is seldom prepared in the same way and is of varying basicity. To completely oxidize glycerine with bichromate in presence of the lower fatty acids, which escape the purification, without at the same time partially oxidizing the latter, is a problem requiring a nice adjustment of conditions. We find that widely varying proportions of sulphuric acid and bichromate are used and that the time of oxidation is not the same. These facts disclose an urgent need for standardization.

It is noteworthy that in all the work of the past on glycerine analysis, which has come to our notice, no checks have been made against pure anhydrous glycerine. In some cases dilute glycerine was used, but its strength was determined either by combustion, a method of little value, or by specific gravity and reference to one of the many specific gravity tables, most of which are inaccurate. The basis of all our researches on the bichromate and acetin methods has been a sample of anhydrous c. p. glycerine, which is shown to be practically anhydrous (within a few hundredths of a per cent.) by a large number of tests. By dilution of this glycerine a new specific gravity table has been prepared.

We have made a detailed series of experiments to establish the most favorable conditions to effect the complete oxidation of glycerine by bichromate. A comparative study has been made of the different purifying agents in use. The acetin method has also been examined at every stage and carefully compared with the bichromate on a number of crudes. Distillation tests have been made in a specially designed laboratory still giving quantitative results which have been compared with the chemical tests.

A paper giving the results of our earlier work was read by the chairman at the May meeting of the Chicago Section in 1910, but has not been published. The committee has held meetings at Lake Mohonk, June 18-20, at New York, Oct. 18, and at Chicago, Dec. 7-8, 1910. The last meeting was attended by Messrs. Allan and Tainsh, delegates from the British Committee on Glycerine Analysis. The British committee called an international conference on glycerine analysis at London, Oct. 25-27, 1910. Representatives from Germany and France were present. The American committee was represented by Mr. Emery and the chairman.

As a result of our researches we have unanimously decided that the acetin method is the basis on which

glycerine should be bought and sold. The bichromate method is of value in factory control and for routine work in the analysis of crudes of known good character. For this reason we have felt it necessary to retain the bichromate method, in a properly standardized form, but we advise against its use in general analytical work.

The British committee, with Dr. O. Hehner as chairman, arrived independently at the same conclusion as ourselves in regard to the respective merits of the two methods. The German committee was soon convinced of the greater accuracy of the acetin process. The international conference was therefore able to devote practically all of the time at its disposal to an exhaustive discussion of the details of the proposed methods. The method which is here given is an International method, inasmuch as the details have been agreed on by all the committees.

Neither the acetin nor the bichromate method is correct in theory or practice on crudes containing trimethylenglycol or polyglycerols. We only know that the acetin is less affected by these substances than the bichromate. They are not precipitated by basic lead acetate or silver salts and are therefore left to exert the full reducing power of the molecule on the bichromate. With the acetin on the other hand, action is proportional to the number of OH groups directly attached to the chain. For example, a crude glycerine containing 80 per cent. glycerol and 1 per cent. trimethylenglycol will show by the bichromate method 81.38% and by the acetin method 80.81 per cent. glycerol. With triglycerol, a 1 per cent. addition would increase the bichromate test by 1.15 per cent. and the acetin by 0.64 per cent. A comparison of the results obtained by the acetin and bichromate methods will therefore often throw light on the nature and quantity of the impurities present.

In the absence of a chemical method which will show glycerol only in such mixtures, we must therefore prefer the acetin method, because it gives the same results as the bichromate on pure glycerine and high-grade crudes and lower or much lower results on bad crudes. In the acetin method to be described the error caused by the presence of polyglycerols is partially offset by the determination of the acetylizable matter in the non-volatile residue at 160° C., which will hold the higher polyglycerols. The lower polyglycerols and trimethylenglycol are volatile at 160° C. and are therefore figured as glycerol. Trimethylenglycol is more volatile than glycerol and may be distilled off with the glycerine in the first portions of the distillate, where it may be determined by the spread between the acetin and bichromate tests.

We have met with some bad crudes which cannot with safety be analyzed by any chemical method known to us. The only method which will give even approximate results on crudes high in glycol or crudes containing still residues is a distillation in a still adapted to quantitative work. A crude containing

a large amount of glycol tested 81.8 per cent. (bichromate), 76.2 per cent. (acetin) and 71.0 per cent. (by distillation). A crude made from still residues showed 73 per cent. by the bichromate method, 48 per cent. by the acetin method, and only 30 per cent. by distillation. These are extreme cases, but serve to show that a marked spread between the acetin and the bichromate tests is an indication that both are probably incorrect.

The acetin test is not looked upon with favor by some chemists on the ground that results are unreliable unless precautions are taken out of the reach of the busy laboratory. This opinion is largely the result of erroneous statements in the text-books and literature. The danger of saponifying triacetin by standing in aqueous solution and during neutralization of the acetic acid is greatly exaggerated. A point in favor of the acetin method is the avoidance of the purification required by the bichromate test. Two of the members of this committee have made the change from the bichromate to the acetin test without any trouble, although they had but little experience with the latter. In their hands the acetin method has given results of greater uniformity and accuracy than the bichromate. Every member of our committee has had by this time some experience with the acetin in comparison with the bichromate method and a few of us have had a very extensive experience, covering several years. It is our opinion that with proper attention to details which are not in the least onerous, chemists will be able to obtain results which are more concordant than those obtainable by the bichromate method and at the same time nearer the actual glycerol present.

A standard method for glycerine analysis has been wanted for a long time, and in order to avoid delay we are publishing our methods in advance of the researches which have led to our conclusions. Papers will follow which will describe our experiments in connection with the acetin and bichromate methods, the quantitative distillation of glycerine, a specific gravity table for glycerine and specifications for c. p. and dynamite glycerine.

The chairman has a quantity of anhydrous c. p. glycerine, which he is prepared to distribute to chemists who wish to standardize their methods. This glycerine has been analyzed by most of the members of the British and American committees. A standard soap lye crude will also be prepared.

It is not possible to carry through as many acetin tests per day as bichromate, but with many crudes the difference between results is so wide, that it is not any longer a question as to which method is the quicker or more convenient. The great increase in the price of crude glycerine, together with a falling off in quality, due to the use of impure fats and greases as well as the introduction of new methods of saponification, make it impossible to defend the bichromate method on the ground of convenience and custom. Valuable as this method has been in the past, it is unable to cope with many crudes of to-day.

METHODS OF CRUDE GLYCERINE ANALYSIS.

Recommended by the International Committee.

SAMPLING.

The most satisfactory method available for sampling crude glycerine liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerine sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salt has taken place. In such cases he shall sample with a sectional sampler (see appendix) then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of the same made in his certificate, together with the temperature of the glycerine. Each drum must be sampled. Glycerine which has deposited salt or other solid matter cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerine to be taken including any deposit.

ANALYSIS.

1. *Determination of Free Caustic Alkali.*—Put 20 grams of the sample into a 100 cc. flask, dilute with approximately 50 cc. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 cc. of phenolphthalein solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 cc. of the clear liquid and titrate with normal acid ($N/1$). Calculate the percentage of Na_2O existing as caustic alkali.

2. *Determination of Ash and Total Alkalinity.*—Weigh 2 to 5 grams of the sample in a platinum dish, burn off the glycerine over a luminous Argand burner or other source of heat,¹ giving a low temperature, to avoid volatilization and the formation of sulphides. When the mass is charred to the point that water will not be colored by soluble organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate the water, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

3. *Determination of Alkali Present as Carbonate.*—Take 10 grams of the sample, dilute with 50 cc. distilled water, add sufficient $N/1$ acid to neutralize the total alkali found at (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and then titrate back with $N/1$ NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O . Deduct the Na_2O found in (1). The difference is the percentage of Na_2O existing as carbonate.

4. *Alkali Combined with Organic Acids.*—The sum of the percentages of Na_2O found at (1) and (3) de-

ducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

5. *Determination of Acidity.*—Take 10 grams of the sample, dilute with 50 cc. distilled water free from carbon dioxide, and titrate with $N/1$ NaOH and phenolphthalein. Express in terms of Na_2O required to neutralize 100 grams.

6. *Determination of Total Residue at 160° C.*—For this determination the crude glycerine should be slightly alkaline with Na_2CO_3 , not exceeding 0.2 per cent. Na_2O , in order to prevent loss of organic acids. To avoid the formation of polyglycerols this alkalinity must not be exceeded.

Ten grams of the sample are put into a 100 cc. flask, diluted with water and the calculated quantity of $N/1$ HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 cc., the contents mixed, and 10 cc. measured into a weighed Petrie or similar dish 2.5 in. in diameter and 0.5 in. deep, which should have a flat bottom. In the case of crude glycerines abnormally high in organic residue a smaller amount should be taken, so that the weight of the organic residue does not materially exceed 30 to 40 milligrams.

The dish is placed on a water bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven¹ measuring 12 ins. cube, having an iron plate 0.75 in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half way up the oven. On these strips the dish containing the glycerine is placed.

If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapor is seen to come off, the dish is removed and allowed to cool.

An addition of 0.5 to 1.0 cc. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spurt. The time taken up to this point cannot be given definitely, nor is it important. Usually two or three hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is

¹ An electric oven suitable for this work, which is readily adjusted to 160° C., has been made for Mr. Low and the chairman, by the Apparatus and Specialty Co., Lansing, Mich. Its size is 9 1/2 × 10 × 16 inches and capacity 8 Petrie dishes. It gives a strong draft at constant temperature.

¹ Carbon is readily burned off completely, without loss of chlorides, in a gas-heated muffle furnace adjusted to a dull red heat.

repeated until a constant loss of 1 to 1.5 mg. per hour is obtained.

In the case of acid glycerine a correction must be made for the alkali added, 1 cc. *N/1* alkali represents an addition of 0.03 gram. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na₂CO₃ to NaCl. The corrected weight multiplied by 100 gives the percentage of total residue at 160° C.

This residue is taken for the determination of the non-volatile acetylizable impurities (see acetin method).

7. *Organic Residue*.—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (it should be noted that alkaline salts of fatty acids are converted to carbonates on ignition and that the CO₂ thus derived is not included in the organic residue).

ACETIN PROCESS FOR THE DETERMINATION OF GLYCEROL.

This process is the one agreed upon at a conference of delegates from the British, French, German and American committees, and has been confirmed by each of the above committees as giving results nearer to the truth than the bichromate method on crudes in general. It is the process to be used (if applicable) whenever only one method is employed. On pure glycerines the results are identical with those obtained by the bichromate process. For the application of this method the crude glycerine should not contain over 60 per cent water.

REAGENTS REQUIRED.

(A) *Best Acetic Anhydride*.—This should be carefully selected. A good sample must not require more than 0.1 cc. normal NaOH for saponification of the impurities when a blank is run on 7.5 cc. Only a slight color should develop during digestion of the blank.

The anhydride may be tested for strength by the following method: Into a weighed stoppered vessel, containing 10 to 20 cc. of water, run about 2 cc. of the anhydride, replace the stopper and weigh. Let stand with occasional shaking, for several hours, to permit the hydrolysis of all the anhydride; then dilute to about 200 cc., add phenolphthalein and titrate with *N/1* NaOH. This gives the total acidity due to free acetic acid and acid formed from the anhydride. It is worthy of note that in the presence of much free anhydride a compound is formed with phenolphthalein, soluble in alkali and acetic acid, but insoluble in neutral solutions. If a turbidity is noticed toward the end of the neutralization it is an indication that the anhydride is incompletely hydrolyzed and inasmuch as the indicator is withdrawn from the solution, results may be incorrect.

Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 cc.) measure about 2 cc. of the sample, stopper, mix, cool and weigh. Wash the contents into about 200 cc. of cold water, and titrate the acidity as before. This yields the acidity due to the original,

performed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated to 100 grams) and double the result, obtaining the cc. *N/1* NaOH per 100 grams of the sample. 1 cc. *N/NaOH* equals 0.0510 anhydride.

(B) *Pure Fused Sodium Acetate*.—The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or desiccator. It is most important that the sodium acetate be anhydrous.

(C) *A Solution of Caustic Soda for Neutralizing, of about N/1 Strength, Free from Carbonate*.—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(D) *N/1 Caustic Soda Free from Carbonate*.—Prepared as above and carefully standardized. Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(E) *N/1 Acid*.—Carefully standardized.

(F) *Phenolphthalein Solution*.—0.5 per cent. phenolphthalein in alcohol and neutralized.

THE METHOD.

In a narrow-mouthed flask (preferably round-bottomed), capacity about 120 cc., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grams of the glycerine. A Grethan or Lunge pipette will be found convenient. Add about 3 grams of the anhydrous sodium acetate, then 7.5 cc. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside diameter. The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapor.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 cc. of distilled water free from carbon dioxide at a temperature of about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapors from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolyzed in hot than in cold water. The contents of the flask may be warmed to, but must not exceed, 80° C., until the solution is complete, except a few dark flocks repre-

senting organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected.

Cool the flask and contents without loosening from the condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask, and filter the contents through an acid-washed filter into a Jena glass flask of about 1 liter capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 cc. of phenolphthalein solution (*F*), then run in caustic soda solution (*C*) or (*D*) until a faint pinkish yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 cc. or a calculated excess of $N/1$ NaOH (*D*) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate the excess of NaOH with $N/1$ acid (*E*) until the pinkish yellow or chosen end-point color just remains.¹ A further addition of the indicator at this point will cause an increase of the pink color; this must be neglected, and the first end-point taken.

From the $N/1$ NaOH consumed calculate the percentage of glycerol (including acetylizable impurities) after making the correction for the blank test described below.

1 cc. $N/1$ NaOH = 0.03069 gram glycerol.

The coefficient of expansion for normal solutions is 0.00033 per cc. for each degree centigrade. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride, sodium acetate and water as in the analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralization. After neutralization it is not necessary to add more than 10 cc. of the $N/1$ alkali (*D*), as this represents the excess usually present after the saponification of the average soap lye crude. In determining the acid equivalent of the $N/1$ NaOH, however, the entire amount taken in the analysis, 50 cc., should be titrated after dilution with 300 cc. water free from carbon dioxide and without boiling.

¹ A precipitate at this point is an indication of the presence of iron or alumina, and high results will be obtained unless a correction is made as described below.

Determination of the Glycerol Value of the Acetylizable Impurities.—The total residue at 160° C. is dissolved in 1 or 2 cc. of water, washed into the acetylizing flask and evaporated to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis. After correcting for the blank, calculate the result to glycerol.

INSTRUCTIONS FOR CALCULATING THE ACTUAL GLYCEROL CONTENT.

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if any are present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylizable impurities are present these are included in this figure.

Trimethylenglycol is more volatile than glycerine and can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and bichromate results on such distillates. The spread multiplied by 1.736 will give the glycol.

BICHROMATE PROCESS FOR GLYCEROL DETERMINATION.

REAGENTS REQUIRED.

(A) *Pure potassium bichromate* powdered and dried in air free from dust or organic vapors, at 110° to 120° C. This is taken as the standard.

(B) *Dilute Bichromate Solution.*—7.4564 grams of the above bichromate are dissolved in distilled water and the solution made up to one liter at 15.5° C.

(C) *Ferrous Ammonium Sulphate.*—It is never safe to assume this salt to be constant in composition and it must be standardized against the bichromate as follows: dissolve 3.7282 grams of bichromate (*A*) in 50 cc. of water. Add 50 cc. of 50 per cent. sulphuric acid (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (*B*). Calculate the value of the ferrous salt in terms of bichromate.

(D) *Silver Carbonate.*—This is prepared as required for each test from 140 cc. of 0.5 per cent. silver sulphate solution by precipitation with about 4.9 cc. $N/1$ sodium carbonate solution (a little less than the calculated quantity of $N/1$ sodium carbonate should be used as an excess prevents rapid settling). Settle, decant and wash once by decantation.

(E) *Subacetate of Lead.*—Boil a 10 per cent. solution of pure lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(F) *Potassium Ferricyanide.*—A very dilute, freshly prepared solution containing about 0.1 per cent.

THE METHOD.

Weigh 20 grams of the glycerine, dilute to 250 cc. and take 25 cc. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about 5 cc. in most cases) of the basic lead acetate (*E*), allow to stand a few minutes, dilute with distilled water to 100 cc., and then add 0.15 cc. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 cc., and return the filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate (in the great majority of cases 5 cc. are ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 cc. of the dilute glycerine should be taken and purified with 6 cc. of the basic acetate). Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 cc. of the clear filtrate into a flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3.7282 grams of the powdered potassium bichromate (*A*). Rinse down the bichromate with 25 cc. of water and let stand with occasional shaking until all the bichromate is dissolved (no reduction will take place in the cold).

Now add 50 cc. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapors, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (*C*), making spot tests on a porcelain plate with the potassium ferricyanide (*F*). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 gram glycerol = 7.4564 grams bichromate.

1 gram bichromate = 0.13411 gram glycerol.

The percentage of glycerol obtained above includes any oxidizable impurities present after the purification. A correction for the non-volatile impurities may be made by running a bichromate test on the residue at 160° C.

NOTES.

(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid, as stipulated.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 cc.

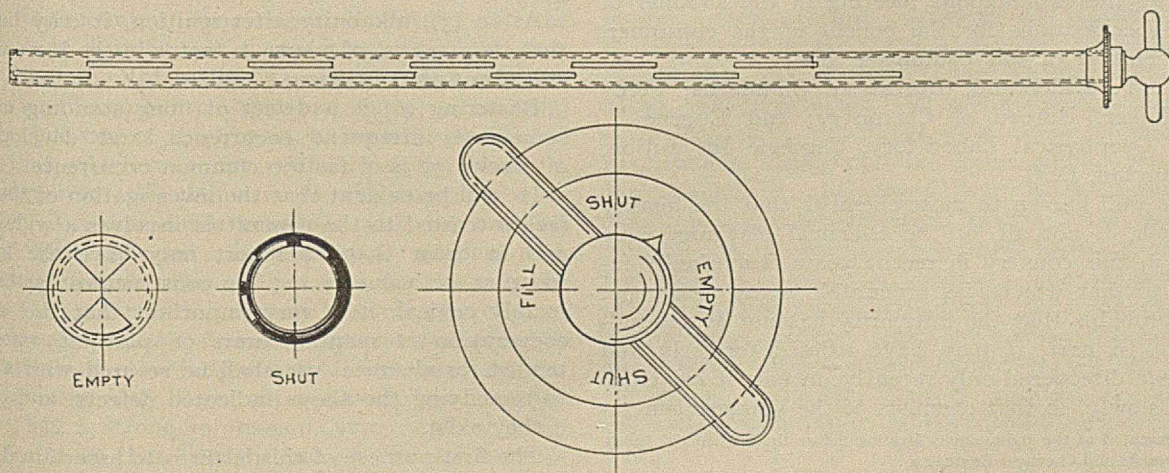
(4) It is sometimes advisable to add a little potassium sulphate to insure a clear filtrate.

APPENDIX.

SAMPLING CRUDE GLYCERINE.

The usual method of sampling crude glycerine hitherto has been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerine contained in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates glycerine runs into the tube very slowly, so that, owing to the time occupied, it is impossible to take a complete section of the crude. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

The sampler which is illustrated herewith has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement the glycerine fills into the sampler almost instantaneously. There are a number of ports cut at the bottom of the sampler which render it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In samplers of larger section (1 in.) it is possible to arrange a third motion whereby the bottom ports



only are open for emptying, but in samplers of smaller dimensions ($\frac{5}{8}$ in.) this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom, the ports are opened for a second or two, then closed and withdrawn, and the sample discharged into the receiving vessel by opening the ports. When the drum contains salt which has deposited, the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum and it is therefore recommended that the drum be sampled before any salt has deposited. A sampler 1 in. in diameter withdraws approximately 10 oz. from a 110-gal. drum. A sampler $\frac{5}{8}$ in. in diameter will withdraw about 5 oz.

PRELIMINARY REPORT OF THE COMMITTEE ON QUALITY OF PLATINUM LABORATORY UTENSILS.¹

In compliance with the authorization accompanying the formation of the above-named committee at the Minneapolis meeting its membership was completed by the selection of Dr. E. T. Allen, of the Geophysical Laboratory, Carnegie Institution.

The committee immediately began to seek information by sending copies of the subjoined letter to the following American firms, who were known or supposed to be or to have been engaged in the manufacture of platinum ware: J. Bishop & Co. Platinum Works, and John C. Entriken, Malvern, Pa., Baker & Co., Inc., American Platinum Works, and Croselmire and Ackor Co., Newark, N. J.

WASHINGTON, D. C.,

January 27, 1911.

Gentlemen:

The Division of Industrial Chemists and Chemical Engineers of the American Chemical Society, when in session at Minneapolis on the last days of December, 1910, established a committee to study the question of the quality of platinum ware and to report, if possible, at the Indianapolis meeting in the summer of 1911, specifications for the benefit of the consumer. The members of this committee are:

Wm. F. Hillebrand, Bureau of Standards; Percy H. Walker, Bureau of Chemistry; and Eugene T. Allen, Geophysical Laboratory, Carnegie Institution, Washington, D. C.

It is well known to most chemists that the quality of much, if not all, of the chemical platinum ware made in this country in recent years is markedly inferior to that which was procurable many years ago. It is probable that the inferiority has not arisen suddenly. In part, it may have existed formerly and has been discovered only recently; in part it has come about slowly, so that chemists of the younger genera-

¹ Presented at the Indianapolis Meeting before the Division of Industrial Chemists and Chemical Engineers.

tion have had less opportunity for comparison than those who have been active for many years. Hence, the protest against the quality of much of the present-day ware has been slow to crystallize.

The objections made to inferior ware, so far as registered up to now, may be stated as follows:

- (1) Undue loss of weight on ignition.
- (2) Undue loss of weight on acid treatment, especially after strong ignition.
- (3) An unsightly appearance of the surface of the ware after strong ignition, especially in the early stages of heating.
- (4) Adherence of crucibles and dishes to triangles, sometimes to such an extent as to leave an indentation of the vessel at the points of contact with the triangle, even when complete cooling has been reached before the two are separated from one another.
- (5) Alkalinity of the surface of the ware after strong ignition.
- (6) Blistering.
- (7) Development of cracks after continued heating.

As causes for (1), an undue loss on ignition, have been pretty generally suggested a content of iridium and perhaps of base metals of low boiling point.

Causes for (2), loss on acid treatment after ignition, are known to reside in an iron content in the first place, and in a content of an alkaline-earth metal (calcium) in the second, these being brought slowly to the surface and there oxidized, so as to give in extreme cases a reddish coating of ferric oxide on the one hand and an alkaline reaction on the other.

The cause of the unsightly surface aspect of the ware in the early stages of treatment (3) is sometimes due to volatile impurities but later seems to be caused by crystallization of the platinum. The question arises: to what extent is this crystallization caused by the presence of an impurity, for instance of a metal giving an alkaline oxide, and consequently, to what extent can it be reduced, if at all, by complete elimination of the impurity?

As to (4), adherence of vessel to triangles, to what extent is this due to an inferior quality of the triangle as contrasted with the vessel, and would it be apparent if the quality of both were good and equally good?

As to (5), alkalinity after ignition, it may be said that its cause is, of course, a factor in the loss on acid treatment after ignition.

Blistering (6) is a defect of long standing and of somewhat infrequent occurrence, and development of cracks (7) is of far too common occurrence.

It will be evident that the investigation of the subject entrusted to the committee involves a wide field; and in order that its report may have the largest measure of value, *i. e.*, be constructive instead of merely critical, it is very important that the willing coöperation of manufacturers of platinum ware intended for chemical use shall be secured with a view to remedying the above indicated defects, and others if they exist.

The first purpose of this letter is to ascertain if your

firm is willing to aid the committee by furnishing such information as it may need in regard to the sources of the platinum entering into different kinds of ware, the methods of refining and the mechanical and chemical treatment to which the platinum is subjected at each step of the processes of conversion into finished ware. The committee would be willing to regard such information as strictly confidential if so requested. With it, progress toward valid conclusions and suggestions would be speedy; but without it, slow and uncertain for lack of adequate and precise data. It is hoped therefore that each American manufacturer of chemical platinum ware will send a thoroughly competent technical delegate to confer with the committee, either in Washington or at some central place to be decided on by mutual agreement.

By such conference at first hand with the firm's representatives, singly or collectively, as may be preferred, it is hoped that simple specifications can be drawn for the consumers' use which it will be quite possible for the manufacturers to meet. This is a case where it is manifestly impossible for the consumer to require from the manufacturer a material of prescribed composition, for he has not at his command the necessary data to serve as a basis for specification, whereas these data are, or should be, at least partly, in possession of the manufacturer. The committee feels strongly that the consumer needs immediate help, and also that the manufacturer can do no greater service to himself than by full and free cooperation with the committee on behalf of the consumer. The alternative will be, no doubt, a large increase in the existing demand for foreign wares in preference to that of American manufacture.

Kindly indicate in some detail your willingness or unwillingness to meet with the committee and to forward its aims as above set forth.

The above inquiries brought forth the information in the first place that John C. Enriken no longer manufactured platinum ware and that Croselmire & Ackor Co. have no manufacturing plant in America. The remaining firms met the request of the committee for interviews by sending separately representatives to Washington. From the lengthy conferences held, considerable information was obtained regarding the sources of the ore and ingot metal that are worked up in this country, their degree of purity, and the processes of refining and manufacture to which they are subjected. Interesting as much of this information was, the committee does not deem it necessary for the purpose of this report to reproduce in detail even that which was not confidential in character. To judge from the claims made, the composition of ordinary American-made crucibles and dishes differs widely with different manufacturers, ranging with respect to iridium from 0.5 per cent. or less to 3 per cent. One maker admitted an iron content of 0.2-0.3 per cent. Little definitely was learned as to the percentages of other impurities. There was manifest reticence in reply to certain questions, but the committee has a strong impression, supported by other evidence than that brought out in the conferences,

that in the past practically no far-reaching refining of ore or imported metal has been practiced in this country, and that, in spite of some statements to the effect that scrap was not worked over for chemical ware, this has been done both at home and abroad, that the practice continued through years has contributed in no small degree to the acknowledged inferiority of most modern chemical ware used in this country, and that this inferiority will increase in degree with time unless stopped. It was admitted by one at least that the sharp competition of recent years was responsible in part for lack of proper control of the composition of chemical ware.

Since it was not possible for the committee to begin its study by making careful analyses of a variety of samples of ware on the market, the most promising line of attack seemed to be to secure samples of their ordinary commercial ware from all the domestic manufacturers, and also if possible of metal specially refined by themselves. These it was proposed to compare among themselves and with foreign-made ware as to behavior on heating, both as regards appearance and stiffness, loss in weight, and tests for iron and alkali. As standards for comparison were taken one crucible from Heraeus, of his own make, of "Thermoelement" platinum, which is claimed to be free from all impurities, and three of his "Tiegel" platinum, containing according to the latest information not over 0.05 per cent. iridium and probably less. These last were made up by one of the American firms, but had a shape different from the crucible of "Thermoelement" platinum made by Heraeus, which it may be remarked belonged to the Bureau of Chemistry.

All the makers expressed themselves as ready to furnish for test several crucibles and triangles of their ware, ordinary and specially refined. Not all of these have been received up to the present time, and if there were no other ground the committee is on this account unable to offer now a complete report.

In order to study the effect of ordinary laboratory conditions, the first tests were made over blast-lamps. It was soon found that the temperatures obtained were markedly dependent on the construction of the lamps and on the gas pressure. Hence, for later tests over blast-lamps one of high efficiency was chosen, giving a temperature, measured by thermocouple, of 1200-1210° in the lower part of the crucible when the crucible was covered, and of about 1100° in the upper part just under the perforated lid, and this lamp alone was afterwards used. The variations of gas pressure could not be overcome conveniently. For this reason, and also to test the continued mechanical and chemical effect of the blast flame in causing loss in weight, it seemed necessary to try the effect of electrical heating. The construction of a resistance furnace that will meet the exacting requirements of the tests contemplated has been found more difficult than was anticipated and is not yet wholly achieved. This is another reason why the committee's report is only preliminary and partial.

The committee is aware that considerable testing of platinum ware has been done by a number of writers¹ and that a portion of the field covered by it has been gone over already by them. As a rule, however, no comparison was made between the ware of different makers, and temperatures were not always controlled by measurement. Further, the experiments were restricted, in the main, to determining losses on ignition. The committee will make no further reference in this report to the work of others, reserving this for a later occasion.

EXPERIMENTAL DATA.

DISCUSSIONS.

Surface Aspect of Ware after Heating.—Leaving out of account the discoloration due to the oxidation of iron, the surface indications shown by ware that has come under the observations of the committee at different times are not easy to describe.

With good ware the crucible becomes uniformly affected by the blast when this envelopes the whole vessel, either taking on a whitish, frosted appearance or becoming uniformly mottled inside and out with crystal plates which do not all reflect the light alike. There is great difference in the size of these plates, from almost microscopic in the case of the frost-like aspect noted to those that are easily apparent to the naked eye. Sometimes, when the plates are large, a decided blue color is imparted to the surface. The crucible of "Thermoelement" platinum of Heraeus which was tested showed only the frosted surface, while his "Tiegel" platinum became in every case coarsely marked. No explanation for this difference has yet been offered, a difference that seems surprising in view of the supposed very slight differences in composition of the two.

On poor ware the surface becomes more or less whitish, sometimes faintly brownish in places, but the discolorations are not uniformly distributed and they often impart an unsightly appearance. As a rule, the lower part of the crucible, where it was hottest, remains bright and from it stretch out more or less fan-shaped areas, the direction of which is affected by that of the flame, *i. e.*, whether this was inclined or applied vertically. The areas often have the appearance of sublimes, such as are produced on charcoal before the blowpipe. Now and then they have been seen starting sharply from a point. On direct and continued application of the flame their appearance and location may undergo change, and they may even disappear entirely.

Surface Alkalinity.—Concerning this singular phenomenon, which was first observed by Dr. H. C. P. Weber, of the Bureau of Standards, before the committee was organized, little definite information has thus far been gained. When manifest it can be de-

tected by applying moist red litmus paper to the surface of the vessel after it has been blasted for several hours. It has been noted in varying degrees of intensity and is not always apparent. The element producing the alkalinity is calcium. Its sources might be lime from the crucibles used for melting the platinum or a lime salt used in polishing. Opinions as to this were conflicting, and the committee has not yet enough evidence at hand to warrant an expression of opinion of its own. The question is to be tested in part by comparison of ware that has been polished with Vienna lime and that which has not been so treated. What effect, if any, the presence of lime has on the quality of the ware is not known, although the observations of Mylius and Hüttner¹ and of Hillebrand² have direct bearing on this point.

Iron Content.—Rouge is sometimes used for polishing ware, and steel enters into its manufacture at more than one stage. These may account for a portion of the iron content of all ordinary ware and for the minute traces that may occur in the specially refined ware, but the evidence all goes to show that the introduction from this source (unless possibly when hot rolling of sheet and hot shaping of utensils is practiced) accounts for but a small fraction of the amount actually present. Its probable sources have already been indicated.

The committee has found that the "Thermoelement" and "Tiegel" platinum of Heraeus are satisfactory with respect to iron. It is either not detectable after long blasting or gives such a faint reaction as to represent a negligible quantity. One American firm has submitted what is claimed to be its own refined ware, which seems to be with respect to iron the equal of the "Tiegel" platinum of Heraeus.

So far as the experience of the members of the committee goes, all the ware supplied by American manufacturers as of their own make, during recent years, has been strongly contaminated by iron. Sometimes, its amount has been so great as to reveal itself after less than a half hour's exposure to a Bunsen burner flame, by a darkening, even reddening, of the inside of the crucible. More often the color change becomes pronounced only after long blasting. In an extreme case as much as 6 milligrams of iron oxide were removed from the surface of a 22-gram dish of German make some years ago by one of the committee members. An amount less than one milligram in weight suffices to impart a very dark color to a crucible of 20 cubic centimeters capacity. Even when the iron does not reveal itself thus, treatment with pure hydrochloric acid or with alkali pyrosulphate will often do so. Renewed heating will invariably bring more iron to the surface of the platinum if originally present. If the heating is done electrically instead of over a blast flame the color change due to iron oxide appears outside as well as inside the crucible. In one case, a few years ago, a dark color due to iron oxide was observed on ware as received from the maker.

Loss in Weight on Ignition.—Aside from a content

¹ Of experimenters in recent years the following may be mentioned: R. W. Hall, *J. Am. Chem. Soc.*, **22**, 494 (1900); Holborn and Henning, *Sitzb. Preuss. Akad. Wiss.*, **1902**, p. 936; Holborn and Austin, *Ibid.*, **1903**, p. 245; Hulett and Berger, *J. Am. Chem. Soc.*, **26**, 1512 (1904); W. C. Heraeus, *Ztschr. angew. Chem.*, **1907**, p. 1892; Mylius and Hüttner, in the general reports of the Phys. Tech. Reichsanstalt, *Ztschr. f. Instrumentenkunde*, **1906-1910**. Hall's paper seems to have been overlooked by the later writers.

¹ *Ztschr. Instrumentenkunde*, **30**, 190 (1910).

² *Bull.* **422**, U. S. Geol. Survey, p. 122.

of volatile base metals, iridium is supposed to be the volatile constituent of platinum which contributes chiefly to the observed loss of weight on strong ignition. This belief is supported by the experience of the committee.

The following set of tests on the ordinary commercial ware submitted by one firm is perhaps typical in general for a grade of ware that is supposed (from the statements made to the committee) to carry about 0.5 per cent. iridium, but further confirmative tests must be made before final conclusions are reached.

A crucible, weighing without cover about 16 grams, lost in four hours, over a vertical blast, 3.4 mg. The temperature inside the crucible and near the bottom was 1180°–1190° C. The rate of loss per hour was 0.85 mg. At 1100° the loss in less than four hours was 1.2 mg., or at the rate of somewhat over 0.3 mg. per hour.

Another crucible of the same lot, but slightly heavier, suffered a loss over the blast in 3 hours at 1200°–1210° of 2.3 mg. (0.77 mg. per hour) and of 1.9 mg. in addition at 1110° in 4.5 hours (0.42 mg. per hour). The surface of the crucible was very unevenly and strongly frosted, in marked contrast to the crucible of refined metal.

Other tests by one of the committee, on purchased domestic ware, showed losses of the same order, in some cases fully 1 milligram per hour at or near 1200°.

Contrasted with these, the "Tiegel" platinum of Heraeus above referred to shows to decided advantage. A crucible weighing about 16 grams lost in 12 hours (heatings of 4 hours each) 2.3 mgs. (0.2 mg. per hour) at temperatures not exactly known but approximating 1200°. At 1100° the loss was 0.9 mg. in 8 hours (0.11 mg. per hour). Another lost at the same rate as the first in 8 hours at 1190°–1210°.

Marked improvement was shown also by crucibles made of metal specially refined in this country, free from iron, and submitted by one firm, the rate of loss per hour being 0.3 mg. at 1200° in 12 hours, and 0.1 mg. at 1100° in 8 hours. The losses in the several periods of heating at 1200° were irregular, due perhaps to marked variations in atmospheric conditions, causing errors in weighing.

The crucible of "Thermoelement" platinum lost in 14 hours at 1200° 2.3 mg. (0.17 mg. per hour), and in 4 hours, at 1100°, 0.2 mg. (0.05 mg. per hour).

The triangles furnished with the crucibles, and of the same composition, suffered corresponding losses.

The last test shows that at the temperatures employed and over a blast-lamp even platinum that is claimed to be free from iridium has a perceptible vapor pressure or forms a volatile oxide, and it is also apparent that for chemical use the "Tiegel" platinum seems to be quite as satisfactory in quality.

The foregoing data may be summarized as follows:

	Rate of loss per hour in mgs.	
	1200°.	1100°.
Ordinary ware (0.5 (?) per cent. Ir).	0.85	0.3
"Tiegel" platinum.....	0.2	0.11
"Thermoelement" platinum.....	0.17	0.05
American refined ware.....	0.3	0.1

These data are not to be taken as rigidly exact, but they are probably fairly indicative. It should be remembered that the crucibles were not polished or wiped between the separate heatings.

From the above and other tests it may be inferred also that there is a sharp rise in the volatility curve for iridium and apparently for platinum also between the temperatures 1100° and 1200°. This point it is the intention of the committee to investigate further. If true, it would seem that for temperatures up to 1100° the volatility loss is of little significance with refined ware, but that it may be of some moment with ordinary commercial ware low in iridium and free from volatile base metals. At higher temperatures and with long-continued heating, however, the losses are appreciable even with the purest ware and are very high with commercial ware.

In this connection it is proper to say that in all probability the maximum temperature of the blast used in the above experiments is above that commonly attained in most laboratories. The gas used was artificial. Attention may be called also to the fact that relatively few substances obtained in chemical analysis require blast ignition and that blasting of an hour's duration is seldom necessary, so that in the majority of cases the volatility loss may be ignored.

Relative Stiffness and Hardness of Ware.—Pure platinum is soft and lacks stiffness. For these reasons it has been common practice to leave a certain amount of iridium in ware made from it or even to add to the amount already present. This addition is especially pronounced in triangles, which may contain 15–20 per cent. of iridium. The crucibles of "Tiegel" platinum made up in this country and also those of American-refined metal showed lack of stiffness in a very objectionable degree. In contrast with them was the crucible of "Thermoelement" platinum which, though not so stiff as the crucibles of commercial ware, was sufficiently so for all practical purposes. The reason for this difference is not yet apparent, but it may be due to the different shape of the crucibles or to a different thickness of the metal. If so the defect mentioned in the American crucibles tested is one that can be easily remedied by the makers.

Triangles.—In order that no error might be introduced by the use of triangles differing in composition from the crucibles, whereby iridium or other metal might pass from the former to the latter, the makers were asked to furnish with the crucibles triangles of the same composition, and this they did.

The refined crucibles and triangles were found to stick together badly while hot, owing to the welding property of pure platinum. They could be separated when cool, but often only by the expenditure of some

force and with danger of tearing out metal from the crucibles. It is probable that, in order to help maintain as far as possible the purity of a vessel of highly refined platinum, it should not be used in conjunction with a platinum triangle of different quality. Sagging, to a much greater degree than with ordinary triangles that have been some time in use, was not observed. The sticking defect is serious enough to take into consideration with refined ware. Therefore, experiments were made to test the temperatures obtainable inside a crucible with triangles of different materials and shapes. Without entering into details, it may be said that with a vertical blast flame the differences were far less than had been expected between triangles of platinum, of clay and of quartz, so that except for particular uses platinum triangles seem to have little advantage over those of clay or quartz when used under the conditions of the tests. The clay triangles with projecting points on which the crucibles rest allow as high a temperature to be reached in the upper part of the crucible as those of platinum. Quartz triangles made in one piece are to be had, but the cheaper ones of nickel or "nichrome" covered with quartz tubing are probably just as serviceable.

A word of caution may be added here with regard to the use of "nichrome" in direct contact with platinum. It has not been shown that there is no contamination from this source and in view of the cost of platinum ware any additional source of contamination is to be guarded against.

Blistering.—The blistering of crucibles seems to be far less frequent now than it was some years ago. It is probable that this defect resulted from past methods of manufacture rather than from other causes, and the committee has not given experimental attention to the subject.

Cracking.—One manufacturer attributed cracking not to the faulty nature of the ware but to careless handling of magnesium-ammonium phosphate, etc., and to heating with reducing flames. Another treated the ware mechanically to lessen the tendency to crack.

Extra Cost of Refined Ware.—The refining of platinum to the extent shown by the "Tiegel" platinum of Heraeus and by the recent product of one of the American manufacturers necessitates a higher charge than we have been accustomed to pay for commercial ware. In the experience of those who have bought the refined ware in this country the extra cost is in the neighborhood of 30 cents per gram. This is a large relative increase, but not excessive in comparison with the advantage gained from having an article that one knows to be free from all objectionable impurities in significant amounts. If platinum can be refined to the extent of removing all or nearly all iron and other base metals without removing all the iridium, the presence of the latter might be no disadvantage when extreme temperatures are not called for. The matter is important, for stiffness is essential to large vessels, and this quality iridium undoubt-

edly imparts to platinum ware. That iron can be so removed without removing the iridium the following experience of one of the committee at the Bureau of Standards appears to show. For the sake of completeness data not relevant to the point in question are included.

Two crucibles, No. 65, bought in 1905, and No. 117, bought from another firm in 1908, but never used before, were first heated electrically at 1250° for several hours. No. 65 showed then no iron, or at most a trace, and lost weight subsequently over the blast at 1100°–1200° at the rate of 0.64 mg. per hour. Crucible No. 117 yielded 1.4 mg. iron oxide after the electrical heating. After cleaning, subsequent blast ignition caused a loss at the rate of 1 mg. per hour for the first 3 hours and of 0.9 mg. for the next 8 hours; the surface became strongly alkaline and showed more iron oxide. From the stiffness of the crucibles and their high loss in weight it is practically certain that both contained iridium, yet the one was free from iron, the other heavily charged. The original source of crucible No. 65 is not known.

CONCLUSIONS AND RECOMMENDATIONS.

Although it were premature to offer anything final in the way of recommendations, the investigation has brought out certain facts and observations which the committee has deemed it wise to lay before chemists in the foregoing pages without waiting for completion of the inquiry. It is hoped that further tests on domestic and foreign ware and a closer study of the literature will enable it to present a more finished report later.

It has been shown that ware of foreign make can be had against which nothing can be brought on the score of iron or other base metal content and in which the loss caused by strong blasting seems to be solely of platinum itself and to be entirely negligible, for all ordinary purposes, up to at least 1100°.

It appears also that American-refined platinum ware can be had of nearly if not quite as good quality and there does not seem to be any reason to think that its quality cannot be still further improved if there is a call for it to be done.

In order to obtain such ware it is only necessary to specify that it must show no marked uneven discoloration on heating and must give no test for iron after prolonged ignition (two hours may be regarded as sufficient) and that the rate of loss per hour at 1100° C. over a period of not less than four hours and preferably longer, shall not exceed, say 0.2 milligram. The makers are granted a fair margin of safety in this latter item. Ware which does not meet these conditions should not be accepted if the purchaser is willing to pay the enhanced cost of the better ware. These specifications are subject to revision.

In conclusion, for the present, the committee tenders its thanks to the manufacturers who were interviewed, and especially to those who submitted samples for test. All of them expressed a desire to further

the objects of the committee's investigation and to furnish ware of the best quality, which each asserted his ability to do.

W. F. HILLEBRAND,
PERCY H WALKER,
E. T. ALLEN.

THE DETERMINATION OF NITROGEN IN COMMERCIAL AMMONIATES OF HIGH NITROGEN CONTENT.

First Report of the Committee on Nitrogen, Division of Fertilizer Chemists, American Chemical Society.

In the fall of 1909, the attention of this committee was directed to the frequent discrepancies between the results of analyses by buyers' and sellers' chemists on samples representing shipments of high-grade commercial ammoniates, especially dried blood. The difference was remarkable in its tendency to higher results by the buyer's chemist. A typical example of this condition was shown in the joint analysis of a sample of dried blood prepared by a seller's chemist, as shown in the following table:

Analyst.	Moisture.	Ammonia.	Nitrogen.	Nitrogen moisture-free basis.
1.....	5.12	17.55	14.45	15.23
2.....	5.92	17.52	14.43	15.29
3.....	..	17.48	14.40	..
4.....	5.12	17.90	14.74	15.54
5.....	4.74	17.87	14.72	15.45
6.....	4.95	17.85	14.70	15.47

Analysts 1, 2 and 3 are sellers' chemists; 4, 5 and 6 represent buyers'.

This table shows several important features. It must be borne in mind that payment is not and cannot be justly based on the analysis on a moisture-free basis. While therefore the latter may be considered the best basis of comparison from an analytical standpoint, so long as only the ammonia or nitrogen content is being compared, the actual ammonia or nitrogen content of the sample is the only real point of contention from a commercial standpoint. From the table it will be seen that the buyers' chemists find, on an average, 0.35 per cent. of ammonia or 0.29 per cent. of nitrogen more than the sellers' chemists. Assuming that the value of dried blood is \$3.00 per "unit" (per cent. of ammonia per ton), there is a difference of \$1.05 in the value per ton based on the respective average analyses obtained. From an analytical standpoint, after reducing the results obtained to a moisture-free basis, this difference is reduced somewhat, namely to 0.23 per cent. ammonia or 0.19 per cent. of nitrogen, but this fact does not alter the commercial discrepancy in the least.

The question at once arose: Is this difference due to differences in men or methods? The samples, particularly in the example quoted, were presumably prepared with every care to make them uniform. To answer the question, if possible, this committee decided to prepare samples of several ammoniates in sufficient quantity, and to obtain the true moisture and nitrogen content of these samples, so that they might serve the important purpose of standard samples. It is only by means of such standard samples that any chemist is able to judge the accuracy of his own work or that of his assistants, and it is not fair

to condemn any method unless such standards are available for final judgment, after the necessary experience with the method in question has been acquired.

Two samples were therefore prepared: one of dried blood, the other of high-grade tankage. To these a third was added later, representing a complete fertilizer composed of the dried blood mentioned above, acid phosphate and muriate of potash. After grinding the samples to a suitable degree of fineness, they were divided as follows: The entire sample was thoroughly mixed in a mechanical mixer, and divided into a number of containers while the mixer was running, placing a spoonful at a time into each container in turn. When the entire sample was divided in this way, the same number of fresh containers was set up and the contents of each container of the first set, after thoroughly mixing, was distributed into the second set as before. Finally each container of the second set was emptied on a porcelain tile, the contents thoroughly mixed, and divided into as many approximately equal parts as there were bottles to fill. Each part was then transferred to one of the bottles.

Requests for coöperative work were sent to all those who had registered in the Division of Fertilizer Chemists and to a number of other chemists, in order to obtain results by all the different methods possible, including the absolute or cupric oxid method and the soda-lime method as well as the various "wet combustion" methods.

To those who signified their willingness to coöperate, a set of the samples was sent together with the following instructions:

"It has been brought to the attention of this committee that there are frequently considerable differences between the analyses by various laboratories on the same shipments of high-grade nitrogenous materials, such as blood, tankage, etc. In order to throw light on this matter, it has been decided to send out to those who are willing to coöperate, three samples which have been prepared very carefully so as to ensure uniformity, and a set of these is being mailed to you under separate cover.

"These samples have been passed through a forty-mesh sieve and the determination should be made on them as received without further reduction or grinding. When weighing, the entire contents of each bottle should be spread on a sheet of glazed paper, and after mixing well, the portions for analysis should be taken from the sample thus spread out, while it is well mixed, so as to obtain truly representative analyses. There is more or less tendency to segregation in samples of this kind, and this is particularly true of the mixed fertilizer.

"In each of these three samples moisture and nitrogen are to be determined by the method or methods commonly in use in your laboratory for this work. Please do not report averages, but individual determinations only.

"In addition to reporting your results, will you please describe in detail the method or methods by which your results were obtained? Also please answer the following questions:

"*Moisture*.—(1) How much was weighed out for each determination? (2) At what temperature was the bath kept? (3) Was the sample dried for a specified number of hours, or to constant weight? (4) If the latter, approximately how long did it take to attain constant weight?

"*Nitrogen*.—(1) How much was weighed out for each determination? (2) In the Kjeldahl, Gunning or similar methods, approximately how long did it take for the solution to become clear or practically colorless? (3) How long after this occurred was digestion continued? (4) Was permanganate used? (5) Have you ever noticed evolution of chlorine when permanganate was added? (6) Was the entire digestion distilled, or an aliquot part, and if so, how much? (7) Approximately how long did the distillation last? (8) Approximately what volume was distilled off?

"It is desired to present as complete a report as possible at the Boston meeting, and the committee therefore asks that the results be sent within twenty days from receipt of samples and instructions."

Reports were received from forty-eight laboratories; many included the work of more than one analyst.

Determination of Moisture.—As the results came in it soon became evident that the determination of moisture, which was also asked for, presented at least as much, if not more difficulty than the nitrogen determination. Much stress was laid on this by many coöperators, as shown by the extensive and painstaking work reported upon, while many others seemed to attach no importance whatever to this feature.

Many reports included the results of a large number of determinations, often under different conditions and often also by different methods. In some cases an attempt was made to show differences in this way by means of single determinations. It is unfortunate, to say the least, that time and energy should be wasted in such attempts, instead of concentrating in one or two definite directions. Some reports included single determinations by one method only. The moisture determinations are summarized in Table 1.

TABLE 1.—DETERMINATION OF MOISTURE.—SUMMARY.

	Dried blood.	Tankage.	Complete fertilizer.
Number of individual determinations.	204	207	192
Number of individual averages.	72	71	65
Mean of individual averages.	6.15	1.56	1.83
Maximum of individual averages.	7.74	2.49	2.99
Minimum of individual averages.	5.07	0.89	1.07
Standard deviation.	0.478	0.345	0.473
Probable error of the mean.	0.0416	0.0292	0.0405
Probable error of the individual averages	0.330	0.230	0.319

A few sets of determinations by the vacuum method and one set by drying in hydrogen were received. A great many results were reported showing the effects of redrying and of drying under various conditions. In these cases only the results of the first drying were included in the averages as being deemed more nearly comparable with the results of drying but once, usually five hours. Aside from these repetitions, few results have been omitted from the averages. Only obviously erroneous results, shown to be so by subsequent work of the respective analysts themselves, were omitted. All the moisture results were

averaged together, because those reported by drying in vacuum were too few in number to furnish an average comparable with that obtained by drying with access of air.

There is a remarkable degree of variation between the various analysts. Atmospheric conditions such as of temperature or humidity appear to have at least as much, if not more, bearing on the results than variations in details of manipulation or drying. In one instance, it was possible to confirm this in the case of the dried blood, where a difference of 1 per cent. was obtained by two analysts in the same laboratory. The higher results were obtained during a wet snow-storm, while the lower were obtained on a bright, crisp, sunny, but cold day. Many series of determinations, on the other hand, showed clearly the effects of gradual absorption of moisture.

The means in Table 1 were calculated from the individual averages rather than from the individual single determinations, although in this way the results of single determinations were given equal weight with the results of duplicate and triplicate determinations. It is unfortunate that not all results were determined in duplicate or triplicate, but it is highly probable that any given number of determinations by a single analyst would give a less accurate and less desirable average than the same number of single determinations by as many analysts. Practically speaking, the former would represent just one set of accidental conditions of determinations, while the latter would represent a large and random assortment of sets of such accidental conditions.

The results summarized in Table 1 were also considered from a statistical standpoint and an attempt to find the measure of concentration of the determinations about the mean was made and expressed as the standard deviation in terms of per cent. of moisture. At the same time the probable error of the mean and of the individual average determinations were also calculated and these values are included in Table 1. It will be seen that these values are of practically the same or very nearly the same order of magnitude for the three samples examined. The significance of these values will be discussed again further on in connection with the determination of nitrogen.

It will be seen from the above results that the determination of moisture, usually considered a very simple one, is in reality a very complex matter dependent upon conditions in a much larger measure perhaps than many other determinations or than is usually supposed to be the case.

Determination of Nitrogen.—The results of the determination of nitrogen have been grouped as far as possible according to the method employed. For the purposes of better comparison the average moisture values obtained by each analyst have been used in the nitrogen tables to calculate the results to a moisture-free basis. In cases where no moisture was determined the average moisture values from Table 1 were used for this purpose.

The result of the absolute or cupric oxid method follow in Table 2.

TABLE 2.—DETERMINATION OF NITROGEN. ABSOLUTE METHOD.

Anal.	Description of method.	Dried blood.				Tankage.				Complete fertilizer.						
		Per cent. average moisture.	Nitrogen.		Per cent. moisture-free basis.	Per cent. average moisture.	Nitrogen.		Per cent. moisture-free basis.	Per cent. average moisture.	Nitrogen.		Per cent. moisture-free basis.			
			Per cent. indiv. determ.	Per cent. mean.			Per cent. indiv. determ.	Per cent. mean.			Per cent. indiv. determ.	Per cent. mean.				
1 B	Closed tube, without use of vacuum pump, CO ₂ from NaHCO ₃ . 0.15-0.25 gram taken for analysis.				
	Preliminary.....	..	16.37	11.88				
	Final.....	..	14.83	11.55				
		..	15.22	9.95				
		..	15.09	10.11				
		..	15.28	10.07				
		6.37	15.33	15.23	16.27	1.93	9.89	10.01	10.21				
2	Open tube, specially long comb. tube, CO ₂ from NaHCO ₃ in special generator.				
	Preliminary.....	..	13.87	9.09	3.79				
	Final.....	..	14.04	8.93				
		..	14.68	9.18	4.17				
		..	14.51	9.24	3.99				
		6.46	..	14.60	15.61	1.51	9.35	9.24	9.38	2.02	3.99	4.05	4.13			
3 B	Open tube, CO ₂ from conc. K ₂ CO ₃ sol. 0.16-0.53 gram taken for analysis.	..	14.10	10.44	3.95				
		6.34	13.93	14.02	14.97	1.46	10.44	10.44	10.59	1.91	4.17	4.06	4.14			
17	Closed tube, CO ₂ from magnesite. 0.2-0.6 gram taken for analysis.	6.10	14.67	14.70	14.69	15.63	1.27	9.22	9.20	9.21	9.35	1.51	4.02	3.95	3.99	4.05
		..	15.10	9.27	4.02	
	Open tube, CO ₂ from NaHCO ₃ .	6.10	15.10	15.10	16.07	9.31	9.29	9.41	1.51	4.16	4.09	4.16		
		..	14.96	9.55		
18	Open tube.	6.11	14.98	14.97	15.94	1.40	9.58	9.56	9.70	1.58	4.38	4.38	4.45			

No attempt has been made to calculate averages from Table 2, as the results are too discordant. That the usual method of combustion is not adapted to this class of materials soon became evident to the analysts concerned. Analyst 2 in particular found that an unusually long time of combustion at a high heat was necessary to get off all the nitrogen, as shown in the difference between his preliminary and final results. It is not to be assumed that anything but nitrogen from the sample was measured in this work, but no explanation has been made of the great discrepancy of results obtained by this method, and we can only conclude that these materials are not adapted to the absolute method as usually carried out.

Only one set of results by the soda-lime method was received which is shown in Table 3.

TABLE 3.—DETERMINATION OF NITROGEN, SODA-LIME METHOD.

	Moisture. Per cent.	Nitrogen, moisture-free basis.	
		Nitrogen. Per cent.	Per cent.
Dried blood.....	6.41	14.48	15.47
Tankage.....	1.33	9.61	9.74
Complete fertilizer.....	1.58	3.98	4.04

The excellent agreement of these results with those obtained by the "wet combustion" methods, as will be shown later, is all the more interesting, since only single determinations were made by this analyst. He states, however, that he has determined nitrogen by this method for sixteen years.

The results by the official Kjeldahl method have been divided into two sets. In Table 4 is shown a summary of the results where potassium permanganate was used to complete oxidation. The summary of the results by the same method without permanganate is shown in Table 5 and the results

by the other "wet combustion" methods are summarized in Tables 6-10.

TABLE 4.—DETERMINATION OF NITROGEN. KJELDAHL METHOD WITH PERMANGANATE.

	No. of analysts.	No. of indiv. determination.	Moist.	Mean.	Nitrogen.		Mean, moisture-free basis.
					Maximum.	Minimum.	
Dried blood.....	27	77	6.13	14.39	14.56	14.11	15.32
Tankage.....	27	81	1.56	9.57	9.80	9.37	9.72
Complete fertilizer....	27	74	1.77	4.06	4.15	3.90	4.13

The results of one analyst only were omitted from Table 4 as they were abnormally high. No explanation could be found for this and although it seems probable that the fault lay with the standard acid and alkali employed, this opinion is purely speculation.

As the results of one analyst are of particular interest in the case of the dried blood and the tankage, indicating a definite tendency towards higher results with increased time of digestion, they have been tabulated together with his results by the Gunning method in Table 8. An attempt to show this tendency was also made by one or two other analysts, although not so clearly and successfully.

TABLE 5.—DETERMINATION OF NITROGEN. KJELDAHL METHOD WITHOUT PERMANGANATE.

	No. of analysts.	No. of indiv. determination.	Moist.	Mean.	Nitrogen.		Mean, moisture-free basis.
					Maximum.	Minimum.	
Dried blood.....	10	23	5.81	14.39	14.54	14.29	15.30
Tankage.....	10	32	1.63	9.51	9.59	9.32	9.66
Complete fertilizer....	10	25	1.95	4.05	4.17	3.92	4.13

A comparison of the individual results by the Kjeldahl method shows a general tendency towards shortening the time of digestion where permanganate was used. On the other hand, the agreement of the results with permanganate is not quite so good as that of the results where permanganate was omitted. It is natural to draw the inference that the use of permanganate does not seem to be a perfectly satisfactory substitute for longer digestion.

TABLE 6.—DETERMINATION OF NITROGEN. KJELDAHL-GUNNING METHOD WITH PERMANGANATE.

	No. of analysts.	No. of indiv. de-termination.	Moist.	Mean.	Nitrogen.		Mean, moisture-free basis.
					Maximum.	Minimum.	
Dried blood.....	5	13	6.15	14.41	14.51	14.33	15.36
Tankage.....	5	14	1.48	9.53	9.66	9.39	9.67
Complete fertilizer....	5	11	2.01	4.02	4.12	3.89	4.10

This table includes a few results obtained with potassium sulphate in addition to mercury and permanganate. The results in this table indicate that this method will yield results agreeing very well with those in Tables 4 and 5, although the time of digestion may be extremely short.

TABLE 7.—DETERMINATION OF NITROGEN. GUNNING METHOD.

	No. of analysts.	No. of indiv. de-termination.	Moist.	Mean.	Nitrogen.		Mean, moisture-free basis.
					Maximum.	Minimum.	
Dried blood.....	15	50	6.25	14.37	14.56	14.26	15.32
Tankage.....	15	42	1.65	9.48	9.66	9.39	9.63
Complete fertilizer....	15	38	1.95	4.06	4.16	3.90	4.13

The individual results in Table 7 indicate that while a short time of digestion in the Gunning method may not necessarily cause low results yet low results are

TABLE 8.—DETERMINATION OF NITROGEN. 1. KJELDAHL METHOD WITH PERMANGANATE. 2. GUNNING METHOD.

Total time of diges- tion.	Dried blood.				Tankage.				Complete fertilizer.			
	Per cent. aver- age moisture.	Nitrogen.		Per cent. mois- ture-free basis.	Per cent. aver- age moisture.	Nitrogen.		Per cent. mois- ture-free basis.	Per cent. aver- age moisture.	Nitrogen.		Per cent. mois- ture-free basis.
	Per cent.	indiv. de- termina- tion.	Per cent. mean.		Per cent.	indiv. de- termina- tion.	Per cent. mean.		Per cent.	indiv. de- termina- tion.	Per cent. mean.	
1 Until clear.....	..	14.34	9.54
2-3 hours.....	..	14.38	9.59
	..	14.43	9.53	4.08
	..	14.48	9.55	4.09	4.09	4.15
	..	14.48	9.48
2 1/2 hrs. after clearing.....	..	14.37	9.30
3 1/2 hrs. after clearing.....	..	14.53	9.44
4 1/2 hrs. after clearing.....	6.11	14.55	14.43	15.37	1.40	9.51	9.49	9.63	1.58
2 Until clear.....	..	14.32	9.56	4.06
2-3 hours.....	..	14.37	9.64	4.05
	..	14.43	9.61	1.58	4.09	4.07	4.13
	..	14.43	9.65
	..	14.43	9.58
2-2 1/2 hrs. longer.....	..	14.42	9.44
3-3 3/4 hrs. longer.....	..	14.58	9.46
4-4 1/2 hrs. longer.....	6.11	14.60	14.45	15.39	1.40	9.60	9.57	9.71

practically always accompanied by a short time of digestion. The inference is that the time of digestion in the Gunning method must be longer than in any other "wet combustion" method, probably not less

than four to five hours. This has been confirmed by the work of Sherman and Falk.¹

The low results of several analysts in the case of the dried blood would seem to indicate clearly too short a time of digestion. The analyst referred to previously, on the other hand, again demonstrates very clearly the tendency of increased time of digestion towards higher results and his results by the Gunning and by the Kjeldahl method are shown in Table 8.

TABLE 9.—DETERMINATION OF NITROGEN. KJELDAHL-GUNNING METHOD.

	No. of analysts.	No. of indiv. de-termination.	Moist.	Mean.	Nitrogen.		Mean, moisture-free basis.
					Maximum.	Minimum.	
Dried blood.....	23	59	6.29	14.47	14.66	14.26	15.44
Tankage.....	23	58	1.67	9.65	9.80	9.41	9.81
Complete fertilizer....	23	58	2.04	4.10	4.21	3.76	4.18

This method, involving the use of both potassium sulphate and mercury, is being used widely outside of official fertilizer control and is also apparently in considerable use for fertilizer control work in the laboratories of fertilizer manufacturers. It shows a distinct tendency towards higher results, and the agreement between the various analysts is perhaps somewhat better than that obtained by the other "wet combustion" methods, since no results had to be omitted from this table.

TABLE 10.—DETERMINATION OF NITROGEN. GUNNING METHOD WITH COPPER SULPHATE.

	No. of analysts.	No. of indiv. de-termination.	Moist.	Mean.	Nitrogen.		Mean, moisture-free basis.
					Maximum.	Minimum.	
Dried blood.....	7	21	5.85	14.42	14.65	14.24	15.38
Tankage.....	7	21	2.26	9.51	9.70	9.39	9.69
Complete fertilizer....	7	18	1.84	4.06	4.17	3.94	4.13

A similar tendency towards higher results, though not so marked as in the Kjeldahl-Gunning method, is shown in the results by the Gunning method with

¹ *J. Am. Chem. Soc.*, 26, 1469 (1904).

copper sulphate which has recently been adopted as official by the A. O. A. C.

TABLE 11.—DETERMINATION OF NITROGEN. KJELDAHL METHOD WITH COPPER SULPHATE.

	No. of analysts.	No. of indiv. determination.	Nitrogen.				Mean moist.-free basis.
			Moist.	Mean.	Maximum.	Minimum.	
Dried blood.....	2	10	5.17	14.44	14.48	14.41	15.23
Tankage.....	2	10	1.11	9.55	9.55	9.55	9.66
Complete fertilizer....	2	10	1.44	4.07	4.09	4.05	4.16

The results by this method are too few in number to afford a satisfactory basis for comparison with other methods. From the results reported, however, no particular advantage is evident from the use of both copper sulphate and mercury.

Attention is also called in this connection to the recent work of Hibbard on the use of copper sulphate.¹

The average results of all the "wet combustion" methods tabulated above are given in the following table.

This table shows very clearly in the case of the dried blood that the lowest results were obtained by the Kjeldahl method with and without permanganate and by the Gunning method, while the highest results were obtained by the Kjeldahl-Gunning method. This is also true in the case of the tankage, except in the Kjeldahl method with permanganate and is also true, though to a lesser degree, in the case of the complete fertilizer. The use of copper sulphate as shown in Tables 9 and 10 also tends towards slightly higher results, but not quite so much as the use of potassium sulphate with mercury, *i. e.*, the Kjeldahl-Gunning method.

Table 9 could be duplicated by other analysts than those who were accustomed to using this method, requests for further work were sent out by the chairman of the committee to a number of analysts who had not reported results by this method, together with the following letter of instructions.

"I am enclosing a tabulation of the range and averages of results obtained on the three standard samples sent out by the Committee on Nitrogen and I should be glad to have your comments after you have looked over these results.

"If you have sufficient of the samples left, will you kindly retest these in triplicate by the following method and report to me within thirty days? If you have not enough left, please notify me at once.

"*Determination of Moisture and Nitrogen.*—When weighing, the entire contents of each bottle should be spread on a sheet of glazed paper and after mixing well, the portions for the determination of moisture as well as for nitrogen should be taken at the same time from the sample thus spread out, mixing again after each weighing, so as to obtain truly representative portions.

"*Moisture.*—Weigh out, in triplicate, portions of approximately 2.5 grams into weighing dishes which can be tightly covered or watch-glasses held together by clips in the usual manner.

"Do not try to weigh out exactly 2.5 grams, but after having placed approximately 2.5 grams in the dish, cover tightly and finish weighing. Dry for four hours, keeping the temperature of the bath as close to 100° C. as possible. The ventilation of the bath should be as efficient as it can possibly be made. Cool in tightly covered dishes in the desiccator for one hour before weighing.

"*Nitrogen.*—Weigh on a nitrogen-free filter paper

TABLE 12.—DETERMINATION OF NITROGEN. GENERAL MEAN VALUES FROM TABLES 4 TO 7.

Table.	Method.	Dried blood.			Tankage.			Complete fertilizer.					
		Per cent. average moisture.	Nitrogen.		Per cent. moisture-free basis.	Per cent. average moisture.	Nitrogen.		Per cent. moisture-free basis.	Per cent. average moisture.	Nitrogen.		Per cent. moisture-free basis.
			Per cent. indiv. determination.	Per cent. mean.			Per cent. indiv. determination.	Per cent. mean.			Per cent. indiv. determination.	Per cent. mean.	
4	Kjeldahl with permanganate.....	6.13	14.38	14.39	15.32	1.56	9.57	9.57	9.72	1.77	4.05	4.06	4.13
5	Kjeldahl without permanganate.....	5.81	14.37	14.39	15.30	1.63	9.45	9.51	9.66	1.95	4.03	4.05	4.13
6	Kjeldahl-Gunning with permanganate....	6.15	14.38	14.41	15.36	1.48	9.52	9.53	9.67	2.01	4.02	4.02	4.10
7	Gunning.....	6.25	14.38	14.37	15.32	1.65	9.48	9.48	9.63	1.95	4.06	4.06	4.13
8	Kjeldahl-Gunning.....	6.29	14.47	14.47	15.44	1.67	9.65	9.81	9.81	2.04	4.03	4.10	4.18
9	Gunning with copper sulphate.....	5.85	14.48	14.42	15.38	2.26	9.54	9.51	9.69	1.84	4.08	4.06	4.13
10	Kjeldahl with copper sulphate.....	5.17	14.46	14.44	15.23	1.11	9.55	9.55	9.66	1.44	4.06	4.07	4.16

In general, however, the agreement of the corresponding nitrogen values from all the tables must be considered quite satisfactory, whether considered as determined or on a moisture-free basis. The greatest variation is shown in the case of the dried blood in Table 11 on a moisture-free basis, but this is due to the coincidence that the only two analysts reporting on this method obtained a much lower moisture value than the average.

In order to determine whether the high results obtained by the Kjeldahl-Gunning method as shown in

(an ash-free 11 cm. filter paper answers this requirement) 1.401 grams of the blood and of the tankage and 2.802 grams of the mixed fertilizer. Also weigh out three portions of 2 grams each of pure sugar in the same manner. To each of these weighed portions add 5 grams of potassium sulphate and 0.7 gram of mercuric oxide (0.5 gram of pure mercury may be substituted for the mercuric oxide).

"Roll up each weighed portion in its filter paper and drop it into the digestion flask, then add 25 cc. of concentrated sulphuric acid and digest, noting approximately the time it takes for the contents to be-

¹ THIS JOURNAL, 2, 463 (1910).

come (a) entirely liquefied, and (b) to become colorless or practically so. Digestion should be continued for two hours after final color has been reached. The general experience with this method has been that the digestion comes to final color in 30-45 minutes and the total digestion can, therefore, be made in from two to two and one-quarter hours.

"Do not use permanganate, but distil the entire digestion. After cooling, dilute with 200 cc. of water, add a little granulated zinc and then a mixture of 25 cc. of a 4 per cent. potassium sulphide solution with the necessary quantity of caustic soda solution. Distil off not less than 200 and not more than 250 cc. Determine the ammonia in the distillate in the usual manner, using cochineal as indicator. Report results as both ammonia and nitrogen, giving your individual results and blanks, not averages."

At the same time a tentative tabulation of the averages obtained up to that time was sent to all coöperators, and in considering the results of this additional work as summarized in Tables 13 and 14, it must be borne in mind that the results of the previous work were known in a general way by those in charge of the various laboratories, if not by analysts actually doing the work, thus affording opportunity for revision where desired.

TABLE 13.—DETERMINATION OF MOISTURE. METHOD AS OUTLINED BY COMMITTEE ON NITROGEN.

	No. of analysts.		Moisture.		
	No. of indiv. determination.	Mean.	Maximum.	Minimum.	
Dried blood.....	12	40	6.57	7.82	5.07
Tankage.....	12	38	2.38	4.73	1.06
Complete fertilizer.....	12	36	2.42	3.51	1.62

These results show a larger variation than the values given in Table 1 and indicate that in many cases considerable moisture had been absorbed by the samples in the meantime. Some of the results shown in this table were obtained on the remainder of the original samples in the possession of the respective analysts, others were obtained on fresh samples supplied by the committee. For this reason a statistical treatment of the results was not attempted.

Criticism was freely made on that part of the direc-

tions which specify that the samples were to be spread out on a glazed paper and thoroughly mixed after the withdrawal of each portion weighed out. This criticism is well founded, particularly if the determinations are made on days when the relative humidity is high and will have to be taken into consideration in formulating methods for future work on this subject. It will have to be remembered, however, that these materials are not homogeneous, that it is not feasible in control work to weigh out other than a factor weight, so as to avoid unnecessary calculation, and that the resulting tendency to unmix must be overcome. It is easily possible for instance, either intentionally or carelessly, to weigh portions of dried blood from the same sample which will differ from each other by 0.5 per cent. of nitrogen or more.

The results of the nitrogen determinations are summarized in Table 14.

TABLE 14.—DETERMINATION OF NITROGEN. KJELDAHL-GUNNING METHOD AS OUTLINED BY COMMITTEE ON NITROGEN.

	No. of analysts.		No. of indiv. determination.	Moist.	Mean.	Nitrogen.		Mean moist.-free basis.
	No. of indiv. determination.	Mean.				Maximum.	Minimum.	
Dried blood.....	16	58	6.62	14.37	14.56	14.05	15.41	
Tankage.....	16	61	2.58	9.51	9.78	9.02	9.76	
Complete fertilizer....	16	39	2.41	4.09	4.17	4.00	4.19	

The individual results summarized above show no improvement in agreement between the various analysts over the previous tables. The averages of the nitrogen results as determined are lower than the averages in Table 9, but this is obviously due to the absorption of moisture by many of the samples reported upon in this table. When, however, the averages on a moisture-free basis are considered, it will be seen that the tendency towards higher average results shown in Table 9 is confirmed. This is shown very clearly in Table 15, which is essentially the same as Table 12 with the data from Tables 13, 14 and 3 added.

In order to show whether the results by any of the methods were more uniform than those obtained by other methods, a comparison of the statistical data calculated from the various tables is given in Table 16.

TABLE 15.—DETERMINATION OF NITROGEN. GENERAL MEAN VALUES FROM TABLES 3, 4 TO 10 AND 14.

Table.	Method.	Dried blood.			Per cent. moisture-free basis.	Tankage.			Per cent. moisture-free basis.	Complete fertilizer.			Per cent. moisture-free basis.
		Per cent. average moisture.	Per cent. indiv. determination.	Per cent. mean.		Per cent. average moisture.	Per cent. indiv. determination.	Per cent. mean.		Per cent. average moisture.	Per cent. indiv. determination.	Per cent. mean.	
3	Soda lime.....	6.41	14.48	...	15.47	1.33	9.61	...	9.74	1.58	3.98	...	4.04
4	Kjeldahl with permanganate.....	6.13	14.38	14.39	15.32	1.56	9.57	9.57	9.72	1.77	4.05	4.06	4.13
5	Kjeldahl without permanganate.....	5.81	14.37	14.39	15.30	1.63	9.45	9.51	9.66	1.95	4.03	4.05	4.13
6	Kjeldahl-Gunning with permanganate.....	6.15	14.38	14.41	15.36	1.48	9.52	9.53	9.67	2.01	4.02	4.02	4.10
7	Gunning.....	6.25	14.38	14.37	15.32	1.65	9.48	9.48	9.63	1.95	4.06	4.06	4.13
8	Kjeldahl-Gunning.....	6.29	14.47	14.47	15.44	1.67	9.65	9.81	9.81	2.04	4.03	4.10	4.18
9	Gunning with copper sulphate.....	5.85	14.48	14.42	15.38	2.26	9.54	9.51	9.69	1.84	4.08	4.06	4.13
10	Kjeldahl with copper sulphate.....	5.17	14.46	14.44	15.23	1.11	9.55	9.55	9.66	1.44	4.06	4.07	4.16
14	Kjeldahl-Gunning as outlined by the committee.....	6.62	14.37	14.37	15.41	2.58	9.52	9.51	9.76	2.41	4.09	4.09	4.19

TABLE 16.—COMPARATIVE STATISTICAL DATA FROM TABLE 1 TO 14.

Table.	Method.	Dried blood.			Tankage.			Complete fertilizer.		
		Per cent. standard deviation.	Per cent. probable error of the mean.	Per cent. probable error of a single determination standard.	Per cent. deviation.	Per cent. probable error of the mean.	Per cent. probable error of a single determination.	Per cent. standard deviation.	Per cent. probable error of the mean.	Per cent. probable error of a single determination.
1	Moisture.....	0.478	0.0416	0.330	0.345	0.0292	0.230	0.473	0.0405	0.319
4	Kjeldahl with permanganate.....	0.142	0.019	0.096	0.108	0.014	0.073	0.062	0.008	0.041
5	Kjeldahl without permanganate.....	0.104	0.0266	0.070	0.140	0.0357	0.0946	0.0864	0.0238	0.0583
6	Kjeldahl-Gunning with permanganate...	0.074	0.022	0.050	0.115	0.035	0.078	0.094	0.028	0.064
7	Gunning.....	0.119	0.022	0.080	0.107	0.019	0.073	0.053	0.012	0.036
8	Kjeldahl-Gunning.....	0.127	0.028	0.086	0.114	0.025	0.077	0.0828	0.018	0.056
9	Gunning with copper sulphate.....	0.167	0.0033	0.142	0.109	0.0088	0.074	0.091	0.0079	0.061
14	Kjeldahl-Gunning.....	0.122	0.0178	0.082	0.118	0.0194	0.080	0.046	0.0083	0.031

The agreement of the various analysts on moisture determinations is shown clearly to be decidedly inferior to the agreement on nitrogen determinations. Moreover, it was not possible to show any degree whatever of correlation between the corresponding moisture and nitrogen determinations. It was to be expected, for instance, that low nitrogen values on the part of any one analyst would be accompanied by correspondingly high moisture values, but no relation of this sort could be demonstrated.

Practically all the corresponding nitrogen data are of the same order of magnitude, and the exceptions are either confined to tables with comparatively few results, or they are of nearly the same order of magnitude as the majority of the data.

The committee does not, therefore, deem it expedient to make recommendations in favor of any particular method. As a matter of fact, it became evident during the progress of the work that the standardization of the samples prepared would ultimately prove to be of more value than any other feature of the work. There is a considerable supply of the samples of dried blood and tankage available. The supply of complete fertilizer has been exhausted, as only a limited number of samples of this material were prepared for the purpose of showing that greater uniformity would be obtainable among different analysts in the case of a material of low nitrogen content than in one of high nitrogen content. A study of the results of this work fully confirms this view, which was, moreover, to be expected from a purely mathematical standpoint.

The data brought out by the questions included in the letter of instructions were not all tabulated.

The arrangement of the tables shows whether permanganate was or was not used in any given case.

The amount weighed out for the determination of nitrogen was very uniform, between 1 and 2 grams.

The time of digestion to colorless, light straw or straw-yellow was variously given as from twenty minutes to three hours, usually from one-half to one and one-half hours. The total time of digestion varied from one to four hours.

No evolution of chlorine was noticed by any one but the analyst who raised the question.

Only eight analysts took aliquot parts of the digestion for distillation. In all other cases the entire digestion was distilled.

The time of distillation and the volume distilled off, where stated, varied considerably and no definite tendency could be observed in a study of the data obtained on these points.

The standard acid and alkali constitute a very important factor in this work. Comparative tests were made by one of the members of the committee with five of the cooperating analysts. In four of these cases the agreement was most excellent, while in the fifth there was a difference, but not sufficient to account for the materially higher results obtained by this particular analyst. Since, however, differences in this respect may become cumulative together with differences from other sources, the committee believes that this phase of the subject requires further study.

The results of this work may be summarized as follows:

First.—Results were reported by forty-eight cooperating laboratories.

Second.—An average of over 220 individual moisture determinations on each of the three samples were received and tabulated.

Third.—The agreement obtained between the results of moisture determinations of the cooperating analysts was much inferior to that obtained in the determination of nitrogen.

Fourth.—In future cooperative work on the determination of moisture, atmospheric conditions will have to be taken into consideration in addition to details of manipulation, apparatus and methods of drying.

Fifth.—Special precautions are necessary in the preparation and packing of samples representing shipments of these and similar commodities in order that changes in the moisture content may be reduced to a minimum.

Sixth.—An average of over 250 individual nitrogen determinations on each of the three samples were received and tabulated.

Seventh.—The absolute or cupric oxid method as usually carried out does not appear to be applicable to dried blood or tankage.

Eighth.—Since only one set of single determinations by the soda-lime method was received, no conclusions can be drawn or comparisons made between this and other methods which would be general in their nature.

Ninth.—The "wet combustion" methods give mean values which agree satisfactorily with each other,

whether these values be considered as determined or whether they be calculated to a moisture-free basis.

Tenth.—The Kjeldahl-Gunning method, *i. e.*, the use of potassium sulphate with mercury, gives consistently higher mean results than any other wet combustion method.

Eleventh.—Since the chances for error in the "wet combustion" method, aside from possible errors in standard acid and alkali, rarely, if ever, tend towards high results, it is safe to assume that the mean of the Kjeldahl-Gunning method gives more nearly the true nitrogen content than the other "wet combustion" methods. The only common sources of error in determining nitrogen by "wet combustion" which would tend towards high results would be contamination with ammonia fumes either during digestion or distillation and the driving over of caustic alkali during distillation as sometimes happen when too great an excess of alkali is used and the contents of the distilling flasks are boiled down too far or when foaming occurs unnoticed. Practically all other ordinary sources of error would tend towards low results, aside from errors in the standard solutions used.

Twelfth.—The Gunning method apparently requires a longer time of digestion than the other "wet combustion" methods. If the total time of digestion in this method is less than four hours, there is danger of low results.

Thirteenth.—In the Kjeldahl method, permanganate apparently enables the operator to shorten the time of digestion, but the use of permanganate is objectionable to many analysts and is unnecessary, if either a longer time of digestion or the use of potassium sulphate in conjunction with mercury (Kjeldahl-Gunning method) be employed.

Fourteenth.—The use of copper sulphate does not appear to represent any advantages over the use of mercury in point of time of digestion, its chief advantage consisting in doing away with the use of sulphid.

The committee is of the opinion that the very large number of individual determinations reported in this work may be safely assumed to form a good basis for approximating the true nitrogen content of the samples in question within narrow limits so far as shown by the "wet combustion" methods. Indeed, for practical purposes and from a commercial standpoint, it may be safely assumed that the true nitrogen values of these samples have been obtained with a satisfactory degree of accuracy, provided that analysts availing themselves of these samples will not attempt to determine the nitrogen without also carefully determining the moisture at the same time.¹

The committee desires to acknowledge its indebtedness to all those who coöperated in this work, and to thank them for the cordial spirit with which our requests were met throughout the work. Special acknowledgment is due to Dr. H. S. Grindley and

¹ For the present, further samples may be obtained upon application to the chairman of this committee, and inasmuch as no funds are available for this purpose, applicants for these samples are requested to remit \$0.15 for each sample desired to cover postage and packing.

Mr. H. H. Mitchell, of the University of Illinois, for their valuable advice and assistance in the statistical study of the numerical results of this work.

Among those who coöperated in this work were the following:

F. G. Allison, College of Agriculture, University of Illinois, Urbana, Ill.

B. W. Bangs, American Agricultural Chemical Company, Carteret, N. J.

G. F. Beyer, Armour & Company, So. Omaha, Neb.

J. E. Breckenridge, American Agricultural Chemical Company, Carteret, N. J.

Dr. J. S. Burd, University of California, Berkeley, California.

L. M. Burghardt, University of Illinois, Urbana, Illinois.

L. S. Bushnell, Armour & Company, Kansas City, Kansas.

Dr. F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Va.

E. Carroll, University of Illinois, Urbana, Illinois.

Professor Cavanaugh, Cornell University, Ithaca, New York.

Paul Collins, New Haven, Conn.

W. D. Cooke, Virginia-Carolina Chemical Company, Richmond, Va.

Dr. C. E. Derick, University of Illinois, Urbana, Illinois.

W. P. Dunne, Morris & Company, Chicago, Illinois.

G. Farnham, Jarecki Chemical Company, Cincinnati, Ohio.

Frederick Fenger, Armour & Company, Chicago, Illinois.

T. B. Ford, Bureau of Standards, Washington, D. C.

Gascoyne & Company, Baltimore, Md.

F. W. Gill, College of Agriculture, University of Illinois, Urbana, Ill.

Geo. Guckenberger, F. C. Broeman & Company, Cincinnati, Ohio.

H. H. Hanson, Maine Agr. Exp. Station, Orono, Maine.

Dr. B. L. Hartwell, Rhode Island Agr. Exp. Station, Kingston, R. I.

P. L. Hibbard, University of California, Berkeley, California.

T. N. Havlin, Morris & Company, E. St. Louis.

O. C. Haworth, Lafayette, Indiana.

C. C. James, Pacific Guano & Fertilizer Company, Honolulu, H. T.

C. H. Jones, Vermont Agr. Exp. Station, Burlington, Vermont.

W. J. Jones, Jr., Indiana State Chemist, Lafayette, Indiana.

Dr. G. E. F. Lundell, Cornell University, Ithaca, New York.

Wilson H. Low, Cudahy Packing Company, So. Omaha, Neb.

A. Lowenstein, Morris & Company, Chicago, Illinois.

Dr. F. J. Maywald, 89 Pine Street, New York. McCandless Laboratory, Atlanta, Ga.

P. L. McCreary, University of California, Berkeley, California.

Dr. A. T. McLeod, University of Chicago, Chicago, Illinois.

W. D. McNally, Armour & Company, National Stock Yards, Illinois.

G. W. Miles, Boston, Mass.

W. C. Moor, Armour & Company, North Ft. Worth, Texas.

E. G. Moore, Morris & Company, Chicago, Illinois.

H. C. Moore, Armour Fertilizer Works, Atlanta, Ga.

F. A. Nantz, Arkansas Cotton Oil Company, Little Rock, Arkansas.

Rudolph Neu, Armour Fertilizer Works, Jacksonville, Florida.

P. K. Nisbet, American Agricultural Chemical Co., No. Weymouth, Mass.

Dr. F. L. Parker, Jr., Parker Laboratory, Charleston, S. C.

C. L. Pfersch, New Jersey Agr. Exp. Station, New Brunswick, New Jersey.

J. R. Powell, Armour Glue Works, Chicago, Illinois.

E. G. Proulx, Lafayette, Indiana.

W. D. Richardson, Swift & Company, Chicago, Illinois.

W. Rodes, Kentucky Agr. Exp. Station, Lexington, Kentucky.

F. Roman, University of Illinois, Urbana, Illinois.

I. R. Rothrock, Armour Fertilizer Works, Baltimore, Md.

Paul Rudnick, Armour & Company, Chicago, Illinois.

O. M. Shedd, Kentucky Agr. Exp. Station, Lexington, Kentucky.

S. H. Sheib, Tennessee Chemical Company, Nashville, Tennessee.

John Short, E. Rauh & Sons, Fertilizer Company, Indianapolis, Ind.

Professor J. F. Snell, McDonald College, Quebec, Canada.

H. D. Spears, Kentucky Agr. Exp. Station, Lexington, Kentucky.

B. E. St. John, Morris & Company, Kansas City.

E. E. Thomas, University of California, Whittier, California.

E. O. Thomas, Norfolk, Va.

T. C. Trescot, Bureau of Chemistry, Washington, D. C.

W. L. Whitehouse, Coe-Mortimer Company, Moosic, Pa.

Dr. T. J. Willard, Kansas Agr. Exp. Station, Manhattan Kansas.

Dr. F. W. Woll, University of Wisconsin, Madison, Wisconsin.

Respectfully submitted,

Committee on Nitrogen,

C. H. JONES,

F. C. ATKINSON,

F. L. PARKER, JR.,

PAUL RUDNICK, *Chairman.*

REPORT OF COMMITTEE ON FERTILIZER LEGISLATION.

JUNE MEETING, A. C. S., 1911.

There has been no material change in the fertilizer laws of the different states since our last meeting.

While the laws are ample to protect both the manufacturers and consumers, there is a tendency among a certain class of representatives from the rural districts to introduce bills in the Legislatures which if enacted would impose useless hardships upon the manufacturers and would afford practically no additional protection to the consumers. Fortunately the "rule of reason" usually prevails, and not many of these proposed regulations are enacted into laws. Such bills as I refer to if they should become laws would necessarily increase the price of fertilizers to the consumers. It is, therefore, for the best interests of all concerned to endeavor as far as possible to encourage the passage of such laws as will protect all interests concerned, and impose the least hardship on the manufacturer.

The matter of most importance at the present time is the examination of fertilizers for the availability of the organic nitrogen contained. The different agricultural departments have taken up this matter and adopted tentative methods of analysis which have been in force during the past season. The New England States, including New York and New Jersey, are using what is known as the alkaline permanganate method, and the Southern States the neutral permanganate with final recourse to the pepsin hydrochloric acid method. It is a well known fact that none of these methods will give satisfactory results on all classes of materials, and the results on the same materials by the different methods are entirely at variance. It is to be hoped that before any method is enacted into a law a more satisfactory process will be devised which will not only give the true value of the different classes of ammoniates, but will give uniform and satisfactory results in the hands of different analysts.

F. B. CARPENTER,
Chairman.

POTASH WORK OF FERTILIZER DIVISION WITH COMPARISON OF OFFICIAL METHOD AS GIVEN IN BULLETIN, 1907, U. S. DEPARTMENT OF AGRICULTURE AND A MODIFIED METHOD.

JUNE MEETING, A. C. S., 1911.

Modified official method which consisted in washing two grams on eleven cm. filter paper with small portions of hot (boiling) water into a 200 cc. flask to about 175 cc., adding two cc. concentrated HCl-Am. and ammonium oxalate and proceeding as in Official Method. Moisture determinations were also asked.

Forty-two samples were sent out and twenty-three replies received. Those taking part in the work were:

P. L. McCreary, University of California, Berkeley, Cal.

P. L. Hibbard, University of California, Berkeley, Cal.

J. S. Burd, University of California, Berkeley, Cal.

W. D. McNally, Armour & Co., E. St. Louis, Ill.

F. N. Smalley, S. C. O. Co., Savannah, Ga.

W. C. Dumas, Lloyd Laboratory, Atlanta, Ga.

F. B. Porter, Swift & Co., Atlanta, Ga.

F. B. Carpenter, V.-C. C. Co., Richmond, Va.
 J. P. Street, Ct. Agr. Exp. Station, New Haven, Ct.
 C. B. Morrison, Ct. Agr. Exp. Station, New Haven, Ct.
 R. B. Roe, Ct. Agr. Exp. Station, New Haven, Ct.
 C. A. Butts, 702-3 Forsyth Bldg., Atlanta, Ga.
 H. B. Battle, Montgomery, Ala.
 McCandless Laboratory, Atlanta, Ga.
 C. H. Jones, Vt. Agr. Exp. Station, Burlington, Vt.
 W. B. Derby, Vt. Agr. Exp. Station, Burlington, Vt.
 E. P. Verner, Parker Laboratory, Charleston, S. C.
 F. A. Nantz, N. O. Acid & Fert. Co., New Orleans,

La.

B. W. Bangs, Am. Agr. Chem. Co., Carteret, N. J.
 J. E. Breckenridge, Am. Agr. Chem. Co., Carteret,

N. J.

M. H. Pingree, Am. Agr. Chem. Co., Baltimore, Md.
 P. K. Nisbet, Am. Agr. Chem. Co., North Weymouth,

Mass.

G. A. Farnham, Jarecki Chem. Co., Cincinnati, O.

L. W. Thurbow, Great Western Sugar Co., Loveland,

Colo.

W. H. Whitehouse, Coe Mortimer Co., Moosic, Pa.

P. Rudnick, Armour & Co., Chicago, Ill.

Names are not in order of number of analyst used in report.

Results were as follows:

Analyst.	Potash official.		Mod. off.		Dif. in favor of mod. off.
	No. 1.	No. 2.	No. 3.	No. 4.	
1	..	7.81	..	8.30	0.49
2	7.04	..	7.62
	7.06	7.05	7.58	7.60	0.55
3	..	7.14	..	7.53	0.39
4	..	7.08	..	7.49	0.41
5	..	7.38	..	7.67	0.29
6	..	7.17	..	7.32	0.15
7	..	7.38	..	8.07	0.69
8	7.42	..	8.01
	7.31	..	8.76
	7.42	7.38	7.95	7.94	0.56
9	7.74	..	8.18
	7.74	..	8.20
	7.70	..	8.16
	7.74	7.73	8.16	8.18	0.45
10	..	7.47	..	8.02	0.45
11	..	7.40	..	8.33	0.93
12	..	7.74	..	7.85	0.11
13	..	7.33	..	7.22	..
14	..	7.90	..	7.98	..
15	7.05	..	7.88
	7.15	..	7.78
	7.08	7.09	7.90	7.85	0.76
16	..	7.67	..	8.09	0.42
17	..	6.59	..	7.12	0.53
18	..	7.72	..	8.24	0.48
19	..	7.64	..	8.22	0.58
20	..	6.78	..	7.21	0.43
	..	6.82	..	7.25	0.43
21	..	6.69	..	7.07	0.38
22	..	7.40	..	7.72	0.32
	..	7.32	..	7.80	0.48
23	..	7.41	..	7.79	0.38
	..	7.40	..	7.77	0.37
	..	7.44	..	7.80	0.36
24	..	7.26	..	7.82	0.56

Average + difference in favor of Modified Official Method, 0.45 per cent.

Moisture determinations were reported at temperatures from 98° to 130°.

Those made at 98-100° were from 3.65 to 5.18. Five hours seemed to be sufficient time to reach constant weight.

Sample contained large percentage of iron and aluminum phosphate, about eight per cent. iron and aluminum oxides, was ground to No. 30 mesh screen and thoroughly mixed. Theoretical amount of potash added was 8.30 per cent. in form of muriate.

Conclusions: Modified Official Method gave average increase in potash soluble in water of 0.45 per cent.

No. 1 and No. 3 column individual determinations, No. 2 and No. 4 averages.

AMERICAN ELECTROCHEMICAL SOCIETY.

The 20th general meeting of the Society will be held in Toronto, Canada, September 21-23, 1911. The preliminary program as far as outlined at this writing is as follows, subject to revision:

THURSDAY, SEPTEMBER 21ST.

Morning Session.

Reading and discussion of papers.

Afternoon Session.

Reading and discussion of papers.

Evening.

Meeting of Board of Directors, followed by smoker and entertainment by Section Q.

FRIDAY, SEPTEMBER 22ND.

Morning Session.

(Probably at some golf club) reading and discussion of papers.

Afternoon.

Golf tournament, etc.

Evening.

Banquet at McConkey's Restaurant.

SATURDAY, SEPTEMBER 23RD.

Morning.

Visit to Canadian General Electric Company's Plant at Peterboro. Return trip through locks to reach town in time to catch 5 P.M. boat out of town.

Members are requested to fill out and mail the cards enclosed in June Bulletin signifying their intention of attending the 20th general meeting, so that the Local Committee can make proper arrangements for their entertainment.

Members having papers to present at this meeting should notify either Chairman Lidbury, of the Papers Committee, or the Secretary before September 1st, sending titles of same so as to secure a place on the program.

W. S. LANDIS, *Assistant Secretary.*

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.,

August 10, 1911.

THE TRAINING OF INDUSTRIAL CHEMISTS IN ENGLAND.

At the annual meeting of the Society of Chemical Industry, held in Sheffield in July, the president, in his address, said that new apparatus, methods, and products appeared with such rapidity that it had become extremely difficult to keep pace with all the applications of science to industry. The tendency of the present age was toward specialization, but too minute subdivision had its disadvantages. There would always, therefore, be a demand for trained men who

had a good knowledge of science generally, and especially of the methods of applying it. It was sometimes alleged that the nature of the training given to students in this country was not practical enough, and that some foreign nations were superior to us in this respect. He did not think the facilities for acquiring knowledge were less in Great Britain than in any other country—in fact, in some of our institutions they were superior—but in one respect many of their students were deficient; they had not been taught to realize that the object of the industrial chemist, like that of the alchemist, was to produce gold, and that every factory operation must yield a profit, failing which it must cease. In this respect probably our German colleagues were more advanced than we were. In all things the practical side must receive careful attention. The more practical knowledge the chemist had in any branch of industry, the more likely was his work to be successful.

AMERICAN GAS INSTITUTE.

Annual meeting, October 18, 19, 20, 21, 1911, St. Louis, Mo. Officers: *President*, Donald McDonald,

Louisville, Ky.; *Secretary*, A. B. Beadle, 29 West 39th St., New York City.

NATIONAL COMMERCIAL GAS ASSOCIATION.

Annual meeting, October 23–28, 1911, Denver. Officers: *President*, C. N. Stannard, Denver; *Secretary*, Louis Stotz, 29 West 39th St., New York City.

MICHIGAN GAS ASSOCIATION.

September 20–22nd. Annual meeting at Detroit, Mich. *Secretary*, Glenn R. Chamberlain, Grand Rapids Gas Light Co., Grand Rapids, Mich.

AMERICAN INSTITUTE OF MINING ENGINEERS.

October 10th. Annual convention at San Francisco, Cal., followed by trip to Japan. *Secretary*, Joseph Struthers, 29 West 39th St., New York City.

AMERICAN MINING CONGRESS.

September 26–29th. Annual session at Chicago, Ill. *Secretary*, J. F. Callbreath, Denver, Colo.

EDUCATIONAL

ANN ARBOR TO CONFER NEW DEGREE.

The degree of Doctor of Public Health was established by the Board of Regents of the University of Michigan. This degree has long been given in England, and it has recently been given by the University of Pennsylvania. At a conference held a short time ago in Chicago, it was agreed, providing the governing bodies consent, that Pennsylvania, Harvard and Michigan, with the beginning of the next college year, offer practically the same courses.

It has been announced that the Board of Trustees of Cumberland University has elected Prof. J. I. D. Hinds to the chair of Chemistry in that institution. Prof. Hinds has for eight or nine years held the chair of Chemistry at Peabody College. It is stated that he will assume the duties of the new position at the opening of the next fall term.

Dr. E. C. Franklin, prof. of organic chemistry, at Stanford University since 1903, has been appointed professor of chemistry in the Hygienic Laboratory of the U. S. Marine Hospital Service.

Prof. H. V. Army, dean of the Cleveland School of Pharmacy of Western Reserve University, has been selected as the successor of Prof. Virgil Coblentz at the N. Y. College of Pharmacy.

Prof. L. H. Bailey, director of the New York State College of Agriculture of Cornell University, has tendered his resignation to the trustees of the University. It is Prof. Bailey's intention to give up teaching.

At the annual meeting of the British Medical Association, the latter part of July, the University of Man-

chester conferred the degree of LL.D. upon Dr. Russell H. Chittenden, professor of physiology at Yale University.

Dr. Emil Godlewski, professor of agricultural chemistry of the University of Krakau, Poland, has been elected a corresponding member of the Paris Academy of Sciences.

Dr. Stewart J. Lloyd, heretofore adjunct professor of chemistry and metallurgy at the University of Alabama, has been advanced to a professorship of chemistry.

Mr. T. F. Winmill, of Magdalen College, Oxford, has been awarded the Mackennon Scholarship by the Royal Society for his researches on structural chemistry.

Dr. Benj. F. Lovelace, professor of chemistry at the University of Alabama, has been elected associate professor of chemistry at Johns Hopkins University.

Prof. Paul Friedlaender, of Darmstadt, has been awarded the Baeyer gold plaque and the Duisberg prize by the Verein Deutscher Chemiker.

Mr. R. C. Forster has supplemented his previous gifts to University College, London, by an additional £30,000 for the chemical laboratory fund.

Prof. Svante Arrhenius, of Stockholm, has been elected an honorary member of the Academy of Sciences in Vienna.

Prof. Paul Ehrlich, of Frankfort, has been awarded the Liebig medal by the Verein Deutscher Chemiker.

NOTES AND CORRESPONDENCE.

To the Editor of the Journal of Industrial and Engineering Chemistry:

In a communication which appeared in the June number of THIS JOURNAL regarding the invention of celluloid, Mr. Edward Worden states that the question whether the credit of the invention belongs to Spill or to the Hyatts is one of fact and not of individual opinion, and goes on in his usual complete and painstaking manner to cite the references, patents and decisions bearing on the subject.

The writer, in reply, begs leave to make use of Mr. Worden's data, to which the reader is referred, but to draw different conclusions from it.

While it is true that Parkes was the first to take out a patent into which the statement may be read that he knew of the solvent action of a solution of camphor in absolute alcohol, yet it was Daniel Spill who brought out the vital fact that nitrocellulose becomes plastic by admixture with camphor, commercial alcohol merely being used as a vehicle, and it is upon this fact that the subsequent development of the industry rests.

Celluloid was made by the Hyatts some years later by an alleged new process and they should be given full credit for the pioneer work which put the industry on a commercial basis (R. C. Schüpphaus, "The Evolution of Smokeless Powder," *J. Soc. Chem. Ind.*, Vol. XIV, No. 6; R. C. Schüpphaus, "Technical Application of Camphor," *J. Soc. Chem. Ind.*, Vol. XXVI, No. 8). The material is now manufactured under several trade names, but the term celluloid has generally come to be used to designate the various products, and it is in this sense that Spill is credited with having invented celluloid. C. M. JOYCE.

ARLINGTON, N. J.,
June 14, 1911.

To the Editor of the Journal of Industrial and Engineering Chemistry:

I should like to correct a typographical error in a paper of mine in the October, 1910, number of THIS JOURNAL on "The Determination of Sugar Lost by Entrainment from Evaporators." In formula II, near the end, the letter I should be a figure 1.

R. S. NORRIS.

HONOLULU, July 31, 1911.

To the Editor of the Journal of Industrial and Engineering Chemistry:

I think attention should be called to the danger of accepting weights for standard solutions and the equivalent values in substances as given in well-known standard works.

The latest edition of Sutton's "Volumetric Analysis" (the 10th ed.) pretends to have carefully revised the text, corrected mistakes and brought values in harmony with the atomic weights to be used in 1911.

Faith in the claim will be rudely broken by a glance at page 395: The quantity of potassium bichromate to be taken to make the standard solution for the

analysis of glycerines is the old figure, familiar for the past 25 years. It was wrong twenty-five years ago, according to tables of atomic weights most in use, and it has remained wrong ever since. It has been reprinted in every book dealing with glycerine analysis and is a good example of how little real revision there is in standard books.

In comparison with the accepted atomic weights of today a glycerine would test about 0.3 per cent. too low on a basis of 100 per cent. glycerine by using 74.86 grams (the figure in Sutton) instead of the accepted figure of today, 74.5641 grams.

The analysis of crude glycerines is difficult enough, and full of enough pitfalls, without having to start on a wrong basis.

The glycerine industry is a large and very important one, and such inaccuracies as reprinted in Sutton should be shown up strongly, both as a guide to the users of the book and as a warning to the publishers. The amount of trouble that can be caused by the use of these incorrect figures is something little appreciated, for while a spread between analysts of 0.3 per cent. might be passed, or even 0.5 per cent., when 0.3 per cent. more is added on trouble is at hand.

WILSON H. LOW.

LABORATORY OF
THE CUDAHY PACKING CO

A FEW LABORATORY HELPS.

Sometimes insignificant things which are developed in any particular laboratory are never taken advantage of by other people for the very reason that they are considered by the originator as so trivial that they are not worth publishing and so do not become known.

It has occurred to me that a few devices which we are constantly using might be of interest to others.

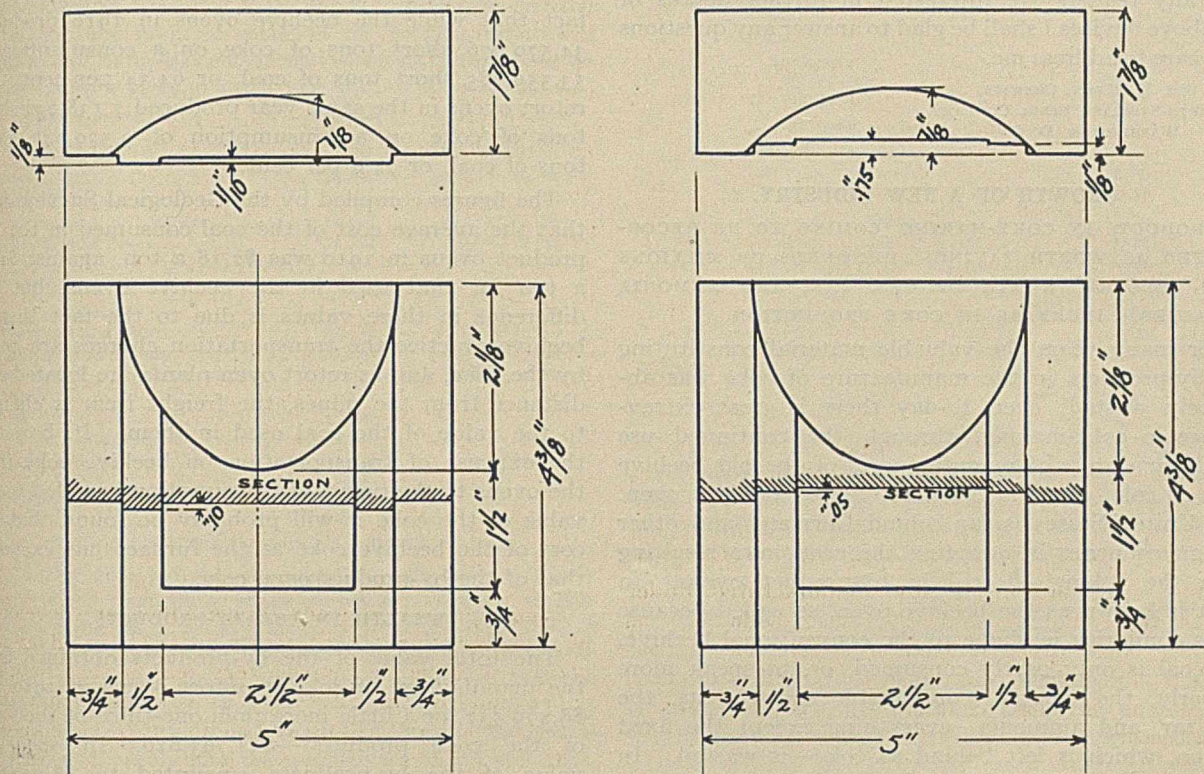
Test Samples.—It is a frequent occurrence in the case of open-hearth alloy steels that the ladle tests as usually taken from a heat are too hard to drill even with the aid of the most modern high-speed steel drills; and sometimes if the carbon content happens to be at all unusual, a good deal of difficulty is experienced in annealing the test to get it into condition to drill. This is particularly undesirable in the case of a rapid test for the melter during the progress of a heat where the delay of even a few minutes might be very costly. This may seem an absurd statement to men who are accustomed to make carbon steel and who judge largely by the fracture, but the conditions are often far different when alloy metals are present, and it often happens that the melters would be at a very considerable disadvantage in securing a uniform product without the assistance of the laboratory in keeping them informed of the changing composition of the metal during the melting.

In order to overcome any possible delay in getting our samples we designed a split mould (see sketch) in which is cast a thin sheet of metal. A ladle sample is drawn from the furnace and poured directly into

the mould, which is knocked apart immediately and the small casting quenched in water. The heavy end of it is then broken off and the thin piece sent to the laboratory where it is crushed to a fine powder in a steel mortar similar to the one described in *Blair*, p. 17, 7th ed. The behavior of the piece during the crushing is a very fair indication of the percentage of carbon. When the metal has reached 0.30 per cent. carbon the brittleness begins to give way to malleableness, and this latter property increases as the carbon decreases beyond this point. The direct

in gasoline keep in excellent condition. The thin coat of paraffine is not enough to be objectionable and yet it is thick enough to cause water or acid spilled upon it to form into a well rounded drop which can be easily brushed off. In fact, if the bench is made to slope a little, the water or acid will run off almost of its own accord.

Gas.—If the location of the laboratory is such that there is no chance to connect with the usual city gas pipes, gasoline gas is the customary substitute. So it was with us, but we have found that by making



DETAIL OF TEST MOULD

combustion method should be used for carbon determination (THIS JOURNAL, 1, 376.)

The moulds are also used in taking the final samples during the casting of the ingots in the pit. The method is not only very rapid but it is also very accurate and the sample obtained is always of uniform analysis.

Boats for Carbon Combustion.—We have had considerable success in using boats made of nickel. It is very easy to make them up and they last quite a long time. Ground quartz is used as a bed for the drillings. In buying nickel sheets for such purpose some care must be used in the selection in order to get nickel free from carbon. We generally use sheets of 0.03 inch thickness.

Benches.—The problem of a bench that will stand the wear of a busy laboratory is not always an easy one. Slate and glass are of course very nice, but they are probably responsible for a good deal of breakage of glassware. We have found that wooden benches painted occasionally with a solution of paraffine

a very slight change in the generator—one which any pipe fitter can readily accomplish—that ordinary producer gas can be substituted for the air supply and mixed with the gasoline gas in such proportions as to enrich it into a very efficient gas. We find the most economical mixture to be 80 per cent. producer gas plus 20 per cent. gasoline gas.

Producer gas is not always available for such a purpose, but in plants where it is employed, its use in this way will not only result in a greater satisfaction but also in a reduction of the gasoline consumption. It should be passed through a scrubber or some equivalent device to remove tarry matter before being piped to the gasoline mixer. No storage tank is necessary other than the mixing chamber which comes with the usual gasoline gas outfit. The only precaution to observe is the insertion of wire gauze at some point in the pipe line to prevent back fire.

Hood Linings.—It is sometimes desirable to build an inexpensive but efficient hood in the laboratory. Such materials as tiling, soapstone or glass are very

much to be preferred, but if a good serviceable structure is desired at small cost a wooden one lined with "Century" asbestos shingles is excellent. These shingles make a nice appearance and are supposed to be acid-proof. Strictly speaking, they do not effectually resist acid under the severe conditions, but when coated with pitch they are very efficient. There is also the further advantage that when thus coated the acid fumes do not condense on the surface and drop down on the work—a thing which frequently occurs in most hoods, especially in humid weather.

If any readers are interested in further details of the above devices I shall be glad to answer any questions they care to address me.

WM. H. KEEN, CHEMIST,
FIRTH-STERLING STEEL COMPANY,
WASHINGTON, D. C.

GROWTH OF A NEW INDUSTRY.

BY-PRODUCTS IN COKE-MAKING COMING TO BE RECOGNIZED AS WORTH SAVING. HUNDREDS OF MILLIONS OF DOLLARS' WORTH OF GAS, TAR, AND AMMONIA WASTED. INCREASE IN COKE PRODUCTION.

For many years the valuable material constituting the by-products in the manufacture of coke was absolutely wasted; even to-day there is great extravagance in coke-making, through the continued use by the majority of manufacturers of the old beehive type of coke oven, rather than the by-product oven. The United States is far behind Germany and other foreign countries in adopting the economies resulting from the coking of coal in by-product ovens. In what is known as the beehive oven, so called because of its similarity in shape to the conventional beehive, the coal is only partly consumed, or, to speak more properly, the volatile, combustible constituents, the gas, tar, and ammonia—everything except the fixed carbon, which is left behind as coke—is wasted. In the by-product ovens these are recovered and used. In Germany little or no coke is now made except in retort or by-product ovens. Hundreds of millions of dollars' worth of these valuable by-products have been wasted by American coke producers, but it is gratifying to note that the improved by-product oven is replacing the wasteful beehive with considerable rapidity.

The first ovens of the by-product type in the United States were built in 1893 at Syracuse, N. Y. From this one plant there has been an increase to 4,078 by-product ovens in 1910, all but 27 of which were in active operation. This is an increase of 164 over the number in operation in 1909 and 399 more than were in operation in 1908.

CONSERVATION OF THE BY-PRODUCTS.

During 1909 and 1910, according to E. W. Parker, of the U. S. Geological Survey, there was more activity in the construction of by-product recovery coking plants than at any time since 1903. At the close of 1909 there were 649 by-product ovens in course of construction, with 300 more contracted for. Of the 649 ovens started in 1909, there were 99 completed and put in blast in 1910. Work on the 300 ovens contracted for in 1909 was begun in 1910.

The production of coke in by-product ovens in 1910 amounted to 7,138,734 short tons, against 6,254,644 tons in 1909 and 4,201,226 tons in 1908. The increase in 1910 over 1909 was 14.13 per cent., whereas the total production of beehive coke increased from 33,060,421 short tons to 34,570,076, a gain of 1,509,655 tons, or only 4.57 per cent. The coke made in by-product ovens in 1910 was 17.12 per cent. of the total production.

ECONOMIES IN THE BY-PRODUCT OVENS.

The efficiency of by-product ovens is shown by the fact that while the beehive ovens in 1910 produced 34,570,076 short tons of coke on a consumption of 53,559,285 short tons of coal, or 64.54 per cent., the retort ovens in the same year produced 7,138,734 short tons of coke on a consumption of 9,529,042 short tons of coal, or 74.9 per cent.

The figures compiled by the Geological Survey show that the average cost of the coal consumed in the by-product ovens in 1910 was \$2.18 a ton, against \$1.01 a ton for that used in the beehive ovens, but the difference in these values is due to the fact that in beehive practice the transportation charges are borne by the coke, and as retort oven plants are located at a distance from the mines, the freight item is charged to the value of the coal used in them. If, however, the expense of transportation on beehive coke from the ovens to the points of consumption is added to the value of the coke it will probably be found that the cost of the beehive coke at the furnace has exceeded that of the by-product oven coke.

WEALTH IN THE BY-PRODUCTS.

The total value of the by-products obtained from the manufacture of coke in retort ovens in 1910 was \$8,479,557, or a little more than one-third of the value of the coke produced—\$24,793,016. In 1909 the value of the by-products amounted to \$8,073,948, and in 1908 to \$7,382,299. The by-products recovered in 1910 consisted of 27,692,858 cubic feet of surplus gas, valued at \$3,017,908; 66,303,214 gallons of tar, valued at \$1,599,453; 70,247,543 pounds of ammonium sulphate, or its equivalent, valued at \$1,841,062; 20,229,421 pounds of anhydrous ammonia, valued at \$1,725,266; and 4,654,282 gallons of ammonia liquor, valued at \$295,868. In addition to these, there is a quantity of light and secondary oil and small quantities of coke breeze recovered, with an estimated value of \$400,000. The value of the recoverable but wasted contents of the coal made into coke in beehive ovens would, at the prices obtained in 1910, have been between \$35,000,000 and \$40,000,000.

If all the coke made in the United States were produced in retort ovens, says Mr. Parker, probably not more than half the number of ovens would be required, say, for 1910, 45,000 ovens. These would yield in gas, over and above that required for the regeneration of the ovens, without by-product recovery, approximately a million horsepower per hour for every day in the year.

CONSULAR AND TRADE NOTES.

MARSEILLAISE PEANUT-OIL INDUSTRY.

The arrivals of peanuts at Marseilles during the calendar year 1910 aggregated 348,016 metric tons, classified as follows: Decorticated, or shelled, nuts, 199,774; undecorticated, or unshelled, nuts, 148,242 tons. Taking into account the weight of the hulls, it may be said that the receipts of decorticated peanuts were practically twice as large as those of peanuts in the shell.

A detailed statement of these imports showing the relative importance and range of values of the different varieties of peanuts sold in the Marseillaise market during 1910 follows, the quantities being given in metric tons of 2,204 pounds:

Articles and countries.	Quantity. Tons.	Range of values per 220 pounds.
<i>Decorticated.</i>		
China.....	24,071	\$6.65 to \$8.21
Mozambique.....	9,485	7.14 to 8.49
Bombay.....	14,821	6.51 to 7.81
Coromandel Coast.....	151,397	5.86 to 7.52
Total.....	199,774	
<i>Undecorticated.</i>		
Rufisque and Sine.....	90,676	\$5.40 to \$6.85
Gambia and Saloum.....	38,696	5.40 to 6.65
Casamance.....	820	5.26 to 6.30
Bissao.....	2,455	6.22 to 6.32
Rio Nunez.....	204
Egypt, India, and Java.....	15,297	5.49 to 6.27
Spain and La Plata.....	94
Total.....	148,242	

USE OF DIFFERENT VARIETIES—PRICES OF OIL.

It will be observed that the unshelled nuts bring relatively higher prices than those which arrive here already shelled. In fact, edible oil is made principally from the West African nuts, the best grades being obtained from the following varieties, in the order named: (1) Senegal nuts: (a) Rufisque Cayor, (b) Nianing, (c) Sine, (d) Saloum; (2) Gambia; (3) Casamance; (4) Rio Nunez (French Guineas). The shelled peanuts enter mostly into the manufacture of industrial oils, although the Mozambique and selected Bombay nuts furnish current grades of edible oil. The Java peanuts are taken up largely by the confectionery trade, important quantities having been re-exported to the United States during the last two years.

Peanut oil ranks next to olive oil in popular favor, being generally preferred in France to cotton oil. It is highly rated as a salad and cooking oil, and is used extensively in the manufacture of margarin and by sardine packers. It is frequently mixed with olive and other vegetable oils. The industrial grades obtained from the Indian nuts and the second pressings of the African varieties are consumed mainly by the soap-making industry, but a certain proportion is also employed for illuminating and lubricating purposes.

The price of peanut oil varies considerably from year to year. The average Marseillaise values, during the last three years, of edible oil made from Gambia nuts, which furnish a good medium quality, were as follows per 100 kilos (220 pounds): In 1907-8, \$18.56; 1908-9, \$14.67; 1909-10, \$16.98. The oil extracted from the Rufisque peanuts is usually worth from 5 to 10 per cent. more than the Gambia oil. The following are the ruling prices at the present time (May 17) per 100 kilos f. o. b. Marseilles, naked: Edible grades—Rufisque selected, \$19.30; Rufisque superfine, \$18.14; Rufisque petite, \$16.40; Gambia, \$17.37; Mozambique, \$16.40; Bombay, \$16.21. Industrial grades—lamp oil, \$15.05; lubricating oil, neutral, \$14.86; soap oil, \$12.64.

PRODUCTION AND PRICE OF PEANUT CAKE.

The Marseillaise mills produced last year 170,000 tons of peanut-oil cake, the values ranging from 14 to 16 francs (\$2.70 to \$3.08) per 100 kilos delivered in bulk, ex-mill. The cake is used for cattle-feeding. About 80,000 tons are exported annually, chiefly to Germany and Scandinavia. The present ruling prices of the various grades of peanut cake and competing products in this market are as follows:

Articles.	Price.
Peanut:	
Rufisque—	
Extra white.....	\$3.03
Ordinary.....	2.70
Coromandel.....	2.60
Sesame:	
Karachi.....	2.60
Indian.....	2.31
Cotton, first quality.....	2.70
Cornmeal.....	4.24
Linseed.....	4.44
Copra:	
Ordinary.....	2.60
Semiwhite.....	2.84
Ceylon.....	2.79
Cochin.....	4.05
Colza, Russian.....	1.93

CLEANING AND PRESSING OF NUTS.

Peanuts in the shell are never ground whole in the Marseillaise mills. On the contrary, expression of the oil is almost invariably preceded by a careful preparation of the nuts, particularly in the case of edible oil. The peanuts are crushed only after having been cleaned and decorticated, and after every effort has been made to remove entirely the germs and the red skin covering the kernels. All these operations are done by machinery.

The peanuts undergo a preliminary cleaning in a "blutoir," or rotary sieve; they are afterwards brought by an elevator to the decortivating machine and passed through grooved rollers, so adjusted as to husk the nuts without crushing the kernels. The separation of the husks and kernels is effected by ventilation. The germs, sprouts, and red skin still adhering to the kernels after the husking process are stripped off by friction against the coarse-wired meshes of a rapidly oscillating sieve, the operation being completed by a ventilator connected with the apparatus. It is extremely difficult, however, to detach entirely the red cuticle from the kernels, and in the case of new-crop nuts it is said to be a practical impossibility.

After the kernels have been cleaned they are ground by a crusher provided with two pairs of rollers. The mass emerging from the rollers falls into a "sasseur," or sifter, which separates the coarse from the fine meal, the remaining stones and other foreign substances having been eliminated by an aspirator. The coarse meal is reground.

PRESSING OF THE MEAL.

The meal is then put into hair bags called "scourtins," and subjected to hydraulic pressure, from 12 to 15 scourtins separated by metal plates being pressed at the same time. A scourtin contains about 10 kilos (22 pounds) of meal. The type of press employed in connection with this method is known as the "presse Marseillaise." Most of the presses of this type are worked under a pressure of 250 atmospheres, or 3,675 pounds to the square inch, but a pressure of 500 atmospheres is not infrequent. A few of the leading Marseille mills have adopted the Anglo-American "cage press," thus avoiding the use of scourtins. While the Marseillaise press crushes only from 1,000

to 1,100 kilos of nuts per day of 24 hours, the capacity of the Anglo-American cage press reaches 2,000 to 2,500 kilos.

The first pressing, which furnishes the high-grade oil, is made without heating the meal. In other words, the meal is pressed cold. This pressing usually lasts about one hour. For the second pressing the scourtins are generally emptied, the meal reground and brought to a temperature of 30° to 50° C. (86° to 122° F.), according to the quality and condition of the nuts. The same amount of pressure is applied as for the first pressing and the same press may be used. A smaller yield but a finer grade of oil results from the second pressing when the supplementary grinding of the meal is dispensed with. In some mills a third pressure is applied, but this is an unusual practice.

YIELD OF OIL.

The yield of oil varies according to the origin and condition of the nuts. The Senegal peanuts in the shell yield about 33 per cent. of their gross weight, the Gambia peanuts 31.5 to 32 per cent. Both of these varieties yield from 21 to 23 per cent. on the first pressing and 10 to 11 per cent. on the second pressing. The average oil yield of the shelled peanuts is about 39 per cent. for the Indian nuts and 42 per cent. for the Mozambique. From 6 to 10 per cent. of oil, with an average of 8 per cent., remains in the cake. A bushel of shelled peanuts weighing 30 pounds should produce on the average about 1 $\frac{1}{8}$ gallons of oil (a little over a gallon on the first pressing) and 16 $\frac{1}{2}$ pounds of cake, hulls not included. These cakes are about 2 feet square by $\frac{3}{4}$ inch thick.

After running from the presses, peanut oil does not need refining, but is simply filtered. It is then fit for consumption as salad oil. Bleaching is resorted to only in order to produce the white oil required in the manufacture of margarin.

Extraction of oil by solvents has not been found profitable in the case of peanut cakes, as these cakes are used exclusively, except when in a damaged condition, as a stock feed, and such solvents as sulphide of carbon and tetrachloride of carbon are considered harmful and depreciate the value of the cake for cattle-feeding purposes. Only a very limited quantity of peanut cake is ground into meal, and this always on special demand.

USE OF HULLS—ANALYSIS OF CAKE.

The hulls are rarely, if ever, mixed with the cake, but they are largely used as fuel by the mill owners. They are also ground separately and disposed of as a by-product of small value. After grinding to meal they are worth from 3 to 3.50 francs (58 to 67 cents) per 100 kilos, packed in bags. Considerable quantities of this meal are shipped to England, where, it is stated, it is mixed with molasses in the manufacture of a compound cake which has lately come into favor as a stock feed. It is stated that the hulls are used to a certain extent in Germany as paper stock.

The following is an official analysis of West African peanut cakes: Moisture, 9.72 per cent.; oil, 5.68 per cent.; feculae and digestible carbohydrates, 36.08 per cent.; protein, 40.05 per cent.; nitrogenous substances other than protein, 1.07 per cent.; crude fiber (not digestible), 3.86 per cent.; mineral substances, 3.54 per cent.

As shown by this analysis, the peanut cake contains an extremely large percentage of nitrogen, which accounts for the fact that use of the meal in army and navy rations and by the working classes has been occasionally advocated.

ADAPTATION OF COTTON-OIL MILLS TO PEANUT CRUSHING

The adaptation of cotton-oil mills to the peanut-oil industry can be accomplished at a moderate expense. The following estimate of the cost of the special equipment required in order to treat 50 metric tons of peanuts per day of 24 hours has been furnished by a Marseillaise firm that makes a specialty of this type of machinery:

	Cost.
One "blutoir," or bolter, total length 4 meters (13.12 feet), complete.....	\$550.05
One decorticating machine, with 3 grooved rollers, and a ventilator to remove the stones and other foreign substances still adhering to the shells; a sieve for the separation of the hulls and kernels; another ventilator for the removal of the shells having passed with the kernels through the sieve, and pulleys.....	868.50
One ventilator, with distributor, for the collection of the undecorticated peanuts having passed with the hulls.....	125.45
One sorting apparatus for the kernels remaining in the waste drawn off by the ventilator of the decorticating machine.....	250.90
One apparatus receiving the kernels from the foregoing and removing the stones and red skins, and separating besides the germs and coarse bran.....	250.90
One elevator to bring the nuts from the "blutoir" to the decorticating machine, 7 meters (22.96 feet) in height.....	140.89
One elevator, to feed the apparatus handling the clean kernels.....	110.97
One elevator to feed the apparatus handling the waste.....	110.98
One endless screw to carry waste from the decorticating machine.....	77.20
One endless screw to carry the clean nuts from the "blutoir" to the decorticating machine.....	77.20
One aspirator for the entire installation.....	144.75
Driving gear for the entire installation.....	231.60
Total cost, delivered quay Marseilles.....	2,939.39

The same installation with wooden frames and supports would cost \$2,316.

A crushing machine complete, with a capacity of 50 metric tons, could be had for \$874.29, divided as follows:

	Cost.
One hopper, with distributor, above crusher....	\$ 67.55
One crusher, comprising 2 pairs of rollers, the first pair measuring 400 millimeters (1.31 feet) in diameter, and 600 millimeters (1.968 feet) in length, and the second pair 600 millimeters both in length and in diameter.....	482.50
One "sasseur," or sifter, placed beneath the crusher, removing the foreign substances and classifying the meal.....	115.80
One aspirator connected with the rollers and the "sasseur".....	208.44

The presses and filters employed in cotton-oil mills are suitable for the peanut-oil industry.

THE RADIUM MARKET.

[From Consul General T. St. John Gaffney, Dresden, Germany.]

Since the discovery of radium and the powerful action of its rays, governments as well as numerous private enterprises have endeavored to discover or acquire suitable sources of this valuable product. While governments are prompted exclusively by scientific motives, private individuals to a very great extent are attracted by the high price, \$80,000 per gram (0.03527 avoirdupois ounce). The cost of producing a gram of radium is about \$2,000, which is low considering the value of the substance.

A radium bank was established in Paris a short time ago, which in 1910 disposed of 1.92 grams of radium of highest activity at \$80,000 per gram. Of that quantity \$15,000 worth has been acquired for industrial purposes and \$139,000 worth for use in therapeutics.

Radium of the highest activity never loses any of its properties. A regular output of radium means a regular increase in the quantity of radium in existence in the world. In consequence of this property, a hiring system has been developed, a procedure which will naturally hamper the development of a market.

The production of radium is dependent to a great extent upon the production of uranium, and as the present output of the latter metal is still needed to meet the demand for uranium-color manufacture, an early increase in the production of radium seems unlikely. The new American production of inferior uranium has also interfered with the market, and a regular increase in the output will cause still further depression.

Radium is found in Luntwengule, Morogoro district, East Africa; Evje N. v. Cristiansund, Norway; Cornwall and South Devon; Joachimsthal in Bohemia; Gilpin County in Colorado; and Kolmlagerstaetten in Sweden. Of all uranium mines only the one at Joachimsthal, which is working regularly, may be depended upon; there the two mines to be taken into account which have an estimated yearly output of 16 to 20 tons of uranium pitch ore, or pitchblende, containing 55 per cent. U_3O_8 . Radium-free uranium color is obtained from this ore, which increases the radium content of the residue. Six tons is the annual production of residue, from which it is reasonable to expect a production of 1.8 grams of radium salt of the highest activity.

The yield in Austria up to the present—3.5 grams—is not derived from the regular production from pitchblende, but from numerous old stocks, which are probably exhausted now. The yearly yield of 1.8 grams of radium salt of the highest activity may, according to present prices, be valued at \$144,000.

[Previous reports on radium appeared in Weekly Consular and Trade Reports for Apr. 16, 1910, and in Daily Consular and Trade Reports for July 21, Aug. 30, Sept. 27, and Nov. 23, 1910.]

PEACE IN THE GERMAN POTASH INDUSTRY.

[From Consul Talbot J. Albert, Brunswick.]

At the conference held recently at Hamburg between the conflicting interests, German and American, in the potassium industry, an agreement has been reached as to prices and rebates.

The agreement has a duration of five and one-half years. During this period the American purchasers of potash, that is to say, the North Trust, the South Trust, and the independents, obligate themselves to make all purchases from the potassium syndicate. The probability of the market being disturbed by outside mines is thought to be remote, as such outsiders would have to organize a sales agency in the United States similar to the German Kali Works owned by the syndicate, which delivers potash salts directly to the buyer. Such an organization would be expensive and difficult to effect.

The basis of prices is practically the same for concentrated salts as that contained in the potassium law, and the same as prevailed in America in 1909 before the syndicate was renewed and before the Schmidtman contracts went into force. The prices, aside from 40 per cent. manure salts, which are sold to the German agriculturists at low prices, are the same as the maximum prices laid down in the law for the domestic consumption. On the other hand, the prices proposed for raw salts, especially for kainit, are higher than the prices formerly paid by Americans to the syndicate. Rebates for most sorts of salts are increased. Formerly a rebate of 9 per cent. on the average was granted the American companies. Now it will be from 11 to 12 per cent.

In reference to certain expenses which may be incurred by the syndicate the right is granted it during the duration of the agreement, five and one-half years, to increase prices 3 per cent.

The agreement is incomplete inasmuch as the Aschersleben and Söllstedt Works belonging to the Schmidtman interests and the Schmidtman International Trust had not united in it. An effort will be made by amicable means to bring the remaining parties into the agreement. If it is not successful, it is thought that their sales contract will be attacked, as they are regarded as in some respects legally indefensible.

EIGHTH INTERNATIONAL COTTON CONGRESS.

[By Commercial Agent Ralph M. Odell.]

The International Cotton Congress which was held in Barcelona, Spain, May 8 to 11, 1911, was a representative gathering of cotton manufacturers from all parts of the world. More than 250 delegates were present, representing every country in which the cotton industry is carried on, with the exception of Japan and Russia.

Papers were read and discussed which related to the subject of cotton manufacturing in all its stages and the problems confronting the industry to-day. Among these subjects may be mentioned the expansion of the present cotton fields and the opening up of new ones in any part of the world where this can be done with success to meet ever-increasing requirements; the more scientific cultivation of the raw material; improvements in the ginning, baling, warehousing, and transporting of cotton, especially American cotton, by which large savings can be effected; the international standardization of grades of cotton, and reforms in the marketing of same; plans for the application of world-wide short-time running, to deal with the over-production of cotton goods and the consequent universal depression in the industry and trade; mill-fire insurance problems; the drafting of a uniform contract for the purchase and sale of yarns and cloth; and the establishment of a table of percentages of moisture to apply to cotton yarns.

THORIUM SYNDICATE SUSPENDED.

[Special Correspondence in London Financial Times.]

For a considerable time past negotiations have been proceeding among the principal European manufacturers of thorium with the view of coming to an arrangement by which production and prices could be regulated, but these have at length been abandoned, as unanimity was found to be unattainable under existing circumstances. The supply of thorium was at one time a virtual monopoly under the control of a powerful Continental syndicate, but the "corner" has at length been broken, and the industry has fallen on evil days from the producer's point of view. Prices have steadily declined for two or three years, and are not unlikely to go considerably lower. This declining tendency is directly attributable to the glutting of the market with monazite sand, the principal raw material from which thorium is produced. The supplies of this sand were entirely controlled by the syndicate, whose exorbitant prices forced the leading makers of incandescent mantles, including the incandescent-light companies, to exert themselves to obtain independent supplies at all costs. In this they were successful and prices fell rapidly. Practically the whole of the supply of monazite sands comes from Brazil, and thorium nitrate is manufactured only in the United States and on the continent of Europe. The yearly consumption of monazite sand for the manufacture of thorium is placed at between 2,000 and 2,500 tons, but for some years the supplies have been equal to double the consumption. The contract between the Brazilian Government and the thorium syndicate has now expired, and a new lease of the fields is about to be arranged. There are numerous offerers, and as the Brazilian Government is not likely to allow any monopoly to acquire control of the supplies a further flooding of the market and consequent decline in prices is feared.

NEW EDITION OF GERMAN TARIFF.

A revised edition of the tariff of the German Customs Union has been published in English by the Bureau of Manufactures (Tariff Series No. 7). This edition includes all corrections up to June, 1911. In view of the fact that the changes, except those embodied in Supplement A to the former edition, and those noted from time to time in the Daily Consular and Trade Reports, are of minor importance. Copies of the new edition will not be sent to persons on the mailing list for tariffs, but may be obtained from the Bureau of Manufactures upon application.

NEW RADIUM SPRING IN BOHEMIA.

[From Consul William J. Pike, Reichenberg, Austria.]

In the neighborhood of Reichenberg a radium spring has been discovered whose waters are remarkably strong in radioactivity. The measurement of experts by the newest apparatus shows an emanation quantity of 18.8 Mache units, which is double the amount of the celebrated Bohemian spring at Teplitz. For medicinal purposes the waters are said to be most satisfactory,

having a temperature of 7.7° C., and a constant flow of sufficient quantity for an important establishment. — *Daily Consular and Trade Reports*, Aug. 7.

In the second quarter of 1911 the American consulate at Cologne, Germany, invoiced \$500,323 worth of aniline salts and dyes to the United States, also \$190,044 of mineral water, and other articles, making up a total of \$1,180,231.

BOOK REVIEWS.

Handboek ten Dienste van de Suikerriet-Cultur en de Riet-suiker-Fabricage op Java. Edited by the United Sugar Experiment Stations of Java. 4 volumes. Amsterdam: J. H. de Bussy.

The first three volumes of the "Handboek" were reviewed in THIS JOURNAL, 1, 380. Those who have read the recent interesting contributions upon the sugar cane industry in different countries written by Mr. H. C. Prinsen Geerligs in *De Indische Mercur* will be glad to know that this entire series of articles with much added information has been incorporated in permanent book form to make a new volume of the "Handboek:" Vol. IV, "De Rietsuikerindustrie in de Verschillende Landen van Productie." Historisch technisch en statistisch overzicht over de productie en den uitvoer van de reit-suiker. By H. C. PRINSEN GEERLIGS, Directeur der Filiale Nederland von het Proefstation voor de Java Suiker Industrie. 1911. 416 pages. Price, bound, f. 7.50.

In the introduction to this new work Mr. Geerligs states that owing to several causes—(chief among which he gives the Brussels Sugar Convention of 1902, the Annexation of Formosa by Japan, and the changed conditions resulting from the Spanish-American War)—the cane sugar industry has entered upon a new period of development. He considers the present moment, therefore, an opportune one in which to review the conditions and future prospects of the industry.

In the first 42 pages of the volume a brief survey of the entire field is given in which connection the author reviews the history of the sugar cane industry from the first legendary mention of the cane in the sacred writings of the Hindoos down to the present day. Special stress is placed upon the influences of such movements as the Crusades, Spanish Colonization, Negro Slavery, The Continental Blockage, The Rise of the Sugar Beet Industry, The Bounty and Cartel System, and the Recent Brussels Convention.

In the second and main division of the work the

conditions of the cane industry in each of some 50 countries are described. The geography and climate of each section, agricultural conditions, methods of cultivation and manufacture, character of labor, conditions of marketing the raw sugar, and statistics of production are thoroughly reviewed. Colored maps of the leading cane-producing countries, photographs of modern factories, and numerous cuts and diagrams give additional value to the descriptive matter of the text.

The typography of the book is excellent, conforming in character to the work of the publishers upon the three previous volumes of the "Handboek."

The many friends of Mr. Geerligs in all parts of the sugar world are pleased to note that his retirement from active labors in Java, in building up the sugar industry of that colony, has brought with it, not a cessation of activities, but the opportunity of rendering even greater services in other ways.

It is hoped that this new addition to the "Handboek" may soon be translated into English for the benefit of those readers, who are unable to find their way in Dutch.

C. A. BROWNE.

"Royaume de Belgique Ministers des Colonies, Bulletin Agricole du Congo Belge." Brussels. December, 1910. Vol. I, No. 2. Price, 5 francs a year.

This is the quarterly agricultural journal of the Office of the Minister for the Colonies. Its contents are almost entirely of an agricultural nature, giving the rules and regulations for setting out of rubber plantations, a review taken from *Technique Moderne* on rubber latex, discussing in detail the various methods of coagulation, the working of raw rubber, the composition of the latex, its valuation and selling methods. An article on dry farming deals principally with the practice in the Western United States, and several articles discuss introduction of live stock into the Belgian Congo. A botanical description (in Dutch) is given of the various commercial rubber trees. The journal is well printed on good paper and is full of illustrations.

R. F. BACON.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

Materials for Permanent Painting. By MAXIMILIAN TOCH. D. Van Nostrand Company. 208 pp. \$2.00 net.

Chemistry of the Essential Oils and Artificial Perfumery. By ERNEST J. PARRY. 2nd Ed. D 8vo. 550 pp. \$3.50. London: Scott, Greenwood & Son.

Manual of Agricultural Chemistry. By HERBERT INGLE. 2nd Ed. D 8vo. 450 pp. \$2.25. Scott Greenwood & Son.

Directory of Chemical Industries throughout the World. 1st Ed. 1911. L 8vo. 727 pp. \$3.75. Berlin. 1911.

Translocation of Plant Food and Elaboration of Plant Material

- in Wheat Seedlings. By J. A. LE CLERC AND J. F. BREAZEALE. U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 138.
- The Dimethyl Sulfate Test of Creosote Oils and Creosote Dips. A Substitute for the Sulfonation Test. By ROBERT M. CHAPIN. U. S. Dept. of Agriculture, Bureau of Animal Industry, Circular 167.
- Application of Physico-chemical Theories to Technical Processes and Methods of Manufacture. By R. KREMAN. \$2.50. Halle. 1911. (German.)
- Detection and Determination of Small Quantities of Ethyl and Methyl Alcohol and of Formic Acid. By RAYMOND F. BACON. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular 74.
- Handbook on the Manufacture of Illuminating Gas. By WILHELM BERTELSMANN. 2 vols. Vol. I. 581 pp. \$5.00. Stuttgart: Ferdinand Enke. (German.)
- Handbook of Chemical Technology. By H. OST. 7th Ed. \$4.00. Hannover: Max Jaenecke. (German.)
- Mixing, Stirring and Kneading and the Machines Used for these Operations. By HERMANN FISCHER. 8vo. 90 pp. \$1.75. Leipzig: Otto Spamer. (German.)
- Theory and Practice of the Gas Industry. By RUDOLF MEWES. 40. 403 pp. \$5.00. Leipzig: H. A. L. Degener. (German.)
- The Patent Laws of All Countries. By J. KOHLER AND M. MINTZ. Vol. II, Part 5. L. 8vo. \$4.25. Berlin. 1911. (German.)
- The Mineral Industry. Vol. XIX. By ALBERT H. FAY. 8vo. 900 pp. \$10.00. New York: McGraw, Hill Book Co.
- Catalysis. By WILHELM OSTWALD. 2nd Ed. 8vo. 39 pp. \$0.50. Leipzig: Akademische Verlagsgesellschaft. (German.)
- Saccharin in Food. U. S. Dept. of Agriculture, Food Inspection Decision No. 138.
- Notices of Judgment, Food and Drugs Act, Nos. 895 to 987. U. S. Dept. of Agriculture.
- Crystallography and Practical Crystal Measurement. By A. E. H. TUTTON. 8vo. 946 pp. \$8.50. The Macmillan Co., New York.
- Rubber. By P. SCHIDROWITZ. 8vo. 290 pp. \$2.75. Methuen & Co., London.
- Metallurgy. By W. BORCHERS. Translation. 8vo. 271 pp. \$3.00. John Wiley & Sons, New York.
- Laboratory Manual of Inorganic Chemistry. By E. C. BINGHAM AND GEO. F. WHITE. 12mo. 147 pp. \$1.00. John Wiley & Sons, New York.
- Technical Methods of Ore Analysis. By ALBERT H. LOW. 5th Ed. John Wiley & Sons, New York.
- Manual of Practical Assaying. By H. V. F. FURMAN AND WM. D. PARDOE. 7th Ed. 8vo. 530 pp. \$3.00. John Wiley & Sons, New York.
- Essentials of Volumetric Analysis. By HENRY W. SCHIMPF. 2nd Ed. 12mo. 358 pp. \$1.50. John Wiley & Sons, New York.
- Short Introduction to the Structure of Iron-Carbon Alloys. By O. KROHNKE. \$1.75. Berlin. 1911. (German.)
- Chemistry of the Albuminoids. By COHNHEIM. 3rd Ed. \$2.75. Brunswick. 1911. (German.)
- Biochemical Metabolism of the Phosphate Ion in Soil. By J. STOKLASA. L. 8vo. 159 pp. \$1.50. Jena. 1911. (German.)
- Textbook of Pharmaceutical Chemistry. By TH. EKECRANTZ. 8vo. 288 pp. \$2.75. Stockholm. 1911. (Swedish.)
- The Methods of Testing of the Austrian Pharmacopoeia. By G. MOSSLER. L. 8vo. \$1.25. Vienna. 1911. (German.)
- Human Food Materials; their Origin, History, Constituents, Use and Action. By C. HARTWICH. \$7.50. Leipzig. 1911. (German.)
- Influence of Low Temperatures (Frost) on the Strength of Mortar, Masonry and Concrete. By H. GEIMER. L. 8vo. 70 pp. \$1.50. Berlin. 1911. (German.)
- Safety Devices in Chemical Plants. By K. HARTMANN. \$4.50. Leipzig. 1911. (German.)
- RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.
- Chemistry and Technology of Petroleum for the Year 1910. By L. GURWITSCH. *Zeitschrift fuer angewandte Chemie*, Vol. XXIV, No. 27, pp. 1249-1256.
- The Acetylation of Cotton Cellulose. By CARL G. SCHWALBE. *Zeitschrift fuer angewandte Chemie*, Vol. XXIV, No. 27, pp. 1256-1260.
- Effect of Various Solvents on Sulfate Scale. By S. S. PECK. *International Sugar Journal*, Vol. XIII, July, pp. 357-359.
- Composition and Examination of the Residues from the Distillation of Fats. By J. MARCUSSON. *Zeitschrift fuer angewandte Chemie*, XXIV, Heft 28, pp. 1297-1302.
- The Analysis of Manganese Bronze. By JAMES R. HUBER. *Metallurgical and Chemical Engineering*, Vol. IX, No. 8, pp. 493-494.
- Treatment of Anode Sludge in Electrolytic Refineries. By EDWARD F. KERN. *Metallurgical and Chemical Engineering*, Vol. IX, No. 8, pp. 417-420.
- The Influence of Impurities in Oxygen when Used for Cutting Iron and Steel. By ALEX. E. TUCKER. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 13, pp. 779-782.
- Observations on Cotton and Nitrated Cotton. By H. DE MOSENTHAL. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 13, pp. 782-786.
- The Analysis of Shellac. By A. C. LANGMUIR AND T. S. WHITE. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 13, pp. 786-789.
- The Viscosity and Fluidity of Emulsions, Crystalline Liquids and Colloidal Solutions. By EUGENE C. BINGHAM AND GEORGE F. WHITE. *Journal of the American Chemical Society*, August, 1911, pp. 1257-1275.
- A New Method for the Separation of Cerium. By C. JAMES AND L. A. PRATT. *Journal of the American Chemical Society*, August, 1911, pp. 1326-1330.
- Volhard's Method for the Estimation of Chlorin in Potable Waters. By A. T. STUART. *Journal of the American Chemical Society*, August, 1911, pp. 1344-1349.
- Some Advantages of the Graphic Method of Recording Results in Routine Analysis. By J. H. RUSSELL. *Journal of the American Leather Chemists' Association*, August, 1911, pp. 382-387.

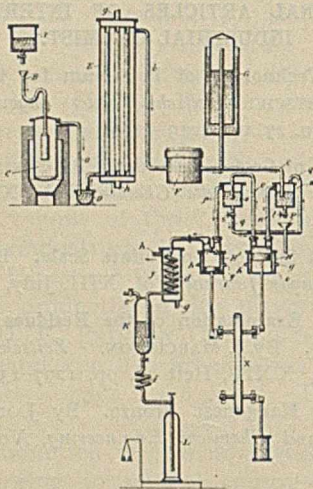
RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Method of Treating Distillation-gases to Produce an Illuminating Liquefied Gas.

U. S. Patent No. 994,369.

Satisfactory results are claimed to be secured by first compressing, after the usual cleaning, the distillation gas used for the purpose at a low stage of compression at normal temperature under water-cooling, then removing the liquid hydrocarbons thereby separated out, and compressing the so treated gas at the higher pressure necessary for its complete liquefaction, finally drawing it off into vessels of suitable material, such as steel. In this manner are avoided over-carburization of the gas and therewith subsequent separating out of fluid hydrocarbons and the loss occasioned thereby in the use of the gas.



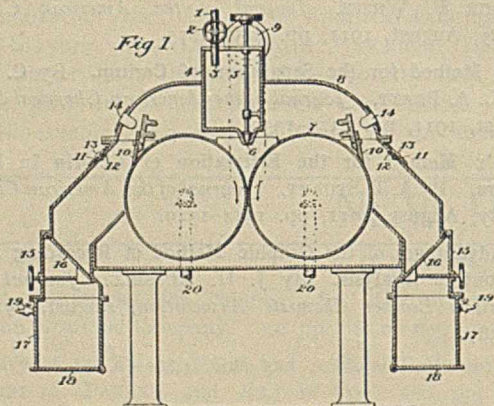
In the carrying out of the foregoing process the liquid hydrocarbons separated under pressure and saturated with gases under pressure should preferably be permitted to escape, at the pressure of the suction pipe, into a vessel inserted in the suction pipe of the apparatus or connected with the suction pipe by a gas-conduit pipe, in order to recover for the process gases set free from the fluid hydrocarbons through reduction of the pressure.

The accompanying illustration shows the apparatus in which the process is carried out.

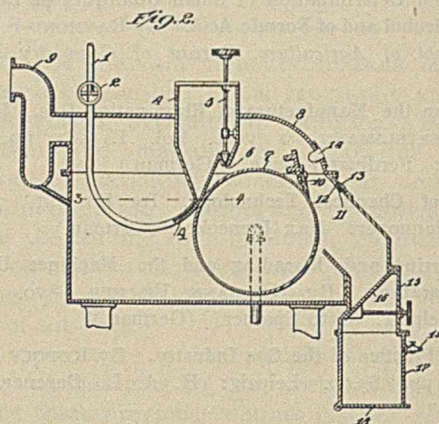
Process of Desiccating the Solid Content of Milk.

U. S. Patent No. 995,303.

The invention has for its object the separation of milk-solids in the form of a fluffy, flaky powder, which upon the addition



of warm water thereto will readily dissolve and emulsify to form a liquid having all the properties of normal milk. These objects the patentee claims to attain by delivering a mass of homogeneously-concentrated milk, free from unconcentrated portions in the form of a thin layer or sheet, to moving heated surfaces initially heated in excess of 5° C. above the boiling



point of the milk at the pressures at which the operation is performed. The layer is cooled during the formation of the same by the inflowing milk in its passage to the receiving receptacle, but without direct contact therewith and is removed in the form of a self-sustaining mass having the identity of a film from the heating surface prior to the complete evaporation of the water therefrom and while still possessing a slightly moist appearance.

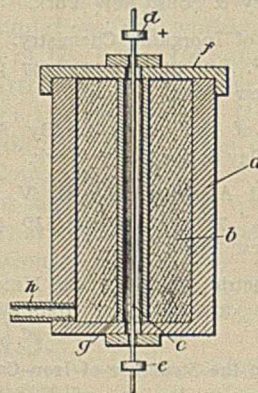
The accompanying illustrations show the apparatus in which the process is carried out.

The inventor is Waitstill H. Swenarton, of Montclair, New Jersey.

Method of Making Nitrogen Compounds.

U. S. Patent No. 996,011.

The method may be carried out by introducing into a suitable receptacle, constructed of material of low heat conductivity, provided with means for introducing nitrogen and containing electrical means of developing a temperature lying between dark red and light yellow, the desired quantity, say 100 kg., of finely



divided calcium carbid. This carbid may be ground to any suitable fineness. A small portion of the carbid immediately adjacent to the electrical heat-developing means is first raised to the temperature required to initiate the reaction at that point between the carbid and the nitrogen then or previously intro-

duced, and the process of conversion starts. The supply of nitrogen being maintained, the heat spontaneously resulting from the reaction between the carbide and nitrogen at this initial stage which we may call the ignition stage of the process is transmitted to an area still more remote from the ignition point and is sufficient to promote the reaction there; and so the reaction continues to spread until conversion of calcium carbide into calcium cyanamid is effected throughout the entire mass. This result will be recognized from the cessation in the consumption of nitrogen, which may be observed in any well-known manner.

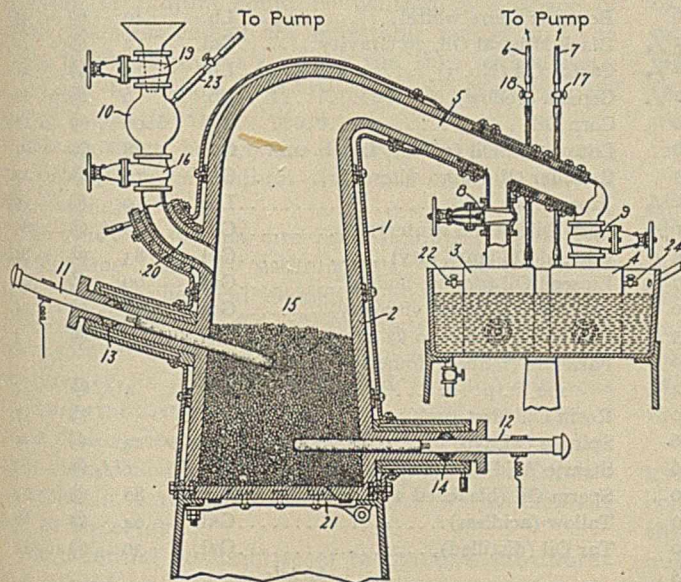
Referring to the accompanying illustration in which the figure is a diagrammatic sectional view of an apparatus suitable for carrying out the invention, *a* represents any suitable receptacle, *b* the material to be acted upon by nitrogen, *c* any suitable means for heating said material: for example, *a* resistor through which a current may be passed; *d* the positive terminal of a work circuit; *e* the negative terminal; *g* a tube or other receptacle through which the resistor *c* may pass; *f* any suitable closure for said receptacle; and *h* suitable means for introducing nitrogen gas.

The inventor is Albert R. Frank, of Halensee, near Berlin, Germany, assignor to Societa Generale Per La Cianamide, of Rome, Italy.

Fractional Distillation of Metals.

U. S. Patent No. 996,474.

The invention aims to provide certain improvements in the treatment of ores so as to effect a reduction of the ore and a purification of the product in one continuous operation. The process is defined in the patent as consisting in reducing the sulfid compound of a volatilizable metal by mixing said com-



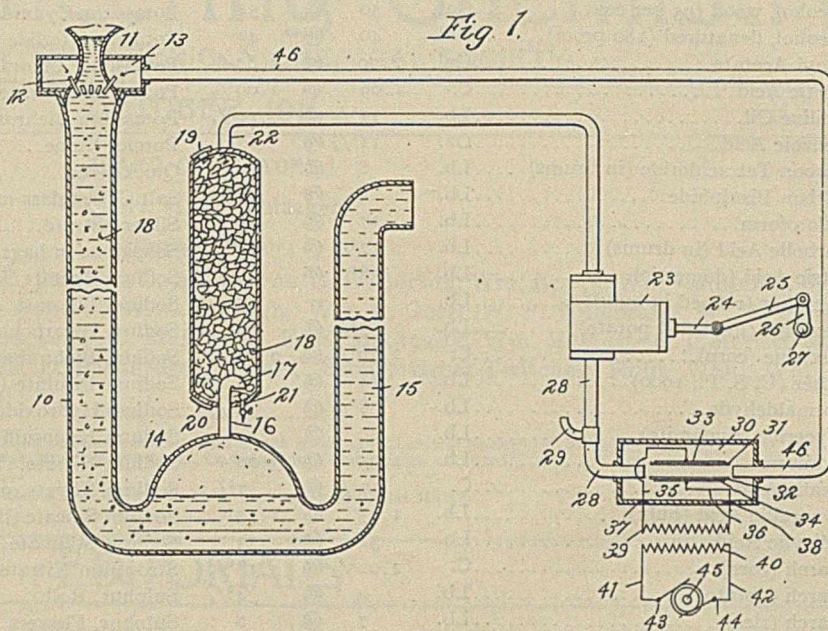
pound with a reaction material which will combine with the sulfur at an elevated temperature to form a relatively stable compound, heating said mixture to the reaction temperature and then removing the reduced metal from the by-products of the reaction by distillation in an attenuated atmosphere.

The inventor is Colin G. Fink, of Schenectady, New York, assignor to General Electric Company.

Apparatus for Purifying Water by Ozone.

U. S. Patent No. 996,560.

The object of the invention is to combine in a single system an efficient means for producing ozone, means for bringing the ozone



produced into intimate contact with the water to be sterilized and means for preparing air for ozonization. The inventor has combined a series of individual devices for performing the several features of the process each peculiarly adapted to its work in combination with the others so that the entire system or apparatus comprises a combination of elements, all coöperating to produce the desired result, and each one assisting the other in addition to doing its own work. In order to avoid the necessity of purifying too large a quantity of air, he has arranged and operates his apparatus in such a manner that the same air, or at least the greater portion of the same air, is used over and over again, only so much new air being admitted into the system at each cycle as will supply the required amount of oxygen to make up for the ozone which has been removed during the cycle by the oxidation of the carbonaceous impurities in the water being treated. In general the system may be described as comprising a water tower in which ozonized air is isothermally compressed by, and comes into intimate contact with, the water being treated; a separating chamber in which the air and ozone, together with the carbon dioxide and other obnoxious gases, are allowed to rise from the water; a lime chamber or tower into which the gases rising from the separating chamber are discharged and through which they pass and wherein the carbon dioxide is removed from the air; a compressed air engine suitably connected with the compressed air coming off of the lime tower and operated by the expansion of said air whereby the air is allowed to do work upon an operating shaft and is thus cooled and dried; and finally the ozone-producing apparatus into which the air thus cooled and dried is allowed to pass for the purpose of having its oxygen converted into ozone. In addition to these general features the system comprises a suitable inlet for additional air which is supplied to the apparatus at each cycle to compensate for the ozone taken up by the carbonaceous impurities of the water.

The inventor is Charles S. Bradley, of New York, assignor to Richard B. Wilson, of that city.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF AUGUST.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 ¹ / ₂ @	23
Acetone (drums).....Lb.	14 ¹ / ₂ @	17
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.70 @	2.83
Acetic Acid.....C.	1.69 @	2.09 ² / ₃
Aniline Oil.....Lb.	11 ¹ / ₂ @	11 ³ / ₄
Benzoic Acid.....Oz.	11 ¹ / ₄ @	12
Carbon Tetrachloride (in drums).....Lb.	8 @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	12 ¹ / ₂ @	14
Citric Acid (domestic).....Lb.	38 ¹ / ₂ @	39
Camphor (refined in bulk).....Lb.		45
Dextrine (imported potato).....Lb.	5 ¹ / ₂ @	7
Dextrine (corn).....C.	2.79 ¹ / ₂ @	2.75
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 ¹ / ₂ @	9 ¹ / ₂
Glycerine (dynamite).....Lb.	20 @	21
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7 ¹ / ₈ @	7 ¹ / ₂
Pyrogallic Acid (bulk).....Lb.	1.25 @	1.55
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	2.02 ¹ / ₂ @	2.18 ¹ / ₂
Starch (potato).....Lb.	4 @	4 ³ / ₄
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 ¹ / ₈ @	5 ¹ / ₄
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	30 ¹ / ₄ @	30 ³ / ₄

Inorganic Chemicals.

Acetate of Lime (gray).....C.	1.87 ¹ / ₂ @	1.92 ¹ / ₂
Acetate of Lead (brown, broken).....Lb.	7 ³ / ₄ @	8
Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 ¹ / ₂ @	3 ¹ / ₄
Ammonium Chloride, gray.....Lb.	5 ³ / ₄ @	6
Arsenic, white.....Lb.	1 ¹ / ₈ @	2 ² / ₈
Ammonium Carbonate, domestic.....Lb.	8 @	8 ³ / ₈
Aluminum Sulphate.....Lb.	90 @	1 ² / ₄
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 ¹ / ₄
Barium Nitrate.....Lb.	5 ¹ / ₂ @	6 ¹ / ₂
Borax, crystals in bags.....Lb.	3 ¹ / ₂ @	4
Boric Acid, crystals.....Lb.	7 @	7 ¹ / ₂
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.17 ¹ / ₂ @	1.25
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	94 @	96
Chalk (light precipitated).....Lb.	4 ¹ / ₂ @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	60 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 ¹ / ₄ @	8 ¹ / ₂
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	81 @	84
Nitric Acid, 36°.....Lb.	3 ³ / ₈ @	4 ¹ / ₄
Nitric Acid, 42°.....Lb.	4 ¹ / ₈ @	5 ¹ / ₂
Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25

Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 ³ / ₈ @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Potassium Nitrate (crude).....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Potassium Bichromate, 50°.....Lb.	7 ³ / ₈ @	7 ¹ / ₄
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	68 ² / ₃ @	70 ¹ / ₃
Salt Cake (glass-makers).....Lb.	62 ¹ / ₂ @	77 ¹ / ₂
Silver Nitrate.....Oz.	34 @	36
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 ¹ / ₄ @	5
Sodium Chlorate.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Sodium Bicarbonate (English).....Lb.	2 ³ / ₄ @	3
Sodium Bichromate.....Lb.	5 ⁵ / ₈ @	5 ¹ / ₂
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 ¹ / ₂
Sodium Hydroxide, 60 per cent.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.		7 ¹ / ₄
Sodium Nitrate, 95 per cent., spot.....C.	2.12 ¹ / ₂ @	2.15
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 ³ / ₄ @	10
Strontium Nitrate.....Lb.	7 ¹ / ₄ @	8
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	85 @	1.00
Talc (American).....Ton	15.00 @	20.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	13 ¹ / ₄ @	13 ¹ / ₂
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 ¹ / ₂
Zinc Chloride (granulated).....Lb.	4 ¹ / ₂ @	4 ¹ / ₄
Zinc Sulphate.....Lb.	2 ¹ / ₄ @	2 ¹ / ₂

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 ¹ / ₂
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	6.06 ² / ₃ @	6.11 ² / ₃
Cottonseed Oil (crude), f. o. b. mill.....Gal.	38 @	40
Cylinder Oil (light, filtered).....Gal.	19 ¹ / ₂ @	20
Japan Wax.....Lb.	9 @	9 ¹ / ₄
Lard Oil (prime winter).....Gal.	78 ¹ / ₃ @	85
Linseed Oil (raw, city).....Gal.	83 @	84
Linseed Oil (double-boiled).....Gal.	90 @	91
Paraffine Oil (high viscosity).....Gal.	23 ¹ / ₂ @	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3 @	3 ¹ / ₄
Paraffine (refined, domestic) 120 @ 122 m. p.....Lb.	4 ¹ / ₂ @	4 ¹ / ₄
Rosin Oil (first run).....Gal.	— @	37
Spindle Oil, No. 1.....Gal.	14 @	14 ¹ / ₂
Stearic Acid (double-pressed).....Lb.	9 ¹ / ₂ @	9 ¹ / ₄
Sperm Oil (bleached winter) 38°.....Gal.	82 @	85
Tallow (acidless).....Gal.	64 @	66
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	20 @	20 ¹ / ₂
Antimony.....Lb.	— @	8
Bismuth.....Lb.	— @	1.80
Copper (electrolytic).....Lb.	12.40 @	12.45
Copper (lake).....Lb.	12 ⁵ / ₈ @	12 ² / ₄
Lead.....Lb.	— @	4.50
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	43.50 @	45.50
Silver.....Oz.	52 ³ / ₄ @	53
Tin.....Lb.	— @	43.43
Zinc.....Lb.	— @	5.95