The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume IV AUGUST, 1912 No. 8

Contributions and communications should be addressed to the Editor, M. C. Whitaker, Columbia University, New York City.

Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly.
Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Penna., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PENNA.

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EDITORIALS

THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

Within a few weeks will occur an event of supreme importance to American Chemists and especially to those interested in the branches of our Science to which THIS JOURNAL is especially devoted:—the meeting, in Washington and New York, of the International Congress of Applied Chemistry. Strictly speaking, this is not the first time that such an organization has met on American soil, since the first impetus to the plan of these international meetings seems to have been derived from the sessions of foreign and American chemists who attended the Columbian Exhibition in Chicago in 1893. Every World's Fair has, in recent years, been accompanied by meetings of specialists in sciences and arts; but it must be remembered that they bear the relation of what is popularly called a side-show to the Exhibition itself. They are more or less haphazard in their relation to the general world of science and there is no continuity of management from one occasion to the next. The various international scientific congresses are autonomous; the experiences gathered at one meeting are utilized in the preparation for the next one; special problems are committed to the care of qualified experts, for the report of authoritative opinion to the next gathering and the way is paved for that general worldwide coöperation in the advancement of knowledge and the perfection of its utilization, which has been within narrower limits the chief virtue of the various national organizations.

It is just 250 years since the Royal Society was incorporated in London,—with the sole exception of the Accademia du Lincei—probably the oldest extant society for the exchange of knowledge between the devotees of exact and natural sciences. For nearly two centuries these societies were not only close corporations but also practically local clubs. The greater diffusion of scientific learning, as well as the increased means of communication by railroad and telephone, led to the establishment of national associations, with more liberal terms of membership, and various associations for the advancement of science, with the added feature that the meetings were never held twice in succession in the same city. A natural outgrowth were the national societies for the promotion of some particular science; since increased specialization made it possible for anybody to follow understandingly the sessions of a general association, which soon met in sections, that naturally led to a demand for a closer form of union of their respective members. So that, in chemistry at least, each great nation now possesses one or more special societies, not restricted as to localities or qualifications, as is the case with the academy or institute. but open to every person interested in the science. At the last annual meeting of the American Chemical Society, there were assembled as many members as would have been deemed a fair attendance for the entire American Association for the Advancement of Science, not so many years ago. It is not necessary to descant here on the advantages of oral discussion, supplemented by the pleasures of social intercourse, which make these general sessions so attractive, any more than it is important to point out the same gregarious instinct, which has led to the successful institution of so many local sections, with their well-attended stated meetings. But we must emphasize the fact that *local* chemical societies led a very precarious existence until the more powerful national organization enabled them to gather strength by coöperation and let them experience the stimulus of generous rivalry.

And now we have entered into a new era, practically with the opening of the XXth Century, that of the utter abolition of national boundaries so far as scientific endeavor is concerned. A new chemical discovery in Paris is known in London, New York and Tokio in far less time than was consumed in the transmission of Priestley's or Cavendish's communications to the Royal Society in London, and the time is rapidly passing when the possession and guarding of a scientific secret could be deemed a national advantage. If it be deemed conducive to international amity that the young men of all nations should meet at the Olympian games, in contests of brawn and motor-nerves, how much more important is it that there be occasional interchanges of thought and knowledge. And yet, we wonder whether the press of New York will afford as many paragraphs to the forthcoming International Congress of Applied Chemistry, for matter supplied to it free of expense, as it has published pages of expensive cablegrams from Stockholm? We do not expect any mobs of frenzied cheerers to throng around the arena of scientific debate; and yet we know that the impression which our foreign visitors will take home of the progress in American science and scientific industry will be of far greater importance to the esteem in which our country will be held abroad, than the number of cups which the Finland will bring home from Stockholm. Our individual responsibility in this Congress is as great as our individual opportunity.

To meet the leaders of chemical knowledge and of chemical manufacture, from abroad as well as home, to listen to a free exchange of thought and practical experience, are privileges for which innumerable chemists have traveled to Berlin, London, Paris, Vienna and Rome. We all now have these chances at home, coupled with the opportunity to benefit by free and generous criticism of whatever we may desire brought to their view. In chemical industry, at least, medieval secretiveness is breaking down in favor of frank exchange of experiences.

That the scientific importance of the approaching Congress is thoroughly realized may be gathered from the fact that upwards of 600 papers have already been accepted and are being printed, ready for distribution at the Congress itself. In view of the stringent rules of acceptance which have been adopted, and the early date set for the submission of the papers themselves, it would probably have been easier for the authors to secure publication in the journals of their respective national chemical societies, had they not recognized the paramount claims of this International scientific gathering.

The American Committee of Arrangements is bending every effort toward making the sessions agreeable to the participants; they are particularly anxious to make this Congress memorable for the promptness with which it shall transact its business, the smoothness with which the machinery of entertaining its members shall revolve and the completeness with which their comfort may be considered. This means as full coöperation on the part of every American chemist as has been cheerfully afforded by the hard-working members of the various committees. It may be taken for granted that every chemist who can get away from his work, no matter in what part of the United States he resides, will be anxious to attend the Congress, not only for the selfish reasons already stated, but also for the patriotic one of adding by his own presence to the prestige of the greatest chemical function which is likely to occur here for many a year.

But it is not fair to the managers that you should leave them in the dark as to your intentions: mere subscription to the Congress does not necessarily mean attendance. Write to the Reception Committee at the Chemists' Club, 52 East 41st Street, New York City, of your purpose to come on; of your probable address; of the ladies who will accompany you. If you desire it, write also the kind of rooms you wish to have reserved for you, with your preference of hotels, as this committee has undertaken to look after all the personal comforts of the members. If you have not even paid your subscription as yet, do not postpone this duty until your arrival here, but attend to it now! Remember that no hostess feels happy if she is in doubt as to the acceptance of a single guest, and that there are all kinds of functions planned for this Congress, which cannot be completely arranged, until the approximate number of participants is ascertained. The man who waits until the last minute unless compelled to do so, "because there is always room for one more," catalyzes more profanity among his colleagues than his conscience can bear. Do your share, in the matter of *time* as well as personal attendance. You will not be sorry.

ORIGINAL PAPERS

THE MANUFACTURE OF CARBON BISULPHIDE.[1]

By Edward R. Taylor.

Received May 22, 1912.

The radical changes that have been made possible by the use of electricity in chemical industries are well exemplified in the advance in the manufacture of carbon bisulphide during the past thirty-five years. Reports have been made on the progress of this work from time to time.[2]

The old retort method of manufacturing bisulphide of carbon was fraught with many annoyances and disagreeable circumstances. Yet at one time I had as many as twelve of them in running condition. With but one retort in a place, economies vanish rapidly. With a number in the same furnace they are not all likely to fail at the same time, but one is constantly taking out and putting in, which keeps the works in a state of confusion all the time. Fortunately, the large dynamo, with its ability to generate electricity in large quantities and at reasonable rates, has come to our aid. In any of the usual retorts we are limited as to sizes of retort by possible heat penetration to the interior. As these old retorts are heated externally, you will appreciate some of the difficulties of their operation.

With the electric retort, however, we can have the heat in the interior, where we want it and keep the shell cool; that is the secret of its great success.

In regard to the development of our electric retort, I had considered numerous ways of conducting electricity into the furnace, and gave up as inadvisable the idea of using movable electrodes as is ordinarily done in furnaces. I concluded if I could substitute for that some electrical conductor in small pieces which would come in between stationary electrodes and stand the brunt of the stress, I would overcome the necessity of moving the electrodes, and this has been so successful that we have been able to run our furnace anywhere from eight months to a year without shutting down, and we have made from 1,500,000 to 2,000,000 pounds of carbon bisulphide in a furnace without cleaning out.

Two large induction type dynamos, made by the Stanley Company, are used in producing the electricity to supply our furnace and have given excellent satisfaction. A waterfall and lake furnish regular water-head for the turbine generator. A Corliss engine helps out the water power. Two cables convey the elec-

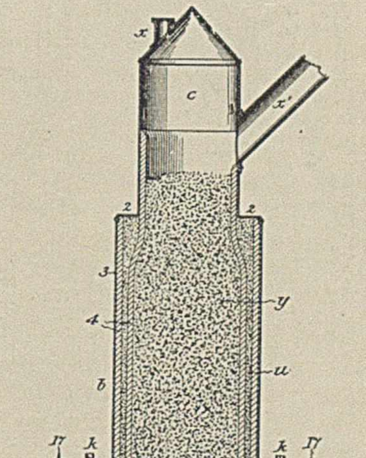

Fig. I.

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[1] Presented before the New York Section of the American Chemical Society, May 10, 1912.

[2] *Trans. Am. Electrochem. Soc.*, **1**, No. 1, 115–7 (1912); *J. Frank. Inst.*, Feb., 1908.

tricity from the dynamos to aluminum bars 6″ wide and $^5/_8$″ thick, which are connected with the insulated electrodes. Aluminum is used in preference to copper because it is less liable to corrosion. Careful and absolute insulation from the shell of the furnace is necessary and possible.

Figs. I and II show the interior construction of the furnace. Each composite electrode in this furnace is composed of twenty-five carbons each 4″ × 4″ × 48,″ making a complete electrode twenty inches square and forty-eight inches long. We use two-phase alternating current and four of these electrodes. In the center of the furnace they are about twelve inches apart.

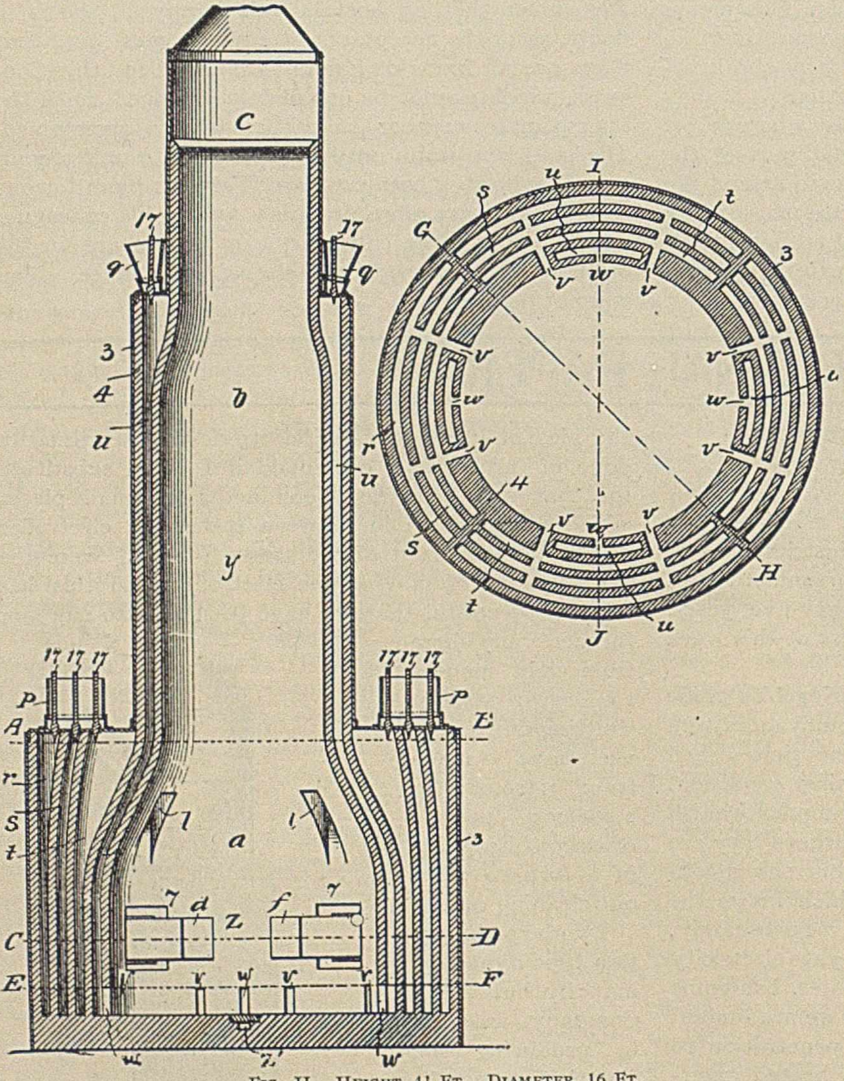


Fig. II. Height, 41 Ft. Diameter, 16 Ft.

Chimneys above each of these electrodes are used to convey broken carbons down upon them and over their ends. Their action breaks up and diffuses the current which, instead of being of one or two arcs, is broken up into a multitude of little ones, but these probably disappear as the furnace heats up. This moderates the intensity of the heat, stops entirely the hissing of the current so common in arc furnaces, and protects from excessive wear the main and more expensive electrodes, which last a year or more without renewal.

They also, if possible, serve a still more important purpose in regulating the current and saving the necessity of moving the electrodes through the walls of the furnace, which would be a very troublesome thing to do in a furnace filled with melted and vaporizing sulphur. This was a problem that presented very serious features in the early thought of a furnace for this purpose. The broken carbons also relieve the intense violence of the heat at the terminals. It will be appreciated that for low temperature work, like the manufacture of bisulphide of carbon, this is very essential. They also facilitate the starting and stopping of the furnace. Indeed the broken carbons are so valuable in this respect that we find we can stop and start at will, even when the furnace has become completely cold, and I cannot emphasize too highly the value of these broken carbons in a furnace of this construction.

To charge the furnace, sulphur is filled in up to the top of the electrodes and broken carbons are added, including the filling of the different chimneys over the several electrodes; the shaft of the furnace is filled with charcoal, and the periphery spaces of the furnace filled up with sulphur.

With the large construction it is easy to feed the cold and crushed sulphur around the periphery of the furnace, allowing it to find its way in the melted state into the interior heat zone.

Being progressively raised in temperature as it approaches the zone of reaction, the level of the melted sulphur is regulated by the amount of current supplied to the furnace and the amount of cold sulphur fed into the periphery.

On combination of the sulphur vapor with the charcoal, the formed bisulphide of carbon rises through the charcoal above it, heating it as it progresses downward towards the reaction zone.

Thus, in this furnace, the heat seeking to escape by radiation is continuously borne back to the reaction zone by the incoming material.

So complete is this return that, when making bisulphide of carbon at the rate of fourteen thousand pounds per twenty-four hours with the room at 16° C., the outside shell of the furnace shows temperatures at different points ranging from 23–64° as a maximum: with yet more power in the furnace, the production would be greater and these readings still lower.

There is very little wear to the interior of the furnace. If electrodes are disposed to get very hot, we feed a little more sulphur than otherwise, and that has a tendency to cool the electrodes.

Sometimes pillars are disposed to form in the cor-

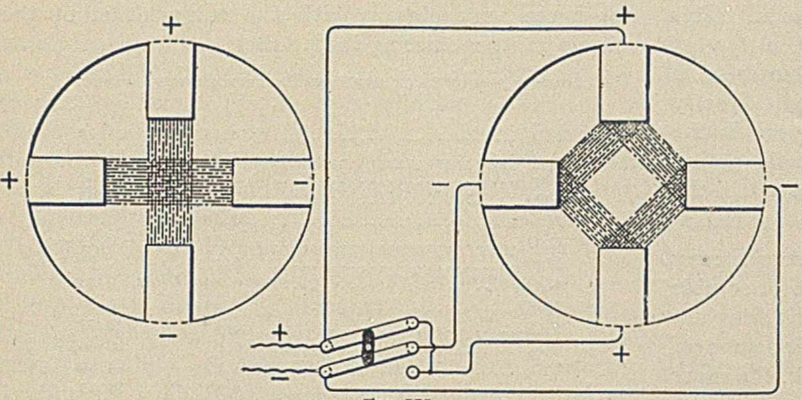
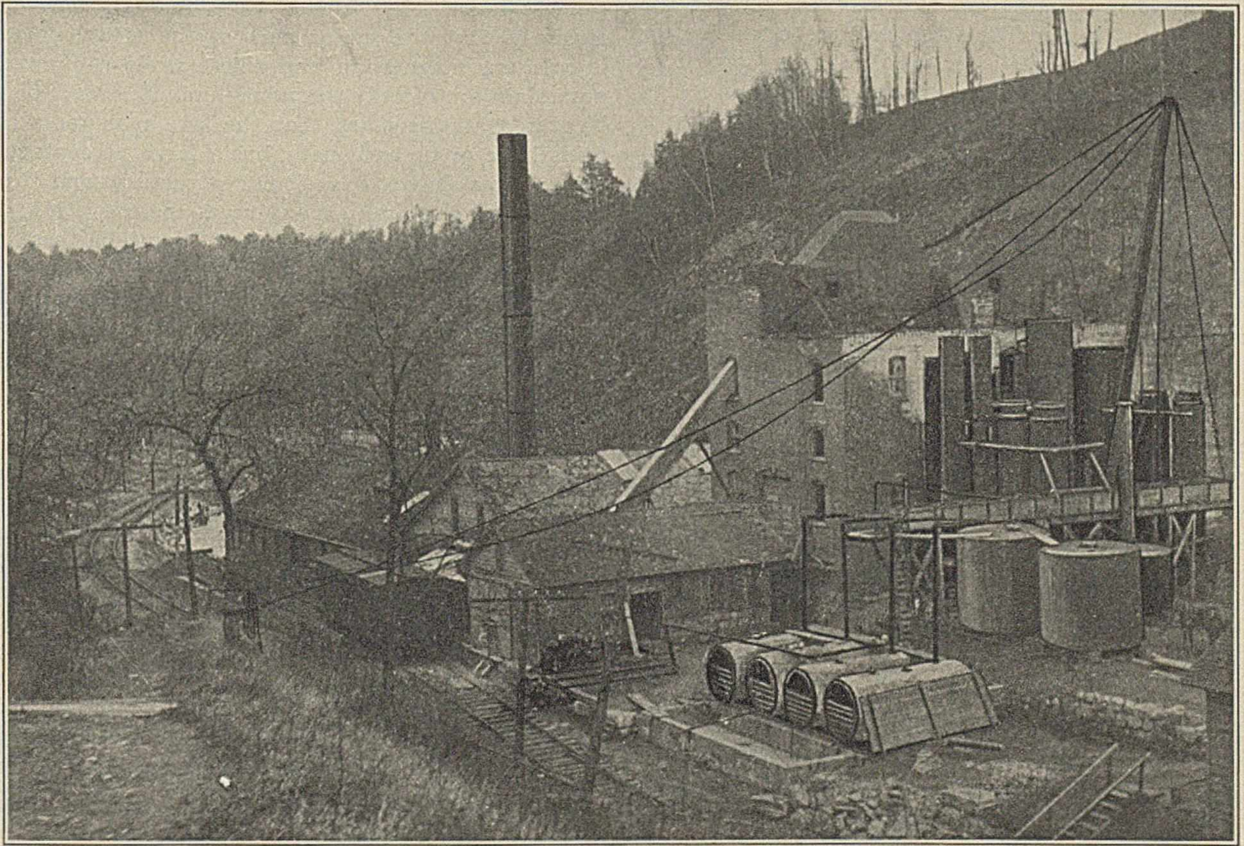


Fig. III.

ners between the electrodes. We use the 2-phase current, with one phase put on one side and the other phase on the other. Now, if pillars form in the corners, and the conductivity of the furnace is not just right, we sometimes change over and run the current to adjacent electrodes to burn out the pillars. This change is shown in Fig. III.

The provision for the sulphur is, I believe, one of the most important features of the furnace structure.



Carbon Bisulphide Plant, Penn Yan, New York.

We are able to lag the furnace from the inside instead of outside, and we lag it with the very materials used in the production of the carbon bisulphide.

Now the more perfectly we can carry this out, and the more completely full all of these channels can be kept with sulphur, the greater the economy will be in the production of the goods. The real fact is I have never yet been able to put enough current into one of these furnaces to enable us to keep all of these perfectly full. I am looking forward in a few weeks to being able to do that, and I anticipate that I shall be able to produce from 25,000–30,000 lbs. of carbon bisulphide in one of these furnaces in twenty-four hours. We have already produced 16,000 lbs. in twenty-four hours, as it is, but with sufficient power to go into the same furnace, it will practically double the output.

Penn Yan, New York.

THE OCCURRENCE OF EFFLORESCENCE ON LAVA BRICKS.

By William McGeorge.

Received March 20, 1912.

It is a common occurrence to see brick walls partially covered with a white film generally most abundant under the eaves and window-sills but more or less scattered over the whole building. This film is composed of soluble salts which, being washed from the interior, on appearance at the surface and subsequent evaporation of the water are deposited as a film. In most cases it is composed of sulphates of calcium, magnesium, potassium or sodium. The carbonates of calcium and magnesium are considered too insoluble to appear and those of sodium and potassium too soluble to remain on the surface of the brick. This film may be attributed to several causes, a few of which are as follows: (1) presence of soluble salts in the materials used, (2) soluble salts formed directly or indirectly through the action of the vapors in the drying kiln, (3) soluble salts formed through the action of the mortar after the bricks have been placed in the wall.

Undoubtedly most of the cases of efflorescence may be traced to cause (1); namely, the presence of soluble matter in the material used. In our case it was noticed that the appearance varied with the degree of porosity or compactness of the finished brick, the more porous brick being covered with a heavy film soon after being placed in the yard. The more compact ones being less easily penetrated by the rains kept their natural appearance longer or did not have so heavy a film.

The Honolulu Lava Brick Company is making brick from dark gray basaltic lava rock such as is used for building purposes in the islands. This rock exists in large quantities on this island (Oahu) and contains a comparatively high percentage of water soluble matter. Their process is essentially as follows: the rock is ground in a mill to a fine powder, to which after the addition of a small per cent. of lime, cement or both, according to formula, enough water is added to dampen the mixture. The whole is then run into a press and pressed into brick. They are then dried in a manner best suited for the setting of the lime or cement. The resulting product has shown excellent physical tests and is a good grade of building brick of gray color. It has been noticed, however, from the beginning, that some of the bricks, soon after being wetted by the rain, became covered with a heavy white efflorescence. At first it makes its appearance in the form of needle-like crystals shooting out from the pores of the brick. Later as the quantity increases the deposit becomes heavy and can be scraped from the surface in large amounts.

Without ascertaining the composition of this film the company tried several methods of eradicating it, which had been recommended by different people. Two of these were addition of barytes which had little or no effect, and the painting of the surface with oil, which in this case did not even have a temporary retaining effect.

Upon making an analysis of this film it was found to be composed essentially of a mixture of sodium and potassium carbonates. The following is a complete analysis:

SiO_2	0.85	H_2O	24.32
Fe_2O_3	..	Na_2O	29.81
Al_2O_3	0.93	K_2O	10.14
P_2O_5	..	SO_3	0.32
CaO	1.56	Cl	0.20
MgO	0.42	CO_2	31.39

It may be seen at a glance that it is composed of extremely soluble constituents. In fact, it may be dissolved by placing in the palm of the hand and rubbing with the finger. On the other hand it does not agree very closely with the composition of the soluble matter existing in the rock.

COMPOSITION OF LAVA AND LAVA DISINTEGRATION PRODUCTS.[1]

	I.	II.
SiO_2	52.15	23.28
Al_2O_3	12.57	33.77
Fe_2O_3	3.36	13.31
FeO	7.07	3.08
Mn_3O_4	0.50	0.40
CaO	8.54	0.16
MgO	6.51	0.09
K_2O	0.84	0.23
Na_2O	2.64	0.29
P_2O_5	0.28	0.32
SO_3	0.61	0.46
TiO_2	4.07	4.49
Vol. matter	0.57	14.53
H_2O	0.37	6.90

[1] From analysis by W. P. Kelley.

The above table shows the effects of weathering and disintegration upon lava rock and incidentally the soluble and insoluble constituents. Column I is an analysis of lava rock and II is its disintegration product taken out of the gulch at the edge of I where the rock was badly disintegrated and most of the soluble matter washed out into the soil. The samples were taken very close to each other and were originally of the same composition. Hence these analyses show conclusively that the major part of the soluble matter is calcium, magnesium and silica, while sodium and potassium are of only secondary importance. It may be stated at this point that the lava rock mass contains little or no carbonate, but a large percentage of these lavas have a vesicular structure and these vesicles or holes are in many cases coated with a film of salts, varying in composition. Some of these are composed of carbonates. While the above table shows the relative solubility of the various ingredients it presents no data which would hinder one from concluding that the sodium and potassium were dissolved out more quickly during the weathering stages than the other ingredients, even though a larger relative percentage of them remains in the residue. If this were true it would account for the small percentage of calcium and magnesium in the film. Accordingly, a set of leaching experiments were run to ascertain if the above were true and to test out the possibility of leaching the ground rock before pressing, thereby removing the soluble matter as far as possible from the material. The results of leaching the ground rock are shown in the following tables, and proved entirely impracticable. Although the soluble matter of which the film is composed decreases, it does so only to a slight extent, while the calcium and magnesium are leached out very rapidly as sulphates.

SOLUBILITY OF CRUSHED LAVA IN HOT H_2O.

	I.	II.	III.	IV.
SiO_2	0.97	17.30	16.05	16.17
CaO	13.75	0.26	0.28	0.27
SO_3	36.48	5.04	3.50	2.28
MgO	3.98	0.18	0.56	0.21
Na_2O	32.10	21.66	34.78	16.10
K_2O	1.86	1.54	5.46	4.65
Res. in 100 cc.	0.9851	0.9516	0.8288	0.7442

The above table shows the results obtained by leaching the ground rock with hot water for eleven days. Leachings were made by allowing the ground rock to remain in an iron tank containing hot water. After one hour the leachings were drawn off and the partial analysis made on this solution is shown in column I. Fresh hot water was then added and allowed to remain twenty four hours and this repeated for eleven days. Column II represents the partial analysis of the solution obtained after one day in contact with the ground rock following the one-hour extraction, column III, that on the fourth day and IV, the eleventh day. Constituents are given in percentages in solids obtained from leaching waters and grams of solids per 100 cc. of solution are shown at the bottom. The first leaching was neutral to litmus and all the rest were decidedly alkaline.

Leaching with cold water was also tried but the experiment was stopped at the end of the third day. A glance at the following table will show that the action of the hot and the cold water was about the same except that the latter was much slower.

Solubility of Crushed Lava in Cold Water.

	1 hr.	2 days.	3 days.
SiO_2	1.44	13.28	15.30
CaO	20.92	6.53	5.16
SO_3	28.26	11.08	10.68
MgO	0.94	6.32	6.04
Na_2O	14.58	21.76	45.52
K_2O	1.78	5.56	6.06
Res. in 100 cc.	0.4637	0.0594	0.0638

This table also shows percentages in the solid matter in the leaching waters and grams of solid matter in 100 cc. Bricks made from the leached rock also developed efflorescence. The major part of the difference between the sum of the constituents recorded in both of the above tables and 100 per cent. is made up of CO_2 and water of crystallization. In the analyses of the extracts, the water and carbon dioxide varied greatly and were not considered to be of sufficient value to warrant their determination.

In addition to these leaching experiments a number of finished bricks were submerged in water to ascertain if a sort of osmosis could be set up within the brick by which a large percentage of the saline matter would be retained in the interior of the brick. They were submerged for various periods and it was found that it gave only temporary benefit.

Barium carbonate and chloride have been used as a means of removing soluble sodium and potassium compounds, their action being to replace the alkalis and form harmless by-products, the alkali compounds being washed out. However, this method has been used only in the wet process and in cases where the percentage of sodium is much less than ours. As stated above when used in our case it had no effect and altered very little the indefiniteness of the time it would take the various weathering agents to remove the salts by the washing of the rain, evaporation and drawing to the surface of more saline matter.

Upon further investigation it was noticed that those bricks to which lime had been added invariably gave a thick efflorescence, increasing with an increase in the percentage of lime added. Then this same rock has been used as a building stone in its natural state and while it is quite porous has rarely shown any of the above efflorescence when used as such. From these facts it appears that the addition of lime is the cause, at least in part, of the trouble. On the other hand it is absolutely necessary to add some binding material to hold the brick together after it comes from the press. While a brick may be made simply by dampening the ground rock and pressing, the corners chip easily upon handling.

Since there seemed to be no chemical means of complete removal or precipitation of the saline matter and addition of lime was partly the cause of the appearance of the film, through its alkaline action on the sodium and potassium and subsequent conversion of these into carbonates, the problem narrowed down to an elimination of the lime, if possible, and the addition of a binding agent which would give a more compact brick as well as one which might have some osmotic properties.

Potassium and sodium are known to occur in basaltic lava in the form of complex silicates. From this fact it is apparent that these silicates are acted upon by the lime, since the bricks after being pressed are run into drying kilns and heated under pressure with steam. The lime, under pressure and at the high temperature of the kiln, reacts with the sodium and potassium in the complex silicates and forms caustic soda and potash as by-products which upon appearance at the surface are converted by the carbon dioxide of the air into carbonates and bicarbonates of the alkalis. If this were true then an elimination of the use of lime as a binding agent should eliminate the trouble. This was done and a small per cent. of cement was used in its stead and the method of drying altered. In this way a more compact brick was obtained and at present writing the alteration is producing decidedly better results.

Thanks are due Mr. W. P. Kelley for valuable suggestions; also for the analyses showing effects of disintegration on lava rock, these analyses being taken from investigations made by him on lava disintegration.

Contribution No. 4, Federal Experiment Station,
Honolulu, Hawaii.

ENAMELS FOR SHEET STEEL.[1]

By Robert D. Landrum.

Received April 4, 1912.

Enamels for sheet steel are boro-silicates of sodium, potassium, calcium and aluminum and are, in every sense of the word, glasses. Such enamels are so compounded that they form a homogeneous, glossy coating on the surface of the sheet steel utensil, which will not be corroded by the acids or alkalies used in cooking and which will resist punishment both by impact and by rapid changes of temperature.

Although an enamel is a glass, the fact that it must adhere to steel and resist the abuse common to cooking utensils makes necessary the addition of other ingredients besides those used in manufacturing ordinary glass. In enamels, ground quartz, flint or sand supply the silica, and feldspar and clay, the alumina. Fluor-

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[1] Delivered before the Chemists' Club of Rochester at the University of Rochester, Rochester, New York, April 1, 1912.

spar or calcite is added to supply the lime and cryolite to render the enamel translucent. Soda ash and pearl ash are fluxes adding sodium oxide or potassium oxide to the product, and borax furnishes the boric anhydride, which adds many desirable qualities, such as greater ductility and elasticity. Sodium or potassium nitrate is used in white enamels and manganese dioxide in dark colored enamels as an oxidizing agent. Oxide of cobalt is used in enamels which come directly in contact with the steel and adds adhesiveness to this coating.

For producing white enamels, oxide of tin is used; for blue, cobalt; for violet and brown, manganese; for gray, nickel; for green, copper or chromium; for yellow, uranium or titanium; and for red, iron, selenium or gold.

Enameling is still held as a secret art, and the formulas are carefully guarded. Most companies allow very few visitors to go through their plants and some keep their employees in ignorance by various schemes. In one American works, each of the enamel raw-materials is given a number. They are ordered, shipped, kept account of, and stored under their respective numbers, and only those in authority even know what materials are used. In this same factory, employees of one department are not allowed in another and after being employed in one department, a man is barred from employment in any other. Some works have the formula for each enamel divided into two parts, one of which is mixed by one man, the other by a second, and certain proportions of each are then mixed together by a third man. In practically all enameling works, the materials are weighed on a scale, the beam of which is hidden from the laborers, who are also generally of foreign birth and are changed frequently.

The "Black Shape."—The sheet steel which is used for enameled ware is as nearly as is possible free from carbon, silicon, sulphur and phosphorus, and its manganese content is generally about 0.2 per cent. These sheets come in squares and oblongs from 27 to 20 gauge and are circled, stamped and spun with as little heat treatment as possible and with the use of a lubricant that can easily be cleaned off. The ears, handles and other trimmings are, as far as is practical, welded on, as riveted joints are difficult to enamel.

Pickling Process.—The surfaces of the completed steel vessels are thoroughly freed from carbonaceous matter by annealing at a low red-heat and are then pickled in hot dilute acid, thoroughly rinsed in water, and then in weak alkali solution. After a quick drying they are ready to be enameled.

The Enamel.—In the making of an enamel, the various raw-materials are loaded from their respective bins into small cars called "dollies." These are filled to a line which approximates the correct weight, then they are pulled on a scale, the beam of which is hidden from the workman, and the enamel-master indicates whether the load is light or heavy, and the workmen correct this by shoveling on more or taking some off. When each of the "dollies" is corrected so that the required amount of material for a mix is in it, all are dumped on a large, hard maple floor, the coarser material on the bottom and the finer on the top. This pile is thoroughly mixed by shoveling, and is loaded into an electric elevator, which hoists it to its bin. There is a bin for each different kind of enamel, and a traveling bucket which holds a melt (about 1200 pounds) carries the mix to the tank furnaces where it is melted into a liquid glass.

These tank furnaces are regenerative, reverberatory furnaces like those used in the manufacture of glass, and natural gas or crude oil is an ideal fuel for them. However, in the older enameling works, coal is used directly, and in the later ones producer-gas is used as a fuel. The temperature required for smelting the different enamels varies from 1000° C. for a glaze to 1300° C. for a ground coat, and, in most enameling works, pyrometers are installed to assist in controlling these temperatures. Each furnace will give seven or eight melts in twenty-four hours.

After the enamel is melted into a liquid glass, a fireclay plug in the front of the furnace is pulled out and the glowing liquid stream plunges out and is caught in a tank of cold running water. The reaction is terrific and the glass mass is torn and shredded, cracking into small pieces like popcorn, each of which is a myriad of microscopic seams and fissures. This "quenching," as the process is called, toughens the enamel and facilitates the process of grinding which comes next.

The water is drained from the tanks, leaving the "enamel frit." This is shoveled into pans (a certain weight to a pan) and is ready for grinding.

In the mill room, the enamel frit is ground in large ball mills for about thirty hours. These mills are cylindrical, about five feet long and six feet in diameter, and are lined with porcelain bricks. The frit is put into them with fifty per cent. of water and several per cent. of white ball-clay. For the white cover-coat enamels, tin oxide is also added. The mill revolves and the constant impact of the flint stones against the glass particles grinds them to an impalpable powder, which mixes with the water and the clay, forming a mass which has the consistency of rich cream. This is loaded into tanks, where it is allowed to age a week or so.

Application of the Enamel.—From the mill room the enamel is taken to the dipping room, where it is put into tanks that are like large dish-pans. These are sunk into tables, and at each tank a slusher works. The slusher takes the stamped-out steel vessel, which has been thoroughly cleaned, and plunges it into the enamel. When taken out, the wet enamel forms a thin film over the entire surface. By a gentle swinging motion, the excess of enamel is thrown off, and the vessel is placed bottom down on three metal points projecting from a board. Three or four vessels are put on a board; these are placed on racks and when the vessels are thoroughly dry they are carried to the furnace room.

The furnace room contains a long bank of muffle-furnaces and in these the ware is put after drying. The temperature in these furnaces is about 1000° C. and here the little powdered particles of enamel are fused together in a solid glass coating over the vessel, the process requiring from three to five minutes.

Each coat is burned separately. For instance, we have a pudding pan that is to be a three-coat white inside, turquoise-blue mottle outside. It is first dipped in the ground coat enamel, the excess is shaken off and the vessel put on a three-pointed rack and dried. After drying, the enamel stands in little grains all over the surface of the ware, adhering to the metal on account of the raw clay ground with it. At this stage every care must be taken, for a scraping, even of the finger nail, would take off some of the powdered particles of the enamel. This pan is then put into the muffle of the furnace, and the heat fuses all the little particles together, leaving a tight-holding vitreous coating all over the surface of the vessel. This fundamental coating is nearly black, due to the oxides of cobalt and nickel which it contains, and shines with a glass-like luster.

After the vessel has cooled at the ordinary temperature of the room, it is again brought to the slushing room, and here is covered with an enamel—this time a white. It goes through the same process as before, except that a black bead is brushed around the rim. On account of the dark color of the first coat showing through, this second coat, after it is burned, has a gray appearance, and is called the "gray coat" or "first white." The vessel is again sent to the slushing room, and is dipped into a white enamel, the excess shaken off, and before drying the blue-green enamel is sprayed on the outside.

This spraying process was at one time done by dipping a wire brush into the wet blue-green enamel and the slusher shaking it over the surface of the vessel, causing the blue enamel to fall in little speckles all over the white enamel. In most factories, however, spraying machines, which work on the principle of an atomizer, have been installed. A tank full of the colored enamel stands over the table and the enamel is forced out through a nozzle in a spray by compressed air. The flowing of the enamel is controlled by the foot of the slusher as he holds the vessel in the spray. The vessel is then dried and the coating is fused in the muffle-furnace, the result being turquoise-blue spots on a white background.

The finished ware is assorted into three lots: firsts, seconds, and job lots. Some of the seconds and job lots are fit for redipping. They may have some little spots where the original vessel was not properly cleaned and where, on account of the rust or dirt, the enamel did not adhere. These spots are filed or are held under a sand-blast until the exposed surface is perfectly clean, and then the vessel is covered with another coat of enamel.

There are schemes for saving money in all manufacturing plants, and in the enameling business a large part of the profit comes from the residues. For instance, every bit of enamel is scraped from the tanks and tables, all sweepings from floors are saved, and all the waste water from the various departments is first carried into catch basins, and every few days these are cleaned and the residue, which has settled to the bottom, is taken out. The residues from all these sources are again melted with the proper amount of fluxing material and coloring matter, and this dark-colored enamel is used for coating the cheaper wares.

A German White Enamel.—In order to give an idea of the composition of a white cover-coat frit, such as is used on cooking utensils, and to show the method used by ceramists to calculate its so-called molecular formula, the following enamel, the formula of which is taken from the 1911[1] edition of the "Taschenbuch für Keramiker," is used:

Feldspar 38.6 per cent., quartz 19.0 per cent., borax 15.4 per cent., cryolite 11.7 per cent., saltpeter 6.5 per cent., calcite 6.5 per cent., fluorspar 1.3 per cent. and magnesium carbonate 1.0 per cent.

Enamel Materials.—All the materials used were practically pure except the feldspar, which was a pegmatite of the following composition:

		Per cent.
Silica	(SiO_2)	70.66
Alumina	Al_2O_3	16.85
Potassium oxide	K_2O	5.93
Sodium oxide	Na_2O	4.61
Lime	CaO	0.52
Carbon dioxide	CO_2	0.41
Moisture	H_2O	1.02

This figures to a "molecular" formula of

$$\left.\begin{matrix} 0.45\ Na_2O \\ 0.39\ K_2O \\ 0.06\ CaO \end{matrix}\right\} Al_2O_3 \left\{\begin{matrix} 7.11\ SiO_2 \\ 0.34\ H_2O \\ 0.06\ CO_2 \end{matrix}\right.$$

the molecular weight of which would be 602.

The other materials used were:

Material.	Formula.	Equivalent weight.
Quartz	SiO_2	60
Borax	$Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$	382
Cryolite	$2Na_3AlF_6$, giving $3Na_2O{\cdot}Al_2O_3{\cdot}6F_2$	420
Saltpeter	$2K_2O{\cdot}N_2O_5$	202
Calcite	$CaO{\cdot}CO_2$	100
Fluorspar	CaF_2, giving $CaO{\cdot}F_2$	78
Magnesium carbonate	$MgO{\cdot}CO_2$	84
Feldspar	(Given above)	602

THE ENAMEL.[2]

Batch Mix. Material.	Per cent. used.	M. W.	Molecular equivalent.[3]	Na_2O.	K_2O.	CaO.	MgO.	Al_2O_3.	SiO_2.	B_2O_3.	F_2.
Feldspar	38.6	602	0.0641	0.0288	0.0250	0.0038	..	0.0641	0.4558	..	..
Quartz	19.0	60	0.3167	..	..	..	..	..	0.3167	..	..
Borax	15.4	382	0.0403	0.0403	..	..	..	..	..	0.0806	..
Cryolite	11.7	420	0.0279	0.0837	..	..	..	0.0279	..	..	0.1674
Saltpeter	6.5	202	0.0322	..	0.0322	..	..	..	..	..	..
Calcite	6.5	100	0.0650	..	..	0.0650	..	..	..	..	..
Fluorspar	1.3	78	0.0167	..	..	0.0167	..	..	..	..	0.0167
Magnesium carbonate	1.0	84	0.0119	..	..	..	0.0119	..	..	..	..
Total	..	..	..	0.1528	0.0572	0.0855	0.0119	0.0920	0.7725	0.0806	0.1841

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[1] Page 18. Published by Keramische Rundschau, Berlin, N. W., 21.

[2] A complete description of the manufacturing of this enamel and of the physical properties of a ware coated with it is given by the writer in "A Comparison of Ten White Enamels" in the *Trans. Am. Ceramic Soc.*, Vol. XIV.

[3] Molecular equivalent equals per cent. used divided by M. W.

The above total corresponds to the following molecular formula of enamel:

$$\left.\begin{array}{l} 0.497\ Na_2O \\ 0.186\ K_2O \\ 0.278\ CaO \\ 0.039\ MgO \end{array}\right\} 0.299\ Al_2O_3 \left\{\begin{array}{l} 2.513\ SiO_2 \\ 0.262\ B_2O_3 \\ 0.599\ F_2 \\ \end{array}\right.$$

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THE PRODUCTION OF EXCESSIVE HYDROGEN SULFID IN SEWAGE DISPOSAL PLANTS AND CONSEQUENT DISINTEGRATION OF THE CONCRETE.[1]

By William M. Barr and R. E. Buchanan.

Received February 15, 1912.

It is well known to those who are familiar with the operation of the septic tank that in the chambers of such tanks, which operate in the absence of light and air, the bacteria produce, in the decomposition of the organic matter of the sewage, quantities of reducing gases. Among the decomposition products is observed more or less hydrogen sulfid gas, resulting in most cases from the decomposition of organic sulfur compounds existing in the sewage. In most tanks of this character the amount of hydrogen sulfid thus liberated is not sufficiently large to cause complaint from excessive odors or to account for the conditions in certain tanks observed by the writers.

Attention was first called to the disintegration of cement mortar in concrete resulting from sewer gases, by Olmstead.[2] The case observed by him occurred in the outfall sewer for Los Angeles, built in 1895. This resulted from the holding back of the sewage in inverted siphons in this sewer, forming, in principle, a septic tank. Beyond this point the neat cement mortar was badly disintegrated and it became necessary to reconstruct the walls and roof of this portion of the sewer. It was observed that the disintegration resulted from the formation of sulfuric acid upon the walls and roof, which attacked the cement, giving calcium sulfate as the final product. It was also observed that the amount of sulfuric acid formed appeared to be too large to have been produced by the organic sulfur compounds in the sewage proper. It was also suggested that the only possible sources of this excessive amount of sulfur were the oil wells and the sulfur which is always present in small quantities in the normal sewage. The report does not indicate that the source of these sulfur compounds was definitely located.

The case of a septic tank in England where a condition similar to the one cited above existed has been reported by Dunn,[3] but no attempt is made to show any relation between this condition and the character of the water supply.

As early as November, 1908, one of us visited the sewage disposal plant of the Inebriate Hospital at Knoxville, Iowa, and observed the following conditions: The concrete composing the roof and walls above the high water line in the dosing chamber was rapidly disintegrating. The under surface of the roof was found to be decomposed to a depth of 2 cm. Quantities of free sulfur were deposited upon the walls, and the calcium compounds of the cement were found to have been converted near the surface into crystals of gypsum. Large quantities of hydrogen sulfid were given off when the dosing chamber discharged, causing complaint of foul odors by neighbors and residents at the hospital. At a later date a similar condition was observed in the septic tank receiving the sewage of the city of Grinnell, Iowa.

In both these cases various measures have been tried to prevent the formation of excessive odors and decomposition of the concrete. A water-softening plant was installed at the Knoxville institution, thinking this might improve conditions, but, except for making the water more desirable for domestic purposes, nothing was achieved. Frequent cleaning of the tank and disinfecting at the time of cleaning did not materially improve conditions.

During the progress of this investigation our attention was called to the septic tank at the State Hospital at Mt. Pleasant, Iowa, and before visiting the place, an analysis of the water supply caused us to predict the condition existing there. A visit showed the septic tank to be in much the same condition as those first studied.

The object of this investigation was to determine the cause of the conditions above noted and to determine whether bacteria were in any measure responsible for the changes, or whether they were purely of a chemical nature. The various observations made by us, together with analyses of the water supplies and the sewage, seemed to point to some definite relationship existing between the compounds of sulfur in the water supply and the formation of excessive hydrogen sulfid, with the consequent formation of sulfuric acid on the walls of the tank.

This was used for a working hypothesis for the following reasons:

First.—The water supplies in the cases observed were found to have an unusually high content of sulfates.

Second.—The odor of hydrogen sulfid was, in all cases, very pronounced about the dosing chamber.

Third.—Free sulfur was found floating on the surface of sewage which had been standing for some time, and quantities of free sulfur were deposited on the walls in various parts of the septic tank.

Fourth.—An abundance of sulfur bacteria was evident upon microscopic examination.

Fifth.—The disintegrating concrete showed much greater amounts of sulfate than the unaffected concrete, and as already stated showed crystals of gypsum on microscopic examination.

A large proportion of proteins contain a considerable percentage of sulfur. When such compounds are decomposed in the absence of oxygen, the sulfur makes its appearance for the most part in combination with hydrogen as hydrogen sulfid. Inasmuch as proteins and the products of hydrolytic cleavage are generally to be found in sewage, it is to be expected that a certain amount of hydrogen sulfid will be de-

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[1] From a Bulletin of the Eng. Expt. Sta., Iowa State College.

[2] *Eng. News*, **44**, 317.

[3] *Cement Eng. News*, **22**, 10.

veloped in such sewage as it passes through an anaërobic septic tank. The quantity so produced is not large and ordinarily little of it escapes into the air. Even in open septic tanks the heavy membrane or scum which usually forms contains many oxidizing bacteria, which may effectually prevent the escape of hydrogen sulfid. In the instances here discussed the amount of hydrogen sulfid evolved cannot be entirely accounted for by the decomposition of such protein substances, for the analyses of the raw sewage show it to be no higher in albuminoid ammonia, that is to say proteins and their decomposition products, than sewage from other disposal plants in which there is no such evolution of this gas.

ANALYSES OF RAW SEWAGE. (Figures show parts per million.)

Sample from	Nitrogen as free ammonia.	Nitrogen as albuminoid ammonia.	Chlorides.	Nitrites.	Nitrates.	Oxygen consumed.	Solids on evaporation.	Solids on ignition.
Hospital for inebriates, Knoxville, Iowa......	21.00	6.50	35.0	none	none	53.31	3040	2484
Hospital for inebriates, Knoxville, Iowa......	32.60	4.60	...	trace	trace	114.7	3902	2624
Grinnell, Ia., city plant....................	6.50	6.00	54.0	high	none	17.18	950	776
Grinnell, Ia., city plant....................	11.50	6.00	122.0	...	...	10.74	1114	894
Knoxville, Ia., city plant[1]..................	25.00	6.00	33.0	trace	none	63.60	800	538
Ames, Ia., city plant[1].......................	18.20	8.20	...	...	...	...	552	251

[1] Excessive hydrogen sulfid was not observed at these plants.

All other plants examined, where the water supply had a smaller sulfate content than that shown for the city of Knoxville in the next table, gave no excessive odor of hydrogen sulfid.

Chemical analyses of the raw sewage and effluents were made to determine the amount of sulfates in solution, and the total sulfates in the raw sewage. These results indicate, first, that the organic matter in normal sewage does not contain enough sulfur to produce the quantities of hydrogen sulfid observed; second, that where the sulfates in the original water supply are high, there is a marked reduction in the amount of mineral sulfates found in the effluent, showing that a portion of these mineral sulfates must have been reduced and removed from solution.

In three cases where excessive hydrogen sulfid was observed these relations were very marked. Several other septic tanks were observed where the sulfates in the water supply ranged from 16 to 143 parts per million as at the Knoxville city plant, and in all such cases very little hydrogen sulfid could be detected at the tank. The Knoxville city plant shows the highest sulfates in the raw sewage of any plant observed where excessive hydrogen sulfid did not appear, and it is doubtful whether this amount of sulfates might not cause trouble in some cases.

ANALYSES OF RAW SEWAGE.

Source of sample.		Total sulfur as SO_4.	Soluble sulfur as SO_4.
Inebriate Hospital, Knoxville, Ia.....	Water supply	1664	1664
Inebriate Hospital, Knoxville, Ia.....	Softened water	1566	1566
Inebriate Hospital, Knoxville, Ia.....	Raw sewage	1552	1533
Inebriate Hospital, Knoxville, Ia.....	Tank effluent	..	965
Grinnell, Ia	Water supply	476	476
Grinnell, Ia.........................	Raw sewage	452	427
Grinnell, Ia.........................	Tank effluent	381	352
State Hospital, Mt. Pleasant, Ia......	Water supply	900	900
State Hospital, Mt. Pleasant, Ia......	Raw Sewage	871	850
State Hospital, Mt. Pleasant, Ia......	Tank effluent	716	690
Knoxville, Ia........................	Water supply	143	143
Knoxville, Ia........................	Raw sewage	163	147
Knoxville, Ia........................	Tank effluent	..	145

The preceding table shows the amount of sulfur in the sewage calculated as SO_4 and the amount in the effluents, showing how it has been removed by reduction to hydrogen sulfid.

The investigations of various European workers, particularly Beyerinck[1] and van Delden,[2] have demonstrated that certain anaërobic bacteria in the presence of organic matter reduce sulfates to sulfids. Each of these investigators isolated specific organisms, which, when inoculated into sterile solutions containing sulfates and a little organic matter, brought about a very considerable evolution of hydrogen sulfid. It was therefore thought possible that the large amount of this gas given off in the septic tank and the dosing chamber might be due in large part at least to a reduction of the sulfates of the water supply. The chemical analyses of these waters show them to be exceptionally high in sulfates. Tests were accordingly made to determine whether or not such sulfates under the septic conditions of this plant would be transformed into sulfids.

The following solutions were prepared in two liter lots, and 500 cc. placed in each of four liter flasks, the solutions in each case being covered by a layer of neutral paraffine oil. This furnished anaërobic conditions for bacterial growth, inasmuch as paraffine oil permits little or no oxygen to penetrate it. After sterilization three of each set of the flasks were inoculated, one being retained as a check. The material used in inoculation was secured from different parts of the septic tank and the dosing chamber of the plant at the Inebriate Hospital at Knoxville. After inoculation the flasks were kept in the laboratory at a temperature of about 18° C.

COMPOSITION OF MEDIA USED.

Material.	Sol. 1.	Sol. 2.	Sol. 3.	Sol. 4.	Sol. 5.	Sol. 6.
Tap water.........	1000 cc.	1000 cc.	1000 cc.	1000 cc.	1000 cc.	1000 cc.
NaCl..............	30 g.	...	...	...	...	...
K_2HPO_4..........	0.5 g.	0.5 g.	0.5 g.	0.5 g	0.5 g.	0.5 g.
Asparagin..........	1.0 g.	1.0 g.	1.0 g.	1.0 g.	1.0 g.	1.0 g.
$MgSO_4$............	8.0 g.	8.0 g.	...	...	...	2.0 g.
Na_2SO_4...........	...	...	2.0 g.	4.0 g.	10.0 g.	...
$FeSO_4$............	0.1 g.	0.1 g.	0.1 g.	0.1 g.	0.1 g.	0.1 g.

The iron in each of the above solutions was added as an indicator. The formation of sulfid was shown by the deposition of black iron sulfid.

Within two or three days the solutions 2, 3, 4, 5 and 6, almost without exception, began to turn gray and within two weeks an abundant precipitate of iron sulfid was visible in all. It is evident, then, that bacteria having the power to reduce sulfates to sulfids were present in numbers in the sewage in question. The quantity of sulfate daily entering the plant justifies

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[1] *Cent. für Bakt., 2nd abt.*, **1**, 1, 49, 104 (1895).

[2] *Ibid.*, **11**, 81, 113 (1903).

the conclusion that much of the hydrogen sulfid developed in the tank is formed by the deoxidation of such sulfates.

Stained mounts were prepared at intervals from each of the flasks described above. At first no bacterial type or organism appeared to predominate; large and small bacilli, cocci, and a few spirilla were present. At the end of the two weeks most of the flasks showed a decided predominance of spirilla. Those containing the highest percentage of hydrogen sulfid were practically pure cultures of this organism.

A medium of the same composition as solution 5 described above, with the addition of 1.5 per cent. agar agar, was used for the purpose of isolation. Different dilutions were plated and the medium covered with paraffine to exclude oxygen. In three or four days black specks appeared in the plates, the areas of discoloration often reaching 10 mm. by the end of the week. Near the center of such areas could be observed small opaque colonies, generally considerably less than 1 mm. in diameter. These colonies were found to consist of the characteristic spirillum noted above. When grown in test tubes containing solution 5 under anaërobic conditions, pure cultures were found to produce a rapid reduction of sulfates to sulfids.

It may be concluded that in the particular sewage of the Knoxville Hospital, this spirillum alone is capable of producing hydrogen sulfid in quantities sufficient to account for the amount present in the dosing chamber and septic tank.

Zelinsky,[1] in 1893, described a motile elongated bacillus (Bacillus Hydrosulfuroum ponticum) obtained at considerable depth from the ooze of the Black Sea. This organism under anaërobic conditions was found to reduce sulfates and sulfites to sulfids.

Beyerinck[2] isolated a specific organism (Spirillum desulfuricans) from canal water. Inoculation of this organism into media containing sulfates resulted in the rapid development of sulfids. Morphologically the organism was from one-half to a full spiral, rather rarely the latter. In the absence of oxygen it is actively motile. It is probable that the organism isolated from the sewage disposal plant at the Knoxville Hospital is the same as the one described by Beyerinck.

Van Delden[3] made a further study of the S. desulfuricans of Beyerinck and also described the form Microspira aestuarii from near the mouth of one of the Holland rivers. The ooze at the bottom of the sea in such places was found to be blackened by sulfids. He made an extensive study of the reduction of sulfur compounds by these organisms in both pure and mixed cultures. M. aestuarii he found to be the more efficient of the two as a reducing agent, producing in the course of seven weeks as much as a gram of hydrogen sulfid per liter of water. Morphologically this organism resembles the former very closely.

Examination of the dosing chambers of the tanks observed showed that the moisture on the walls was strongly acid with sulfuric acid. A considerable portion of this acid was doubtless produced by atmospheric oxidation of the hydrogen sulfid, which of itself might account for the formation of the sulfuric acid and the sulfates found in the concrete. The bacterial study, however, shows another agent which aids materially in the oxidation of the hydrogen sulfid.

The work of Winogradsky, Engelman, Miyoshi, and others has shown that certain groups of bacteria under aërobic conditions may utilize hydrogen sulfid by direct or indirect oxidation as a source of energy. The first evidence of such oxidation is frequently the accumulation within the bacterial cell of granules of free sulfur. These may be recognized microscopically by their relatively high refractive index, by their solubility in carbon disulfid and by the characteristic crystals which form when such solutions are allowed to dry upon a glass slide. These organisms are found later to further oxidize this free sulfur, the final product being sulfuric acid. The organic food requirements of these bacteria seem to be very small; indeed, many apparently utilize the carbon dioxide of the atmosphere and very simple compounds of nitrogen.

In examination of the septic tanks in question one of these oxidizing sulfur organisms (Beggiatoa) was found growing abundantly in some places on the surface of the scum. Disintegrating concrete, moreover, was covered by a luxuriant growth of moulds and bacteria. A comparison of the chemical analysis of sound concrete, and that which has undergone partial disintegrations, hows a notable increase in the amount of sulfate present in the latter. It should be noted further that the concrete below the water line of the septic tank and dosing chamber had disintegrated little or none at all. It seemed evident, therefore, that hydrogen sulfid alone could not be the immediate cause of such disintegration, for it is constantly present in the sewage in contact with those walls. Inasmuch as bacteria, however, seemed to thrive in the moisture generally present on the under side of the roof and on the walls, it seemed probable that much of the hydrogen sulfid arising from the sewage is absorbed and then converted into sulfuric acid through the agency of bacteria.

ANALYSIS OF DISINTEGRATED CEMENT WALL IN SEPTIC TANK AT GRINNELL, IOWA, SHOWING VARIATION IN SULFUR CONTENT OF DIFFERENT PARTS OF CONCRETE.

	Free sulfur.	Sulfates (SO_4).
First or outer[1] layer, 1/4-inch thick	19.7%	1.2%
Second layer, immediately beneath first	7.2	21.0
Third layer, one inch below surface	0.27	6.75

One hundred cm. flasks containing various sulfids were inoculated with material from the disintegrated concrete and examined from time to time. In some of these flasks Beggiatoa filaments developed, showing their characteristic sulfur granules within the cells. However, active oxidation of the sulfids to sulfates occurred in the other flasks in the absence of Beggiatoa, apparently through the agency of other bacteria which swarmed in such cultures.

The following solution was prepared to determine definitely whether or not such bacteria were actually

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[1] *Proc. Rus. Phys. Chem. Soc.*, Fasc. 5.

[2] *Loc. cit.*, 1895.

[3] *Loc. cit.*, 1903.

[1] This layer consisted chiefly of a deposit of free sulfur.

capable of oxidizing sulfids to sulfates. Freshly precipitated, chemically pure iron sulfid and calcium carbonate were added in equal amounts in 100 cc. flasks. To each of these flasks was then added 5 cc. of Knop's solution and after sterilization five were inoculated, the remainder being retained as checks. Within a week the inoculated solutions became cloudy, the uninoculated remaining clear. Stained amounts showed the presence of a capsulated rod showing polar staining in all inoculated flasks. This organism was present in all these flasks in practically pure cultures. Comparative analyses of the contents of the check and of these flasks showed that in those in which bacteria had been developed, between two and three times as much sulfate was present as in the check. The presence of this organism in the solution undoubtedly was the cause of the rapid oxidation of the sulfids which took place. However, the organism has not as yet been isolated in pure cultures and quantitative studies made of its oxidizing power.

The data at hand are sufficient to convince us that bacteria may be responsible, in part at least, for the oxidation of sulfids to sulfates under the conditions as they exist in the sewage disposal plants here discussed.

As rapidly as sulfuric acid is produced by bacteria working in and on the concrete or by atmospheric oxidation, it reacts with the calcium compounds of the cement, forming calcium sulfate. This takes up water of crystallization and swells considerably, the result being a cracking and pulverizing action and a consequent disintegration.

Careful search has failed to reveal any account of bacterial disintegration of concrete through the action of sulfids or sulfates. R. Grieg Smith[1] investigated the disintegration of concrete in the open canals that convey the city water supply of Sidney, New South Wales. He was led to study the action of nitrifying bacteria on concrete through the work of Stutzer and Hartleb, who suggest that such forms might assist in the disintegration of the cement of water reservoirs. He concludes, however, that "there is considerable room for doubt regarding the action of microörganisms on cement. There is more reason to believe that the action is purely chemical." His conclusions would seem to agree with those of Tannatt and Burke,[2] who found disintegration of concrete tile to take place when in contact with soil rich in sulfates. That even in alkali regions bacteria may have something to do with concrete disintegration is evidenced from the work here recorded and the statement of Schreiner, Oswald and Failyer[3] to the effect that hydrogen sulfid is produced in the drainage waters from gypsum alkali lands and from iron pyrites.

SUMMARY.

1. In three of the sewage disposal plants observed, *viz*: Grinnell, State Inebriate Hospital, and State Hospital at Mt. Pleasant, large quantities of hydrogen sulfid are evolved. This sulfid is produced in two ways: (*a*) by the bacterial decomposition of sulfur containing proteins and related compounds, and (*b*) by the reduction of sulfates which are contained in unusual amounts in the water supplies used. Of the two the second seems to be the more important.

2. The organism chiefly responsible for the reduction of sulfates and evolution of hydrogen sulfid is a spiral bacterium closely related to, if not identical with, *Spirillum desulfuricans.*

3. The hydrogen sulfid which escapes as gas from the sewage, particularly in the dosing chamber, is partially dissolved in the moisture on the under side of the roof and concrete walls. Here it is oxidized to sulfuric acid partly by atmospheric oxidation and partly by bacterial action. The sulfuric acid acts upon the calcium compounds of the concrete forming calcium sulfate, and breaking down the concrete. There is often deposited an excess of free sulfur which the oxidizing agencies have not converted to sulfate.

4. The exact species of the organisms responsible for the conversion of hydrogen sulfid into sulfuric acid have not been determined. That bacteria, however, in mixed cultures may bring about this change has been demonstrated. Beggiatoa and a bacillus have been isolated and are probably the most important organisms in bringing about this change.

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[1] *Cent. f. Bakt., 2nd Abt.,* **8,** 377 (1902).

[2] "The Effect of Alkali on Portland Cement," Bull. Mont. Agr. Exp. Sta., 1908.

[3] Bull. U. S. Dept. Agr., Bur. of Soils, 1906.

MARKING PORCELAIN AND SILICA CRUCIBLES, ETC.[1]

By P. A. YODER.

Received April 4, 1912.

INTRODUCTION.

In the analytical laboratory there often is occasion to put upon crucibles, etc., permanent distinguishing marks which will stand ignition and mild treatment with acids and alkalis. The blue pencil or the brush and china paints which are frequently used for this purpose, the markings being burned in, often give results so crude as to be quite unsatisfactory, especially for articles that are before one's eyes daily for years. Moreover, the blue-pencil marks and many china colors lack permanence, and when applied to silica wares do not adhere satisfactorily. The writer has worked out two methods, one for marking with platinum and the other for the application of china paints, both by the use of rubber type.

THE PLATINUM PROCESS.

The crucibles are cleaned by heating for half an hour with nitric acid, one part concentrated acid to one part of water. A sizing is prepared consisting of a hot 5 per cent. solution of gelatin. The parts of the crucibles to be marked are dipped into this sizing and set aside to drain and dry. When the gelatin is dry, the desired number is stamped on with a solution of platinic chlorid containing 12 to 15 per cent. of platinum—*i. e.*, about 32 to 40 per cent. of the hydrated, crystallized chloroplatinic acid. The pad holding the solution may be made of six or eight folds of smooth linen or muslin and need not be much larger than the type used. This pad is nearly

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[1] *Circular* **93,** Bureau of Chemistry, United States Department of Agriculture.

saturated with a few drops of the platinic chloride solution. Too much of the solution causes blurring and too little of it or too dilute a solution results in dim numbers. After the numbers are dry the crucibles are gently heated until the platinum is reduced and the gelatin burned off. This is most conveniently accomplished in a muffle. Finally, the numbers are heated for one-half minute in the flame of the blast lamp—*i. e.*, for one-half minute from the time it attains the temperature of the flame.

If the wares are cleaned and fired as directed, the markings adhere well. The figures become more prominent if burnished by use of a china painter's burnishing stone, if available, or of seashore sand, or less advantageously of a silica soap. The deposit is resistant to single acids, but not to alkalis. In some experiments library paste was substituted with good results for the gelatin sizing. Gold and mixtures of gold and platinum solutions may be applied similarly, but there is more danger of volatilizing the gold chloride before reduction takes place, and thereby causing a spreading of the deposit. The resulting figures also are less conspicuous than when platinum is used. This method of getting the deposit of platinum or gold may possibly find use also in decorating chinaware. If the solution is applied with a brush, a quill, or a glass stylus, it may be more dilute. The same method applied to silica wares also gives very satisfactory results.

APPLICATION OF CHINA COLORS BY USE OF RUBBER STAMPS.

Paints mixed in oil are not satisfactory for use with rubber stamps because the type leaves on the porcelain a rim of thickened paint while the main surface of contact is relatively bare. The method finally adopted is to stamp the wares to be marked with a sizing or varnish similar to that which painters use for applying gold leaf. "Fat oil"—*i. e.*, partly oxidized linseed oil, supplied by paint dealers—proved very satisfactory for this purpose. While this sizing is still sticky, the dry pigment is dusted on with a camel's-hair brush. After the varnish has set, the excess of pigment is wiped off and the crucible is fired at a strong red heat, preferably in a muffle. The "fat oil" dries slowly. This is an advantage because then some time may be allowed between its application and the dusting on of the pigment, for the irregular layer on the porcelain to draw out by surface tension into a smoother one. Standing over night at room temperature, or for one hour in a drying oven at 100° C., suffices for the varnish to set. The pad used for "inking" the type may consist of several thicknesses of linen cloth and is nearly saturated with this varnish. Too much varnish on the pad must be avoided, as it results in figures with ragged outlines. This varnish may readily be cleaned from the rubber type, before it has set, by use of a 10 per cent. alcoholic solution of caustic potash applied with a small bristle brush.

COLOR TESTS.

Seeking a prominent color and one resistant to both acids and alkalis, a series of tests was made with samples of overglaze blues, blacks, and reds supplied by a dealer and one blue prepared by the writer. These were stamped onto porcelain crucibles as above described. The heat used in firing was a red heat slightly lower than that at which the colored figures on the white background disappeared (the radiation plus reflection from a colored surface equaling that from a white surface). In one test they were brought from a dull red to the above temperature during the course of one hour and then cooled. This sufficed to make the blacks and the reds resistant to nitric acid (35 per cent.) and to sodium hydroxide solution (10 per cent.), but the blues were appreciably soluble in the acid. To make the blues resistant, they had to be fired to a higher temperature or held at the above maximum temperature for about an hour. To test the permanence of the markings, the acid and the alkali were each applied five minutes cold, followed by five minutes at a boiling temperature. Of the seven blacks tried, two—*viz.*, a lettering black and a blue black—gave especially good effects in that they yielded a very strong black. Of the same samples when applied to silica dishes and fired as indicated, both the blacks and the reds were again resistant to both nitric acid and alkali, but the blues, even when fired more strongly, came off very readily in nitric acid.

In these tests an electric muffle was used. In heating porcelain crucibles to a high temperature in gas muffles in which the muffle chambers were not thoroughly sealed off from the gas chambers, and occasionally also in the electric muffle, a brown stain developed on the porcelain. This could readily be removed by heating the crucible half a minute in the blast flame, most conveniently in a suitable chimney.

In applying the rubber stamp to the crucibles it is difficult to avoid a sliding motion that blurs the imprint. This may be prevented by using a suitable guide or a steadying support. The writer found it convenient to rest both the inverted crucible and the type holder on a smooth surface while making the impression. In numbering crucibles, etc., it is often advantageous to have the number on three sides so as to make it visible, no matter which way the crucible is turned.

LABORATORY U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON.

ON THE QUANTITATIVE ESTIMATION OF SODIUM HYDROXIDE IN "BLACK LIQUOR."

By EDWIN SUTERMEISTER AND HAROLD R. RAFSKY.

Received January 16, 1912.

In the manufacture of cellulose by the soda process wood is digested under pressure with a solution of sodium hydroxide. The liquid separated from the resulting pulp is called "black liquor," and contains the sodium hydroxide unconsumed in the reaction, together with the sodium salts of acids formed by the decomposition of the wood. A precise evaluation of this residual sodium hydroxide would give valuable information on the exact consumption of caustic soda by wood, and perhaps help to explain the chemistry of the digestion process.

PRESENT METHOD.

The method now employed is simply one of titration with acid, using a solution of phenolphthalein as an outside indicator.[1] In detail: 25 cc. of black liquor are diluted with 300 cc. of water; 10 cc. of a concentrated $BaCl_2$ solution (400 grams to liter) are added to precipitate carbonates and the organic acid radicles which yield insoluble barium salts, and the solution is titrated with N acid (HCl, HNO_3 or H_2SO_4). The end point is determined by removing drops of the solution at intervals during the titration and allowing them to fall gently from a stirring rod into a solution of phenolphthalein in water just covering the bottom of a beaker. When a drop fails to develop a red color in the indicator solution immediately surrounding it, the end point is considered to be reached. This method is approximate only, but checks within 5 per cent. can generally be obtained; *e. g.*, three successive titrations required respectively 5.00, 4.90, 5.11 cc. *N* acid.

The difficulties in arriving at the end point are: first, the distinguishing of the red color of the indicator from the brown of the drop; and, second, the slow development of the red color around the drop. The real trouble, however—dependent, perhaps, on the two just mentioned—is that the end point recorded varies with the working conditions. Thus if the titration is carried out at dilutions other than the one given above, widely differing values are obtained, as is shown in the following table which gives the results of titrating 25 cc. of black liquor at different dilutions:

Total vol. of diluted black liquor.	Individual titrations. N acid.	Average.
39 cc.	3.50 cc. 3.42 cc.	3.46 cc.
88 cc.	3.67 cc. 3.60 cc.	3.63 cc.
185 cc.	3.56 cc. 3.70 cc. 3.60 cc.	3.62 cc.
435 cc.	4.13 cc. 4.62 cc. 4.30 cc. 4.74 cc.	4.45 cc.
835 cc.	5.00 cc. 4.90 cc. 5.11 cc.	5.00 cc.
1635 cc.	4.92 cc. 5.15 cc.	5.03 cc.

Again, if there is added to a black liquor (which has been analyzed by the present method) a known amount of NaOH and this "fortified" black liquor is then titrated, the increase of acid used in titration is smaller than the amount equivalent to the NaOH added. For instance: to a black liquor titrating 6.39 cc. acid, NaOH was added equivalent to 8.28 cc. acid, and duplicate titrations of this "fortified" black liquor showed readings of 13.54 and 13.64 cc., an average of 13.59 cc., while the calculated result is 14.67 cc.

One possible explanation of these inconsistencies is that the OH ions are adsorbed by the colloids present. Another theory supposes the presence of an organic complex which combines with OH ions, the resulting molecule having but a small dissociation constant. On increasing the concentration of OH ions (as in a "fortified" black liquor) the dissociation is checked, whereas a decrease in the concentration of OH ions (as in dilution) increases the dissociation and hence the total amount of OH ions present.

ATTEMPTS TO IMPROVE PRESENT METHOD.

The following is a description of numerous attempts to improve our original method, and is published in the hope of bringing forth some more successful method, or of starting a discussion and stimulating further work along this line.

Preliminary Experiments.—Small test tubes, partly filled with a solution of phenolphthalein in water, were tried for the examination of the individual test drops, but no satisfactory end point was obtainable. The idea of using phenolphthalein directly in the solution to be titrated, after the addition of a white substance such as $BaSO_4$ or China clay to lighten the color, proved a failure as the color change was gradual and indefinite.

Elimination of Precipitate.—We next sought to eliminate the voluminous precipitate produced on addition of $BaCl_2$, in order to obtain a clear liquid for titration. Ordinary settling, filtration, and centrifugal filtration proved unsatisfactory, but in a Babcock centrifuge a clear orange colored solution was secured by adding clay to the regular titration mixture and centrifuging for 7 or 8 minutes. This clear liquid when poured off and titrated with phenolphthalein directly did not give very close duplicates, *e. g.*, 13.76 and 14.64 cc. *N*/10 HCl.

Indicators Tried.—As we were unable to decolorize the clear centrifuged solution with charcoal, we directed our attention to procuring a better indicator. Litmus, Congo red, and lacmoid, with blue-red or red-blue color change were unavailable as the orange color of the solution interfered with the end point. A mixture of dyes, the color of which was practically complementary to the orange shade, was added in an attempt to produce a gray—so that an indicator could be used to better advantage—but the dyes changed color, owing to the action of the alkaline solution, and satisfactory results were not obtained. A mixture of phenolphthalein and malachite green showed some promise but was finally discarded as the malachite green when used in sufficient amount to cover the orange color tended both to precipitate in neutral solution and to mask the last traces of the red of the phenolphthalein. We found, however, that by using an *excess* of phenolphthalein alone we arrived at a satisfactory and definite end point. Our method was to add a few drops of indicator, titrate to disappearance of red, add a large excess of indicator, and again titrate to the disappearance of red, repeating this operation till no red color developed on addition of more indicator.

Determination of Ratio.—Up to this point we were titrating a portion of the clear liquid obtained by precipitating the black liquor with $BaCl_2$ and centri-

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[1] For the basic idea involved in this method we are indebted to Mr. Chas. N. Waite, of Wilmington, Del.

fuging. It now became necessary to determine the ratio of the NaOH in the portion used to that in the entire volume of clear liquor and precipitate.

The first method attempted was to find the total amount of NaOH present in the entire mixture (20 cc. $BaCl_2$, 50 cc. black liquor, 20 grams clay, and 175 cc. of water) by titrating the entire quantity of centrifuged liquor in the usual way and then repeatedly extracting the sludge with water, and centrifuging till the final extraction gave no test with phenolphthalein. As the total volume of the solution was too large to work with conveniently, one-fifth was taken. This idea worked well until the third extraction with water when the clay did not drag down the sludge, but left it in suspension making titration impossible. Addition of more clay was of no avail, and consequently as the sludge still reacted strongly alkaline, the method was abandoned.

The problem was next attacked on the theory that if a known amount of NaOH were added to a black liquor and the mixture centrifuged as usual the same percentage of the added NaOH as of that originally present would be found in the clear liquor. Having determined what percentage of the added NaOH was present in the centrifuged liquor titrated we could then calculate the total amount of NaOH present in the original sample of black liquor.

With this basic idea, we made up the following two mixtures: 25 cc. of black liquor, 10 grams of clay, and 50 cc. of $BaCl_2$; and 25 cc. of black liquor, 10 grams of clay, 45 cc. of $BaCl_2$ and 5 cc. NaOH (= 48.80 cc. $N/5$ HCl). These were centrifuged under the same conditions and 10 cc. of each of the centrifuged liquors titrated. The first titration (2.12 cc. $N/5$ HCl) represented the amount of NaOH present from the black liquor; the second (8.80 cc. $N/5$ HCl) the amount of NaOH present from the black liquor plus added NaOH. Thus the added NaOH present in the 10 cc. of centrifuged liquor = 8.80—2.12 = 6.68 cc. $N/5$ HCl. The percentage of the total added NaOH present in the 10 cc. of centrifuged liquor $= \frac{6.68}{48.80} = 13.7$ per cent.

According to the above theory only 13.7 per cent. of the NaOH present in the original black liquor is to be found in 10 cc. of the clear centrifuged liquor and as this 13.7 per cent. is represented by 2.12 cc. $N/5$ acid the total amount of NaOH present would be equivalent to 15.48 cc. $N/5$ or 3.09 cc. N acid. A series of similar tests were made of which the following is a summary: two determinations of pure black liquor, carried out in the manner outlined above, gave as titrations for 10 cc. of the centrifuged liquor 2.14, 2.10, and 2.19, 2.14, 2.12 cc. $N/5$ acid; average, 2.14 cc. $N/5$ HCl. The table below gives the results of four tests on "fortified" black liquors, *i. e.*, black liquors to which NaOH has been added. All figures given, except the last column, indicate $N/5$ acid used.

	Titration 10 cc. centrifuged fortified black liquor.	Value of NaOH present from black liquor.	Value of NaOH present from added NaOH (I-II)	Value of total NaOH added.	Per cent. total added NaOH present in 10 cc. centrifuged liquor $\frac{(III)}{(IV)}$	Calculated value of NaOH in original black liquor $\left(\frac{(II)}{V}.100\right)$	NaOH value of original black liquor in terms of N acid.
1........	8.82 8.79	2.14	6.66	48.80	13.65	15.68	3.14
2........	8.71 8.67	2.14	6.55	48.80	13.42	15.94	3.19
3........	15.45 15.45	2.14	13.31	97.60	13.63	15.70	3.14
4........	22.55 22.54	2.14	20.40	146.40	13.92	15.37	3.07

Average = 3.14 cc. *N* acid

The average of the four values found below is 3.14 cc. N HCl for the titer of 25 cc. of black liquor. The peculiar part, however, for which we can assign no reason is: that by titrating according to our original method we get a value of from 6–7 cc. N acid for the titer of the same volume of black liquor. Until we can explain why this discrepancy occurs, we cannot proceed further with this method.

In the above series of determinations we centrifuged the mixtures 12 minutes, poured off equal quantities of clear liquor, and centrifuged again for 3 minutes, which left a perfectly clear liquid for titration.

Electrometric Method.—A problem very similar to the one at hand, *i. e.*, the determination of the acidity of tan liquors, has reached a successful solution by the employment of the electrometric method of titration, as reported by Sand and Law[1] and by Sand, Law and Wood.[2] They measure the voltage of a cell, one arm of which is a normal calomel electrode, and the other a hydrogen electrode dipping into the tan liquor to be titrated. Acid is added to the tan liquor until a potential of 0.69 volt is registered, which indicates neutrality.

Through the kindness of Dr. Geo. S. Forbes, of Harvard University, one of the writers was permitted to use apparatus and space in his laboratory to test out this method. We are also indebted to Dr. Forbes for much valuable advice and assistance. The work reported below was carried out very roughly, the object being merely to test the applicability of the method for our use. Our apparatus consisted of a cell similar to that employed in the tan liquor determination, the potential of which was measured by the compensation method using a potentiometer box. We employed a D'Arsonval galvanometer and although this tended to polarize the hydrogen electrode, for approximate work it proved more convenient than an electrometer.

As we were uncertain as to the magnitude of a possible reducing action of black liquor on the hydrogen electrode, we could not assume that the potential corresponding to a given concentration of a pure NaOH solution would necessarily indicate the same concentration of NaOH in the black liquor solution. To test this point we titrated a black liquor according to our original method to get the approximate concentration of NaOH; then we made up a pure NaOH solution of similar concentration (0.026 N), and read off the potentials of the two solutions in the cell.

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[1] *J. Soc. Chem. Ind.*, **30**, 1, 3.

[2] *Ibid.*, **30**, 14, 872.

Calculated potential	1.00 volt
Black liquor	0.97–0.98 volt
Alkali	0.99 volt

The above potential in the alkali, and especially in the case of the black liquor, was not reached for several minutes.

Another determination of a solution one-tenth as strong, 0.0026 N, gave a voltage of 0.91 in the black liquor. The calculated voltage is 0.94.

Both the above determinations indicated that the reducing action of the black liquor did not greatly affect the hydrogen electrode in alkaline solution so we next tried the direct titration of the black liquor.

For this purpose we took 25 cc. black liquor, 10 cc. $BaCl_2$ (400 grams to liter), and 200 cc. water. A similar mixture by our old method titrated 13.1 cc. $N/2$ acid. The first titration registered no sudden fall of potential but rather a steady diminution of voltage up to 28.6 cc. acid (as much as was added) and a second trial resulted similarly. When, however, about 10 cc. concentrated HCl was added, the colloids coagulated and the voltage dropped to 0.33.

To make certain that the H electrode had not been affected by its immersion in the black liquor, immediately after the above titration it was placed in a neutral KCl solution and the voltage found to be above 0.6 volt. In contrast with the black liquor titration above, at the neutral point in the titration of an NaOH solution, as indicated by phenolphthalein, the addition of an extra quarter cc. of $N/2$ acid causes a very sharp diminution of the potential of the cell. From the determinations given above we concluded that the electrometric method was, as applied, inapplicable in our case.

SUMMARY.

The present method for the determination of NaOH content of black liquors is one of titration with acid, using phenolphthalein as an outside indicator.

In the attempt to improve this method, the more important ideas worked upon were:

1. The elimination by centrifugal action of the precipitate formed by $BaCl_2$ and the subsequent titration of the clear liquor.
2. The use of various indicators, and the successful method of employing phenolphthalein.
3. The determination of a ratio between the centrifuged liquor and the sample of black liquor taken.
4. Electrometric method.

None of the methods or modifications thus far tested has proved entirely satisfactory, and the original method, although it gives only approximate results, is the best one at present available.

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THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

By Charles Baskerville and W. A. Hamor.

Received December 12, 1911.

(Concluded from July No.)

VIII. The Examination of Anaesthetic Chloroform.

10. THE DETERMINATION OF THE ACIDITY OF CHLOROFORM.

Chloroform of all grades should always be examined for the presence of acids.[1] In this way it may be ascertained whether the chloroform under examination has been purified by a method serving to eliminate any acids resulting during manufacture or used during purification; if in a tin container, whether the proper care has been exercised in capping; and, since the water extract is usually tested, the extent of any oxidation, either of alcohol or chloroform, may be determined.

The *Codex Medicamentarius Hamburgensis* of 1847 required that anaesthetic chloroform (density 1.48) should not afford a water extract possessing an acid reaction towards litmus. This test has met with general favor, and is essentially the one usually recommended.[2]

It has been proposed, however, that the chloroform be allowed to evaporate spontaneously after the addition of a drop of neutral litmus solution;[3] and that pieces of pith steeped in Congo red solution be used for the detection of acids in chloroform.[4]

Vulpius[5] found that several chloroform samples which satisfied the conditions of the silver nitrate[6] and litmus paper tests showed an acid reaction when treated as follows: To 1 cc. of water, 1 drop of phenolphthalein solution and 1 drop of centinormal potassium

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[1] The possible contaminants of this class are: hydrochloric, hypochlorous, sulphuric, acetic and formic acids; of these, however, only hydrochloric and acetic acids are probable now. There are cases on record which indicate that samples of chloroform may sometimes contain free hydrochloric acid; in all such instances, all of which are extreme in the case of anaesthetic chloroform, either the chloroform originally contained no preservative or had been very carelessly stored for protracted periods of time.

[2] Acids, free chlorine and chlorides are all extracted from chloroform by water, so that when the sample is shaken with, say, twice its volume of water for about 5 minutes, free acids may be detected, when present in appreciable amounts, by blue litmus paper. The detection of the products of the oxidation of pure chloroform will be referred to specifically in the next section.

Brown (*Pharm. J.*, [3] **25,** 865) stated that a water extract of the chloroform under examination should be neutral to litmus; Gay (*Loc. cit.*) recommended that when 6 cc. are shaken with 3 cc. of water, the water extract should not redden litmus paper; Regnault (*Mon. Sci.*, [3] **5,** 417) also recommended that chloroform should be neutral ro litmus; White (*Pharm. J.*, [4] **25,** 540) directed that 5 mils be agitated with 10 mils of water, and that the water layer stand the test with litmus; and Krauch (*Testing of Chemical Reagents*, **1902,** 77) gives a test wherein 2 parts of chloroform are shaken with 3 parts of water, the latter being then tested with blue iitmus paper. See also Linke, *Apoth.-Ztg.*, **25,** 285.

The pharmacopoeias of Spain and France require that chloroform shall be completely neutral to litmus solution; the pharmacopoeias of Switzerland and Austria direct that the chloroform be agitated with an equal volume of water, and that the latter should then not redden litmus or be rendered turbid by silver nitrate solution, while the Danish pharmacopoeia directs that the test be made on the aqueous extract obtained by agitating 10 cc. of chloroform with 5 cc. of water. Practically the same test recommended in the *Codex Medicamentarius Hamburgensis* of 1847 is in the *Deutsches Arzneibuch* of 1910. The *Pharmacopoeia of Japan* of 1907 requires that the sample be shaken with one-half its volume of water, and that the aqueous extract should not redden blue litmus paper. It was specified in the sixth revision of the *Pharmacopoeia of the United States* (1882) that if 5 cc. of purified chloroform be thoroughly agitated with 10 cc. of distilled water, the latter, when separated, should not affect litmus paper (blue).

[3] It was required in the fifth revision of the *Pharmacopoeia of the United States* (**1873,** p. 78) that when 1 fluidrachm of chloroform was evaporated spontaneously with 1 drop of a neutral water solution of litmus, the color of the indicator must not be reddened; it was stated that the result of the test is the same if the chloroform, contained in a white glass bottle, had been previously exposed to direct sunlight for 10 hours. A similar test is given in the *National Dispensatory* of **1887** (p. 439) for incipient decomposition.

[4] A change to "blue" results in the presence of acids. Concerning this test, see *Lancet*, **1907**, I, 1033.

[5] *Arch. Pharm.*, [3] **25,** 998.

[6] This test will be discussed in the next section.

hydroxide solution were added, and the whole was shaken with 5 cc. of the chloroform: in four cases the solution was decolorized in two minutes. On the addition of a second drop of the potassium hydroxide solution, decolorization again occurred, and with one sample this was the case after the addition of two more drops of the alkali.[1] Accordingly, Vulpius suggested as a further check on the purity of chloroform that 10 cc. repeatedly shaken in a stoppered bottle it nearly fills with 2 cc. of water colored with 2 drops of phenolphthalein solution, and 1 drop of decinormal potassium hydroxide solution should not decolorize the latter in 24 hours.[2]

We have found that when 20 cc. of *pure* anaesthetic chloroform are thoroughly agitated with 10 cc. of water and 2 drops of phenolphthalein solution, and then titrated with *N*/100 potassium hydroxide solution, added drop by drop, 0.10 cc. of the standard alkali produces a temporary alkaline reaction; but the dissociation of the phenolphthalein alkali is retarded, and the red color disappears on agitation, 0.2 cc. of *N*/100 potassium hydroxide being required to produce a faint, yet decided, alkaline reaction permanent for 15 minutes, when the mixture is shaken 30 seconds after the addition of each drop of alkali.

The following results were obtained with various samples of chloroform:

Description.	U. S. P. test for acidity.	Cc. *N*/100 KOH required as by above test.	Gms. acid, calculated as acetic, per 100 cc. of sample.
A. Salicylid-chloroform; 0.25 per cent. alcohol	Negative	0.2 cc.	None
B. "Chloroform purified;" 0.5 cc. absolute alcohol in 100 cc.	Negative	0.3 cc.	0.0003 g.
C. "Chloroform medicinale Pictet"	Negative	0.2 cc.	None
D. "Purified chloroform;" of full U. S. P. quality	Negative	0.25 cc.	0.00015 g.
E. "Chloroform e chloral," "absolutely pure;" 0.3 cc. absolute alcohol in 100 cc.	Negative	0.25 cc.	0.00015 g.
F. "Chloroform pure;" 0.56 cc. absolute alcohol in 100 cc.	Negative	0.20 cc.	None
G. "Chloroform, U. S. P.;" 0.7 cc. absolute alcohol in 100 cc.	Negative	0.20 cc.	None
H. A 5 lb. unopened tin of chloroform, supposed to be of U. S. P. quality, but 17 mo. old	Negative	0.35 cc.	0.00045 g.
I. A 125 cc. tin of "chloroform for anaesthesia," six years old	Negative	0.50 cc.	0.0009 g.
J. A tin containing 6 ounces of "chloroformum purificatum," made in 1863 or shortly before	Negative	0.35 cc.	0.00045 g.
K. A sample of anaesthetic chloroform prepared by the manufacturers of I; conforming with all the requirements of the U. S. P. but the sulphuric acid test	Negative	0.25 cc.	0.00015 g.
L. "Purified chloroform," prepared from carbon tetrachloride; 0.74 cc. absolute alcohol in 100 cc.	Negative	0.20 cc.	None
M. "Purified chloroform, U. S. P.;" 0.8 cc. absolute alcohol in 100 cc.	Negative	0.30 cc.	0.0003 g.
N. "Commercial chloroform," the source of M	Negative	0.25 cc.	0.00015 g.

We have been led to conclude that—

(*a*) Whereas litmus is sufficiently sensitive for use in the detection of hydrochloric acid in chloroform,[1] phenolphthalein[2] should always be employed as the indicator in testing anaesthetic chloroforms, since in this case acetic acid is the usual contaminating acid.[3]

(*b*) The amount of *N*/100 potassium hydroxide solution required for neutralization should always be determined. Using 20 cc. of the sample under examination, 10 cc. of water, and 2 drops of phenolphthalein, and titrating as directed above, no more than 0.20 cc. of *N*/100 alkali should be required.

II. THE DECOMPOSITION PRODUCTS OF PURE CHLOROFORM.

(*a*) *The Detection of Carbonyl Chloride.*

Chloroform containing carbonyl chloride gives rise to toxic effects upon administration;[4] and although it is now improbable that accidents can occur from the presence of the oxidation products of pure chloroform, since the necessary precautions are generally exercised in practice to guard against their presence, yet cases have been recorded[5] which show that anaesthetic chloroform which has been carelessly stored for long periods should always be examined for carbonyl chloride as well as the other products of oxidation. When, for any reason, pure chloroform is required for an investigation, it should always be tested for the presence of carbonyl chloride immediately before use.[6]

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[1] From these results, Vulpius concluded that the substance giving the acid reaction was more soluble in chloroform than in water, whence the aqueous extract remained neutral to litmus paper. Vulpius did not consider the influence of alcohol, which was undoubtedly present in the samples examined by him, on the dissociation of phenolphthalein alkali.

[2] On the test of Vulpius, see Werner, *Arch. Pharm.*, [3] **25**, 1113.

[1] This, of course, applies generally to the examination of pure chloroform.

[2] Congo red is also very sensitive for this purpose, and may be used when chloroform is being tested qualitatively.

[3] The results obtained on Nos. H, I and J lend strong support to the view of the authors as to the oxidation of anaesthetic chloroform and particularly as to the rôle of alcohol in preservation. None of these samples contained hydrochloric acid or carbonyl chloride.

[4] Carbonyl chloride has an irritating action upon mucous membranes, besides possessing the poisonous properties of carbon monoxide (Dragendorff, *Ermittelung von Giften*, **1895**, p. 62; Kobert-Friedburg, *Practical Toxicology*, **1897**, p. 127). For a full discussion of the toxicological action of carbonyl chloride, see Müller, *Z. angew. Chem.*, **23**, 1489.

[5] For example, Ramsay (*Brit. Assn. Rept.*, **1892**; *J. Soc. Chem. Ind.*, **11**, 772) found that the only impurity in a number of samples of chloroform received from hospitals where death had occurred was carbonyl chloride. It was found to be impossible to look for an unknown impurity in a number of small samples of chloroform; therefore, he exposed a large quantity of "perfectly pure" chloroform to daylight in the presence of air. After "some" months, a considerable quantity of carbonyl chloride was formed, no other product, excepting a trace of hydrochloric acid, having been detected. It was found to be possible to test for carbonyl chloride by pouring a barium hydroxide solution on the surface of a suspected sample, when a white film would appear at the line of division between the chloroform and the water solution. Most of the samples received by Ramsay gave this test, and it was significant that most of the samples were the products of large consignments to hospitals. Ramsay was inclined to believe that the cause of death was the spasmodic contraction of the glottis produced by the carbonyl chloride after the lungs had been thoroughly charged with chloroform. Dott (*Pharm. J.*, [3] **22**, 1080), however, thought that it is in the highest degree improbable that accidents have occurred in the administration of chloroform from the presence of carbonyl chloride. In his opinion, if the amount were considerable, the surgeon would observe the contamination, while if only traces were present, evidence is lacking to show that these would be dangerous. The authors found that samples of anaesthetic chloroform of U. S. P. grade in no case gave a reaction indicative of carbonyl chloride, and even after storage under good conditions for almost two years, such chloroform contained no carbonyl chloride.

[6] For a case in point, see the experiences of Lowry and Magson (*Trans. Chem. Soc.*, **93**, 121), who, in their studies on dynamic isomerism, found that the presence and production of carbonyl chloride in chloroform solutions by the action of air and light would afford a sufficient explanation of all the anomalous results which have been obtained on the arrest of isomeric change in acid chloroform solutions. They found that the active agent in arresting the isomeric change of nitrocamphor dissolved in chloroform is carbonyl chloride.

Carbonyl chloride may often be recognized in samples of decomposed pure chloroform by its peculiar nauseous smell, which is quite different from that of chlorine or hydrochloric acid.[1] If necessary, carbonyl chloride may be detected in the presence of chlorine by agitating the sample of decomposed chloroform with mercury, which combines with the free chlorine, but does not act upon carbonyl chloride, and thus the peculiar odor of this compound becomes more easily recognizable.[2] After the removal of free chlorine by agitation with mercury, moist blue litmus paper is no longer bleached. Prior to the elimination of free chlorine, the reddening of moistened litmus paper may be masked by the action of free chlorine.[3]

Ramsay[4] proposed a test for the direct detection of carbonyl chloride in chloroform which we have found to be satisfactory, providing the proper precautions are observed. This consists in adding clear barium hydroxide solution to the chloroform and allowing the mixture to stand several hours in a stoppered vessel; if carbonyl chloride is present, a white film of barium carbonate forms at the junction of the two liquids.[5] In testing for the presence of carbonyl chloride, whenever a direct test is deemed necessary, the authors operate as follows: To 15 cc. of the sample, contained in a dry glass-stoppered tube of 25 cc. capacity, sufficient of a perfectly clear 1 : 19 barium hydroxide solution is added to fill the tube; after allowing the mixture to stand 3 hours in a dark place, without agitation, the observation as to the formation of a film of barium carbonate is made.

Other direct tests which have been proposed for the detection of carbonyl chloride are the amidophenetol test of Scholvien[6] and the bilirubin test of Pouchet.[7] The barium hydroxide test is, however, entirely satisfactory whenever it is considered necessary to definitely establish the presence of carbonyl chloride; but in general it is sufficient to test the aqueous extract of the chloroform under examination for hydrochloric acid and then make a quantitative determination.[1]

(*b*) *The Detection of Hydrochloric Acid.*

Hydrochloric acid and chlorides are not likely contaminants of anaesthetic chloroform at the present time, but pure chloroform should always be examined for their presence. Carbonyl chloride, free chlorine and hydrochloric acid may be recognized in one operation by shaking the sample with silver nitrate solution, which, in the presence of any of these impurities, will produce a white precipitate, whereas pure chloroform gives no reaction with silver nitrate, either in aqueous or alcoholic solution. This is essentially the test generally recommended.[2]

Samples of pure, anaesthetic or commercial chloroform which possess no acid reaction, as determined by titration with *N*/100 potassium hydroxide solution, are assuredly free from carbonyl chloride, chlorine and hydrochloric acid, but pure and anaesthetic chloroforms should also comply with the following test: When 10 cc. of the sample are agitated with 5 cc. of water for 5 minutes, the water extract should not become turbid or give any precipitate upon the addition of silver nitrate solution (absence of hydrochloric acid, chlorides, etc.) and no reduction should occur on warming (absence of acetaldehyde, formic acid and formates, etc.).

(*c*) *The Detection of Chlorine.*

It is generally considered that chlorine is a contaminant of anaesthetic chloroform, and accordingly tests are usually specified for its detection. For example, free chlorine and hypochlorous acid are distinguished from hydrochloric acid by their power of bleaching instead of merely reddening litmus, and by liberating

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[1] The authors exhibited samples of chloroform which contained carbonyl chloride; these samples fumed in the air and possessed the characteristic odor of carbonyl chloride.

[2] Carbonyl chloride is unaffected by shaking with mercury, but mercury combines with free chlorine (see Martindale's *Extra Pharmacopoeia*, 9th ed., 126).

[3] On these points, see Schacht and Biltz, *Pharm. J.*, **1893**, 1005.

[4] *Loc. cit.* Ramsay also stated that carbonyl chloride may be removed by agitation with slaked lime, but this has been denied (*Brit. Med. J.*, March 16, 1900).

[5] This test is given in the *Nueva Farmacopea Mexicana*, **1904**, 477. In the seventh revision of the *Pharmacopoeia of the United States* (**1893**, 88), the following test was specified: If to about 5 cc. of chloroform contained in a dry test tube of about 10 cc. capacity, about 4 cc. of perfectly clear barium hydrate T. S. be added without agitation, and the test tube be then corked and set aside in a dark place for six hours, no film should be visible at the line of contact of the two liquids.

[6] *Ber. Pharm. Ges.*, **3**, 213. A drop of amidophenetol is dissolved in benzene (anhydrous and free from carbon disulphide) and the suspected chloroform is added to this solution; if carbonyl chloride is present, there is said to be produced an immediate turbidity and later a separation of crystals of diparaphenetol carbamide, insoluble in chloroform. Instead of amidophenetol, Scholvien found that aniline may be used, in which case diphenylcarbamide is formed. In this connection, it may be indicated that Schmidt (*J. prakt. Chem.*, [2] **5**, 35) found that carbonyl chloride reacted with benzamide, giving, among other products, benzonitrile.

[7] *Nouveaux Remedes*, **1904**, No. 13, 289. Pouchet found that if a little of the chloroform under examination is mixed with bilirubin, this dissolves with a green color in the presence of carbonyl chloride and with a brown color in its absence. Merck (*Annual Report*, **18**, 45), however, regarded zinc chloride and starch solution as a more sensitive reagent.

[1] Cf. *Z. anal. Chem.*, **33**, 488. See *Acidity*.

[2] Regnault (*Mon. Sci.*, [3] **12**, 262; *J. pharm. chim.*, [4] **29**, 402) stated that no precipitate should result with silver nitrate; Brown (*Pharm. J.*, [3] **25**, 865) recommended shaking the sample with an equal volume of silver nitrate solution, when no turbidity should be produced; Behal and Francois (*J. pharm. chim.*, [6] **5**, 417) advised that chloroform should neither precipitate nor reduce silver nitrate; White (*Pharm. J.*, [4] **25**, 540) agitates 5 mils of chloroform with 10 mils of water, then tests the water extract; and Krauch (*Testing of Chemical Reagents*, **1902**, p. 77) shakes 2 parts of chloroform with 3 parts of water, and requires that the water extract shall not produce a turbidity on being carefully poured over a solution of silver nitrate in an equal volume of water.

The silver nitrate test has had pharmacopoeial recognition since 1847, when it was required by the *Codex Medicamentarius Hamburgensis* that the water extract should give no precipitate with silver nitrate. The *British Pharmacopoeia* (**1908**, 75) gives the following test for the presence of chlorides: The addition of 4 drops of silver nitrate solution should not produce more than a very slight opalescence in the aqueous portion obtained by shaking chloroform with twice its volume of water for 5 minutes. The *Deutsches Arzneibuch* (**1910**, 118) requires that the water extract of chloroform should not yield any turbidity with test solution of silver nitrate. The silver nitrate test is also given in the pharmacopoeias of Switzerland, Austria, France, Spain, Sweden, Italy, Chili, and Japan. The pharmacopoeias of Switzerland and Austria direct that the chloroform be agitated with an equal volume of water, and that the latter should not then be rendered turbid by silver nitrate solution; the Danish pharmacopoeia requires that the test be made on the aqueous extract obtained by agitating 10 cc. of chloroform with 5 cc. of water; the French *Codex* (**1908**, 148) gives the silver nitrate test for the presence of hydrochloric acid, also stating that no reduction should occur on warming (formates or aldehyde derivatives); the *Pharmacopoea Svecica* (**1908**, 76) specifies that the test be conducted on the water extract, as does the *Farmacopoea Oficial Espanola* (**1905**, 198); and the *Farmacopea Chilena* (**1886**, 147) requires that no precipitation or reduction should occur when the test is applied. The *Pharmacopoeia of Japan* (**1907**, 84) directs that the chloroform be shaken with one-half its volume of water, and that water be carefully poured into a solution of silver nitrate diluted with equal parts of water, when no turbidity should be produced.

iodine from a solution of potassium iodide,[1] zinc iodide[2] or cadmium iodide[3] when the sample or its water extract is shaken with the reagent.

Since free chlorine can only result either through careless purification of chloroform or from the photochemical decomposition of carbonyl chloride, we can now only suspect its presence in pure chloroform which has undergone oxidation. Moreover, it is highly probable that reactions due to hydrogen dioxide have been attributed to free chlorine; and that, especially where potassium iodide was the reagent used, hydrochloric acid and carbonyl chloride were sometimes the cause of the reactions observed. While both pure and anaesthetic chloroform should, of course, give no reaction with potassium or zinc iodide, these reagents lack the reliability required for specific tests, and a 10 per cent. solution of cadmium potassium iodide is considerably more efficient. When this reagent is used, a response is indicative or either the presence of chlorine or hydrogen dioxide, and pure and anaesthetic chloroform should give a negative result in all cases.

12. THE DETECTION OF CHLORINE SUBSTITUTION PRODUCTS.

(a) *"Chlorinated Decomposition Products."*

The *British Pharmacopoeia* and the *Pharmacopoeia of the United States* give tests for the detection of "odorous decomposition products" and "chlorinated decomposition products" in anaesthetic chloroform.[4] Anaesthetic chloroform which has been properly purified and stored should comply with these requirements,[1] although there are on record instances[2] which show that officinal chloroform of the present pharmacopoeial grade occasionally contains "chlorinated decomposition products," probably resulting from the careless storage, especially for protracted periods of time, of insufficiently pure products.

The phrase "chlorinated decomposition products" is indefinite and rather vague, but it includes a class of compounds, resulting either from manufacture ("chlorinated oils," previously referred to; chlorine substitution products decomposable by sulphuric acid; etc.), in which case such contamination is only likely when the chloroform has not been purified by a process serving for their elimination; or from the oxidation of anaesthetic chloroform (chlorinated derivatives of the oxidation products of alcohol, chlorocarbonic ether, etc.). In the latter case, the formation of such compounds can only result after the oxidation of the alcohol has reached a maximum, and consequently their occurrence is only likely in samples which have been stored for long periods of time under conditions conducive to oxidation.

(b) *The Occurrence of Ethyl Chloride in Chloroform.*

Until 1904, it was generally assumed that commercial chloroform prepared from acetone was identical with that made from alcohol, although the clinical experiences of some English anaesthetists indicated that the anaesthetic chloroform prepared therefrom is distinctly inferior to the product from alcohol. For example, it was observed that the patient often had an undue tendency to cough and hold the breath, and the prolongation of the time of induction thus effected increased the danger of an overdose. In 1904, Wade and Finnemore[3] published the results of their investigation as to the existence of a volatile impurity in chloroform prepared from alcohol. They found that the presence of a minute quantity of ethyl chloride in chloroform made from alcohol, probably about 0.05 per cent. (about 2 cc. per Winchester quart), would account for its physical behavior; and they stated that they had substantiated by clinical experience the conclusion that the volatile substance which "improves" the anaesthetic properties of chloroform made from alcohol, but is absent from chloroform made from acetone, is ethyl chloride. According to Wade and Finnemore, "acetone chloroform" to which a small quantity of ethyl chloride had been added was therapeutically identical with chloroform made from alcohol.[4]

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[1] Potassium iodide is the specified reagent in the pharmacopoeias of Austria, Chili, Denmark, Sweden, Switzerland, and the United States. The Austrian pharmacopoeia requires that no violet color result; the Chili pharmacopoeia that no color result; and the Danish pharmacopoeia that no color be produced on mixing 5 cc. of chloroform with 20 cc. of water and a crystal of potassium iodide. The potassium iodide test is also given in the *Pharmacopoea Croatico-Slavonica* (**1888**, 163), where it is stated that no rose color should result; and in the Finland Pharmacopoeia, where it is required that no violet color result. The *Pharmacopoeia of the United States* (**1905**, 99) specifies that the sample be well shaken with twice its volume of water, and that the water extract be then tested with litmus paper, silver nitrate solution and potassium iodide solution.

[2] The zinc iodide-starch test was recommended by Schwarz and Will (*Pharm. Ztg.*, **1888**, 551); Brown (*Pharm. J.*, [3] **23**, 229) proposed that zinc iodide and starch be used to detect the first signs of decomposition; later Brown (*Ibid.*, [3] **25**, 865) recommended that on shaking with an equal volume of zinc iodide and starch solution, no color should be imparted to the chloroform—a test which he found to be more delicate than that with sirup of iodide of iron and starch; and Krauch (*Testing of Chemical Reagents*, **1902**, 78) states that on shaking with zinc iodide and starch solution, no blue coloration must occur. It has been also considered that the presence of free chlorine is sufficiently indicated by the coloration of moistened test paper charged with zinc iodide and starch when it is immersed in the atmosphere of the container.

The *Deutsches Arzneibuch* (**1910**, 118) states that when the water extract of chloroform is shaken with zinc iodide and starch solution, the latter should not become blue or colored. The *Pharmacopoeia of Japan* (**1907**, 84) requires that chloroform acquire no coloration on shaking with a solution of zinc iodide and starch, and that the latter acquire no blue coloration.

[3] The *British Pharmacopoeia* (**1908**, 75) directs that the aqueous portion obtained by shaking chloroform with twice its volume of water for 5 minutes should not afford any color with 1 cc. of cadmium iodide T. S. and 2 drops of mucilage of starch. The same reagents are required in Belgium.

[4] The *British Pharmacopoeia* requires that 2 cc. of the sulphuric acid liquid, obtained on shaking chloroform with 1/10 its volume of sulphuric acid for 20 minutes, and then set aside for 15 minutes, when diluted with $2^1/_2$ times its volume of water, should remain clear, almost colorless, and should possess a pleasant odor; that the liquid should still retain its transparency and freedom from color, even when further diluted with 10 cc. of water and stirred with a glass rod, and the transparency should not be more than slightly diminished on the addition of 4 drops of silver nitrate solution; and that the addition of silver nitrate solution should not more than slightly diminish the transparency of the aqueous portion obtained by shaking the sulphuric acid—treated chloroform with twice its volume of water. The *Pharmacopoeia of the United States* gives a similar test. See Section 3(*a*).—*The Test with Sulphuric Acid.*

[1] The authors have experimentally demonstrated that this is the case.

[2] For example, Ohliger (*Proc. Mich. Pharm. Assn.*, **1906**, 47) reported chloroform with "chlorinated compounds" and "carbonizable impurities" present; and Caspari (*Proc. Mo. Pharm. Assn.*, **1906**, 100) examined seven samples of chloroform, out of which two contained "chlorinated decomposition products."

[3] *J. Chem. Soc.*, **85**, 938.

[4] It has therefore been proposed to add a minute of ethyl chloride to chloroform made from acetone (*Schweiz. Wochschr.*, **47**, 302). It has been stated that the addition of 0.25 per cent. of ethyl chloride to chloroform prepared from acetone renders it physiologically identical with the product from alcohol (*Trans. Soc. Anaesth.*, **7**, 89). In fact, there has been

Dott[1] confirmed the observation that a small proportion of ethyl chloride is formed in preparing chloroform from ethyl alcohol. He found that, unlike most impurities, it is not removed by washing with water,[2] treatment with sulphuric acid, or with soda solution.

While ethyl chloride, when present in small proportions in anaesthetic chloroform, is not, strictly speaking, an objectionable impurity, and although it may, according to some, prevent a prolongation of the period of induction, yet anaesthetic chloroform manufactured from acetone in this country has been found by American anaesthetists to be fully as satisfactory as that from other sources, and this may be said to be general when the chloroform is properly made from purified acetone and the product is carefully purified. When chloroform is prepared from alcohol, ethyl chloride may be easily formed in the course of chlorination, while it is difficult to conceive how it could be formed from acetone under these conditions; but ethyl chloride comes over with the first distillate on rectifying. The anaesthetist should know the preparation he is using, and if he desires chloroform containing ethyl chloride he should specify "chloraethoform" or a similar preparation. Anaesthetic chloroform should, without exception, be free from contamination with ethyl chloride, for each compound exerts its specific physiological action.

Since the boiling point of anaesthetic chloroform may be lowered 2° C. by the presence of 0.1 per cent. of ethyl chloride, this impurity may be detected by fractionation.

(*c*) *The Occurrence of Ethylene Chloride in Chloroform.*

Ethylene chloride has, in the past, been regarded as a contaminant of chloroform, and several tests have been proposed for its detection[3]; but its presence in anaesthetic chloroform is not to be expected now.[4] The isomer, ethylidene chloride, is, however, a probable contaminant of chloroform prepared from alcohol,[5] since it is more difficult to eliminate by rectification; and even though it is said to possess anaesthetic properties similar to those of chloroform, its presence should be known for the reasons indicated in the case of ethyl chloride.[1]

(*d*) *The Detection of Carbon Tetrachloride.*

Chloroform is now being manufactured from carbon tetrachloride; therefore the detection of this likely contaminant should be considered, although we have so far been unable to find a chemical method which is suitable for the recognition of probable amounts in anaesthetic chloroform.[2] The method given in the French *Codex*[3] is unsatisfactory, and the manufacturers of chloroform from carbon tetrachloride state that they are aware of no method of determining the presence of carbon tetrachloride in chloroform except by the specific gravity—that is, by taking some chloroform which is known to be pure and diluting it with various percentages of pure carbon tetrachloride, they have found that a scale may be made which is of sufficient accuracy for the purpose. It it true that mixtures of pure chloroform and pure carbon tetrachloride may be determined in this way, and the method is undoubtedly suitable for factory control, yet it is highly desirable that a method be found which is applicable in the presence of the variables of anaesthetic chloroform and is of sufficient delicacy for the detection of small amounts. Since it has been stated that all chloroform contains traces of dichlormethane,[4] the detection of this compound is likewise of importance.[5]

Since the variables of anaesthetic chloroform of the present pharmacopoeial grade also render the determination of small amounts of carbon tetrachloride by means of the boiling point[6] and conductivity methods, and by an estimation of total chlorine, inapplicable, an investigation was made to ascertain whether carbon

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placed on the market a preparation of chloroform containing 0.25 per cent. of ethyl chloride, called "chloraethoform" (*Chem. and Drug.*, **1904**, 1289).

[1] *J. Soc. Chem. Ind.*, **27**, 272.

[2] In 1875, Normandy-Noad (*Commercial Chemical Analysis*, p. 122) stated that "hydrochloric ether" may be recognized in chloroform by shaking the latter with water, then decanting the aqueous extract and distilling it from a water-bath. They mention that the odor of the ether is very evident in the portions which first come over.

Others state that the presence of ethyl chloride may be recognized by distilling the chloroform with water on a water bath, when the first portions of the distillate will possess a distinct odor of the foreign body.

[3] Hager (*Kommentar*, **1865**, 443) stated that the test with sodium serves for the detection of alcohol and ethylene chloride; he also reported that ethylene chloride may be detected by means of potassium hydroxide, ethylene being evolved. It has been proposed that ethylene chloride be detected in chloroform by drying the sample by agitation with dry potassium carbonate, and then adding potassium, which produces chlor-ethylene, a gas possessing an alliaceous odor, in the presence of the impurity.

On the boiling points of mixtures of ethylene chloride and chloroform, see Wulf, *Inaugural Dissert.*, Berlin, June 26, 1885.

Keppeler (*Anaesthetica; Loc. cit.*), in one of the 101 fatal cases of chloroform administration collected by him, states that allyl chloride was found in the chloroform, although the same chloroform had been used without bad effect in other cases.

[4] Any ethylene chloride present in the crude product is removed by means of the rectification processes now in use.

[5] See Krämer, *Ber.*, **3**, 257; and Regnault, *Ann. chim. phys.*, [2] **71**, 355.

[1] Allen (*Commercial Organic Analysis*, **1**, 235) considered it very doubtful whether the substance in chloroform of the formula $C_2H_4Cl_2$ is always ethylene chloride, but that it is probably more frequently the isomer $CH_3.CHCl_2$.

Ethylidene chloride possesses an odor and taste similar to those of chloroform, a boiling point of 58–60°, and is difficult to detect when present in chloroform in small amounts. On its conduct with sodium, potassium, and potassium hydroxide, see Tollens, *Ann.*, **137**, 311.

[2] The investigation is being continued in this laboratory.

[3] **1908**, 148. The method given is as follows: Agitate 1 part of chloroform with 100 parts of water previously saturated with carbon tetrachloride, and finally with 20 parts of this same water; the carbon tetrachloride, if it is present in sensible proportions, will remain undissolved, while the chloroform dissolves completely.

This test is evidently based upon the one proposed by Robineau and Rollin (*Mon. Sci.*, [4] **1**, 341), who found that when 400 cc. of water, previously saturated with carbon tetrachloride, are shaken with 1 cc. of the chloroform in question, the liquid will become turbid even in the presence of 0.1 per cent. of carbon tetrachloride. The same authors mention another test which is of no value. 1 cc. of the chloroform to be tested is put in a sealed tube with 10 cc. of sodium carbonate (36° Bé.) and 10 cc. of water, and the mixture is heated for 7–8 hours at 100° C. Sodium carbonate does not attack carbon tetrachloride, consequently the appearance of oily drops shows the presence of this compound.

The test mentioned by Margosches ("Der Tetrachlorkohlenstoff," p. 78) for distinguishing chloroform from carbon tetrachloride—that based on the fact that chloroform is immediately intensely colored by the addition of wood-tar pitch, whereas no coloration results in the case of carbon tetrachloride—is not suitable for proving the presence of carbon tetrachloride in chloroform.

[4] See Section VI, 6.

[5] The physiological action of dichlormethane requires investigation.

[6] In this connection it should be mentioned that Haywood (*J. Phys. Chem.*, **3**, 318) found that chloroform, otherwise pure, containing 7.8 per cent. of carbon tetrachloride, boils at 62° at 758.1 mm.

tetrachloride might be determined in anaesthetic chloroform by reduction, or rather by a method based upon the probably different degrees of reducibility of carbon tetrachloride and chloroform, and then determining the hydrochloric acid formed. For this purpose, zinc and sulphuric acid[1] and copper-zinc couple[2] are unsuitable; accordingly finely-divided iron was first tried as the reducing agent, since it has been stated that the reduction of carbon tetrachloride by means of this agent may be readily controlled, so that little or no reduction to dichlormethane occurs.[3]

In the experiments with reduced iron, varying amounts (0.5–10 g.) of the latter were added to mixtures of water (10–50 cc.) and anaesthetic chloroform (20–150 cc.) containing known amounts of carbon tetrachloride, both with and without the addition of small amounts of sulphuric acid, and the reaction was studied at various temperatures during different periods of time. In every experiment a blank anaesthetic chloroform free from carbon tetrachloride was run under the same conditions. In these experiments it was invariably found that chloroform also underwent reduction, as shown by the formation of hydrochloric acid, and it is concluded that the presence of likely amounts of carbon tetrachloride in anaesthetic chloroform cannot be recognized with accuracy by such a method. Palladium hydride gave similar results.

It should be mentioned here that carbon disulphide—a possible contaminant of commercial chloroform prepared from commercial carbon tetrachloride—may be recognized in chloroform by means of the method of Schmitz-Dumont[4] for the detection of this compound in carbon tetrachloride.

13. SCHEME FOR THE EXAMINATION OF CHLOROFORM FOR ANAESTHETIC AND ANALYTICAL PURPOSES, WITH PARTICULAR REFERENCE TO THE DETECTION OF AVOIDABLE IMPURITIES.

1. Specific Gravity. The specific gravity should be determined by means of a pycnometer at 15° C. (see discussion under *Specific Gravity* and *Alcohol*).

2. Odor. In the case of *anaesthetic chloroform*, 100 cc. of the sample are slowly evaporated over a water-bath until about 10 cc. remain in the flask. This residuum should be colorless and should possess no foreign odor; and when it is allowed to evaporate on filter paper, at room temperature, there should result no odor of fusel oil, empyreumatic matter, or other substances than *chloroform* and *ethyl alcohol*, as the last portions disappear. If a decided odor is imparted to the filter paper after the evaporation of the residue, or if any foreign odor is observed during the course of evaporation, the chloroform should be rejected; but for further information, may be tested for such impurities as fusel oil, chlorinated derivatives of alcohol, acetone, or the higher alcohols, extractive matter, etc.

Pure chloroform should also comply with this requirement, except that as the last portions of the residuum evaporate on filter paper, no odor of other substances than *chloroform* should be apparent.

3. Residue. When 100 cc. of either *pure* or *anaesthetic* chloroform are allowed to evaporate in a platinum dish at 100° C., there should be left no weighable residue. In every case this should be determined gravimetrically and not by vision.

4. Organic Impurities. When 20 cc. of *anaesthetic chloroform* are mixed with 15 cc. of concentrated sulphuric acid in a glass-stoppered tube of 50 cc. capacity which has been previously rinsed with concentrated sulphuric acid, no visible coloration should be imparted to the mixture after the addition of 0.4 cc. of pure 40 per cent. formaldehyde solution, and then shaking throughout a period of five minutes.

Pure chloroform should, of course, also comply with this test; in fact, in this case, no coloration should result even after one hour, providing the mixture is allowed to stand in the dark.

5. Water. *Pure chloroform* and *anhydrous anaesthetic chloroform* should comply with the following test: When 20 cc. of the sample are boiled over one gram of clean crystals of calcium carbide, and the vapors evolved are passed into ammoniacal silver nitrate solution, no acetylene reaction should result.

Anaesthetic chloroform should readily conform to this test: When 10 cc, of the sample are agitated with an equal volume of paraffin oil (sp. gr. 0.880), the oil should dissolve to a clear solution without any evidence of a turbidity.

6. Alcohol. *Pure chloroform* should possess a correct specific gravity and should comply with the following: 10 cc. are shaken in a separatory funnel with 4 cc. of concentrated sulphuric acid; the extraction is again repeated with 4 cc. of sulphuric acid, and finally with 2 cc. The sulphuric acid solution is now mixed with 40 cc. of water, and the diluted solution is gently distilled until the distillate amounts to about 20 cc. To 10 cc. of the distillate, 6 drops of a 10 per cent. solution of potassium hydroxide are added and the liquid is warmed to about 50° C. A solution of potassium iodide fully saturated with free iodine is next added, drop by drop, with agitation, until the liquid becomes permanently yellowish brown in color, when it is carefully decolorized with potassium hydroxide solution. No iodoform should be deposited at the bottom of the tube. This test is not peculiar to alcohol, being produced also by acetaldehyde, propyl alcohol, acetone, etc.; but *pure chloroform* should give an absolute non-response. As confirmatory tests, apply tests 1(*a*), 1(*b*) and 3(*b*) of Section 5.

In the case of *anaesthetic chloroform* and *commercial chloroform*, an indication as to the amount of alcohol present may be had from the density of the sample as determined in 1; but no definite conclusions should be arrived at until a quantitative estimation of the alcohol has been made by the method of Nicloux as elaborated by the authors [see 1(*a*), Section 5] or as modified by Behal and François.

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[1] These reagents convert chloroform into dichlormethane (Geuther, *Ann.*, **107,** 212; Richardson, *Chem. News*, **18,** 60).

[2] Owing to the presence of water and alcohol in anaesthetic chloroform (Gladstone and Tribe, *J. Chem. Soc.*, **28,** 508).

[3] Smith, U. S. Patent 753,325, March 1, 1904.

[4] *Chem. Ztg.*, **21,** 487, 510. When this test is applied to chloroform, it is necessary to run a blank test on *pure* anaesthetic chloroform, for metallic silver is precipitated in all cases by reduction, and consequently this precipitate must be distinguished from silver sulphide. Generally, if the precipitate possesses no black color, it may be assumed that no carbon disulphide is present. This method is the best available for the purpose.

Inghilleri (*Gazz. chim. ital.*, **39,** I, 634) found that carbon disulphide and ammonium carbonate form ammonium thiocyanate quantitatively when heated for four hours in alcohol at ordinary pressure. We found, however, that this method does not serve for the detection of such traces of carbon disulphide as are likely to occur in commercial chloroform prepared from carbon tetrachloride. When carbon disulphide is added to anaesthetic chloroform, and the method of Inghilleri is applied, the former does not undergo quantitative conversion into ammonium thiocyanate, and, in addition to the latter, we have found that ammonium thiocarbamate is formed, especially when a considerable amount of alcohol is present.

7. Acetone.

Pure chloroform complying with the iodoform test (6, *supra*) is assuredly free from acetone.

Anaesthetic chloroform should give a negative reaction in all cases when the following exclusion test is applied: 10 cc. of the sample are agitated with 5 drops of a 0.5 per cent. sodium nitroprusside solution and 2 cc. of ammonium hydroxide (sp. gr. 0.925), and the mixture is then allowed to stand for several minutes. Chloroform containing up to 1 per cent. of alcohol may impart a yellowish brown color to the supernatant liquid on agitation, but when acetone is present an amethystine color results. This test must be conducted in the cold. After application to the suspected chloroform direct, the first 10 per cent. distillate and the 10 per cent. residuum, obtained by allowing 100 cc. of the sample to slowly distil, should be tested. When the proportion of acetone to chloroform is 1 : 500, the amethyst color is marked; but in the presence of 1 part in 1000, the coloration is not distinct until the mixture of chloroform with ammonium hydroxide and sodium nitroprusside has been saturated with ammonium sulphate, shaken and then allowed to rest for five minutes. It is advisable, in all cases, to run a blank test on *pure* anaesthetic chloroform for comparison. Since acetaldehyde is generally present in fresh and properly stored samples of anaesthetic chloroform in proportions greater than 1 : 3300, usually the reaction is not interfered with by this substance, but in every case the sample should be examined for the presence of acetaldehyde, and if it complies with test 8(*a*), a positive reaction upon applying the acetone test may be said to be solely indicative of the presence of acetone.

8. Acetaldehyde.

(*a*) *Chloroform of all grades* should pass this exclusion test: 5 cc. of the sample are agitated with 5 cc. of the reagent of François (see Section 9A) in a glass-stoppered tube; no coloration should result even after 15 minutes. The presence of 3 parts of acetaldehyde by volume in 10,000 of chloroform may thus be made evident and smaller amounts may, of course, be detected by resorting to fractionation.

(*b*) *Pure chloroform* giving a negative reaction on the application of test 6 may be regarded as free from acetaldehyde; but it should, in addition, give no response when 5 cc. are agitated with 5 cc. of Nessler's reagent, U. S. P., and the mixture is allowed to stand 5 minutes.

When 10 cc. of *anaesthetic chloroform* are agitated with 10 cc. of water and 5 drops of Nessler's reagent, U. S. P., and the mixture is then allowed to stand for 5 minutes, there should result no precipitate, and the reagent should assume *no coloration*, although it may become opalescent or slightly turbid.

9. Acidity.

When 20 cc. of either *pure or anaesthetic chloroform* are thoroughly agitated with 10 cc. of water and 2 drops of phenolphthalein solution and then titrated with $N/100$ potassium hydroxide solution, added drop by drop, not more than 0.2 cc. of standard alkali solution should be required to produce a faint but decided alkaline reaction permanent for 15 minutes, when the mixture is shaken 30 seconds after the addition of each drop of alkali. If the presence of free acid is indicated, the sample should be rejected, but for further information may be examined for the oxidation products of pure chloroform and alcohol.

10. The Decomposition Products of Pure Chloroform.

(*a*) *Carbonyl chloride.* To 15 cc. of the sample, contained in a dry glass-stoppered tube of 25 cc. capacity, sufficient of a perfectly clear 1 : 19 barium hydroxide solution is added to fill the tube; after allowing the mixture to stand three hours in a dark place without agitation, the observation as to the formation of a film of barium carbonate is made.

(*b*) *Hydrochloric acid and Chlorides.* Samples of chloroform complying with 9 are assuredly free from carbonyl chloride, hydrochloric acid and chlorine; but pure and anaesthetic chloroforms should also conform to the following test: When 10 cc. of the sample are agitated with 5 cc. of water for 5 minutes, the water extract should not become turbid or give any precipitate upon the addition of silver nitrate solution (absence of hydrochloric acid, chlorides, etc.), and no reduction should occur on warming (absence of acetaldehyde, formic acid and formates, etc.).

(*c*) *Chlorine* (*and Hydrogen dioxide*). When 10 cc. of the sample are agitated during 15 minutes with 10 cc. of a 10 per cent. cadmium potassium iodide solution, there should result no liberation of iodine as determined by the addition of starch solution. *Chloroform of all grades should give a negative reaction with this test.*

11. The Decomposition Products of Anaesthetic Chloroform.

(*a*) The detection of *acetaldehyde* has already been referred to (8).

(*b*) *Anaesthetic chloroform* failing to comply with test 9, and which contains none of the substances referred to in 10 (this will generally be found to be the case), should be rejected, since then the indication is that *acetic acid* is present.

(*c*) When 20 cc. of *anaesthetic chloroform* are shaken during 20 minutes with 15 cc. of concentrated sulphuric acid in a glass-stoppered tube of 50 cc. capacity previously rinsed with sulphuric acid, and 2 cc. are diluted with 5 cc. of water, the liquid should remain colorless and clear, and should possess no odor foreign to anaesthetic chloroform (chloroform and alcohol); and the liquid should retain its transparency and colorless state when further diluted with 10 cc. of water, and the transparency should not be diminished on the addition of 5 drops of silver nitrate solution. A positive result is indicative of the presence of chlorinated derivatives of the oxidation products of alcohol, etc. [see Section 12(*a*)].

14. THE DEGREES OF PURITY OF AMERICAN CHLOROFORMS.

The main impurities contained in American anaesthetic chloroforms are, besides water, impurities decomposable by sulphuric acid and traces of the oxidation products of ethyl alcohol. As previously mentioned, the presence of small amounts of ethyl alcohol is necessary; but anaesthetic chloroform should contain but mere traces of water, and it is desirable that it be absolutely water-free. The necessary precautions should be taken by manufacturers to guard against the presence of organic impurities as well as of extractive matter—a common contaminant of anaesthetic chloroform contained in unprotected cork stoppered bottles.

The following table will serve to show the comparative purity of various samples of chloroform. Nos. 1–9 were samples of anaesthetic chloroform, supposed to be of the present U. S. P. grade and such as are now being supplied to the trade;[1] No. 10 was a sample, stated to be of U. S. P. quality, contained in a tin and 17 months old; No. 11 was a sample of "Chloroform for Anaesthesia," contained in a sealed tin, and 6 years old;[2] and No. 12 was an unopened tin

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[1] All of these samples, with the exception of No. 6, were manufactured in the United States. These samples were obtained through the courtesy of the various manufacturers, to whom the authors desire to acknowledge their indebtedness.

[2] This sample was kindly supplied by Surgeon-General Torney, U. S. A. It was dated November 1, 1905.

COMPARATIVE PURITY OF VARIOUS SAMPLES OF CHLOROFORM.

All samples gave tests for water present in permissible amounts; negative acidity tests, U. S. P.; negative tests for chlorides and for oxidation products of pure chloroform.

No.	*Source.*	*Grade.*	*Density at 25/25°.*	*Odor.*	*Residue in g. per liter.*
1	Acetone...............	Anaesthetic	1.4827	Normal	..
2	Acetone...............	Anaesthetic	1.4730	Normal	None
3	. ...	Anaesthetic	1.4772	Normal	None
4	Acetone...............	Anaesthetic	1.4806	Normal	None
5	Acetone...............	Anaesthetic	1.4770	Normal	..
6	Chloral...............	Anaesthetic	1.4839	Normal	..
7	Acetone...............	Anaesthetic	1.4756	Normal	..
8	Acetone...............	Anaesthetic	1.4750	Normal	..
9	Carbon tetrachloride..	Anaesthetic	1.4773	Normal	..
10	....	Anaesthetic	1.4751	Slightly pungent	0.0220
11	Acetone...............	Anaesthetic	1.4722	Normal	None
12	Alcohol...............	Anaesthetic	1.4747	Fruity	..
13	Acetone...............	Analytical	1.4752	Normal	0.0165
14	Acetone...............	Commercial	1.4846	Normal	0.0705

No.	*Extractive matter.*	*Sulphuric acid test.*	*Formalin-sulphuric acid test.*	*Absolute ethyl alcohol in cc. per 100 cc.*	*Higher alcohols.*
1	Present from cork..	Faint	Faint brown	0.50	Not detected
2	Absent....	Negative	Faint yellow	0.97	Not detected
3	Absent...........	Negative	Marked brown	0.77	Not detected
4	Absent...........	Negative	Negative	0.56	Not detected
5	Absent...........	Negative	Brown color	0.70	Not detected
6	Present from luting	Marked	....	0.30	Not detected
7	Present from cork..	Decided	....	0.80	Not detected
8	Indefinite.........	Faint	Very faint yellow	0.84	Not detected
9	Trace.............	Very faint	Faint yellow	0.74	Not detected
10	Trace.............	Faint	....	0.84	Not detected
11	Absent...........	Marked	....	0.83	Present
12	Present...........	Pronounced	....	0.60	Propyl
13	Present from cork..	Faint	....	0.69	Not detected
14	Present...........	Marked	....	..	Not detected

No.	*Acetone.*	*Acetal-dehyde.*	*Acetic acid in g. per 100 cc.*	*"Odorous decomposition products."*	*"Chlorinated decomposition products."*
1	Absent.......	...	0.0003	Absent	Absent
2	Absent.......	Trace	0.0001	Absent	Absent
3	....	Trace	...	Absent	Absent
4	Not detected..	Trace	Absent	Absent	Absent
5	Not detected..	....	Absent	Absent	Absent
6	....	Trace	0.00015	Faint reaction	Trace
7	Not detected..	Trace	0.00015	Absent	Very faint reaction
8	Not detected..	Trace	0.00030	Absent	Present
9	....	Absent	Absent	Absent	Absent
10	....	Present	0.00045	Absent	Present
11	Not detected..	About 1 : 3300	0.0009	Absent	Present
12	....	1 : 2000	0.00045	Present	Absent
13	Not detected..	Trace	...	Absent	Faint reaction
14	Not detected..	Trace	...	Absent	Faint reaction

of "Chloroformum Purificatum," manufactured in 1863 or shortly before.[1] The last two samples are of particular interest, since, so far as the authors are aware, they were the oldest samples of chloroform ever examined.

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[1] This sample was also furnished by Surgeon-General Torney, U. S. A., who stated that the chloroform was taken out of a pannier of the variety issued during the Civil War, along with records, etc., which bore the date of 1863. To quote from his letter of transmittal: "I presume that the chloroform was made at that period, or before, and I may say that it is the last survivor, so far as I know, of the chloroform supplied at that period." It is important to note that this tin of chloroform possessed a smaller air space than No. 11, the container being almost full; this, no doubt, accounts for the difference in oxidation of the alcohol in the two samples.

ON THE STARCH OF GLUTINOUS RICE AND ITS HYDROLYSIS BY DIASTASE.

By YOSHIO TANAKA.

Received February 12, 1912.

While it is well known that starch granules or their solutions are colored intensely blue by a dilute solution of iodine, there is another variety of starch which gives a pure red coloration with the same reagent. Kreusler[1] discovered the presence of such starch in glutinous rice. This variety of starch seems to be quite widely distributed in plants. The writer has found that the starches of "mochi-awa" (glutinous millet), "mochi-kibi" (glutinous variety of Panicum miliaceum L.), "morokoshi" (Andropogon Sorghum Brot. var. vulgaris Hack.) and "nien kaoling" (glutinous variety of "kaoliang") are also colored red by iodine solution.

The peculiar nature of the starch of glutinous rice has been investigated by several authors. Kreusler thought that the red coloration of the starch in glutinous rice, produced by iodine, might be due either to some substance which hindered the ordinary blue coloration of starch, or to some special modification of starch. F. W. Dafert[2] considered that the starch of glutinous rice contains erythroglanulose—the main part of which consisted of erythrodextrin. R. W. Atkinson[3] held that the red coloration was more probably due to special albuminoids than to dextrin. J. Shimoyama[4] attributed this reaction to the presence of a large quantity of Nageli's amylodextrin.

Notwithstanding all these investigations the nature of the starch of glutinous rice is not yet clearly explained and, therefore, research to ascertain the constituents of the starch is not only interesting but necessary from both scientific and practical points of view.

Glutinous rice (Japanese mochi-gome)—Oryza glutinosa—has long been widely used in Japan such as in preparing "Mochi" (a kind of cake prepared by kneading steamed glutinous rice), "Ame" (a sweet prepared by saccharification of cooked glutinous rice by means of malt), "Mirin" (a liquor which is prepared from steamed glutinous rice, koji and spirit), etc.

Since the glutinous rice obtained in the market generally contains common rice, the latter must be removed when the glutinous rice starch is to be used for investigation. The author prepared the starch according to the ordinary process, from glutinous rice, from which common rice had been carefully removed. The separation of common rice from glutinous rice can easily be effected as the former is translucent while the latter is opaque.

The glutinous rice starch forms a white, tasteless and odorless powder; examined under the microscope the granules are almost identical in shape and size with those of the starch obtained from common rice.

BEHAVIOR OF GLUTINOUS-RICE-STARCH WITH IODINE.

A fine red coloration of glutinous-rice-starch with

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[1] U. Kreusler, *Jahres-Bericht chem.-tech.*, **1885**, 657.

[2] F. W. Dafert, *Ibid.*, **1886**, 610.

[3] R. W. Atkinson, *Chem. Sake Brew.*, **1882**, 2.

[4] J. Shimoyama, *J. Shimoyama's Pharm. Chem.*

iodine is observable only after the structure of the starch cell has been destroyed, either by heat or mechanical means. The color produced by iodine with intact grains is a dirty reddish brown. It is, therefore, true that the inner contents of the starch cell alone are colored pure red by iodine, just as the granulose of common starch is colored blue by iodine.

The author made comparative tests on ungelatinized starches obtained from different sources as to their color reactions toward iodine in presence of water. Three grams of each starch were shaken up with 100 cc. of *N*/20000 and *N*/1000 iodine solutions respectively. After ten minutes the color reactions were observed as follows:

Ungelatinized starch from:	Reaction with N/20000 iodine solution.	Reaction with N/1000 iodine solution.
Glutinous rice	Light red	Reddish brown
Common rice	Light red	Purplish blue
Potato	Light purplish red	Blue
Sweet potato	Light purplish red	Blue

The author then tried to ascertain whether or not glutinous rice starch contains common starch.

It is known that common starch possesses greater affinity for iodine than erythrodextrins, therefore, a minute quantity of the former can be detected to a certain extent even in the presence of a larger amount of the latter if a weak iodine solution is carefully added, drop by drop. Again, common starch possesses also greater affinity for iodine than glutinous rice starch, and therefore, the above method may also be applied in order to detect the presence of a small quantity of common starch in glutinous rice starch. Experiments based on the above method led the author to think that glutinous rice starch does not contain common starch, since no blue coloration could be observed with the gelatinized solution of the starch.

The author observed very interesting facts about the coloration of both common starch and the starch of glutinous rice. When glutinous rice starch is suspended in *N*/100 iodine solution without gelatinization and then sodium sulphate is added to saturation, the red coloration which first appeared discolored to a dark tint with a bluish shade. When the blue starch-iodide obtained with potato starch is treated with carbon bisulphide, chloroform or a careful proportion of sodium thiosulphate, the blue coloration turned into a violet or reddish tint. These facts suggest the probability that what is generally known as starch-iodide is not at all a definite chemical compound but a solid solution of iodine in starch. The intensity and shade of color relates to the degree of quantity of iodine therein dissolved, the larger the quantity dissolved the more bluish it appears, while in the least quantity it will appear red. The solubilities of iodine in various starches may be dependent upon the nature of the starch. This view, I believe, can be confirmed by the fact that the blue colored starch iodide is changed into a red compound when it is washed with a potassium iodide solution or with alcohol.

ABSENCE OF ERYTHRODEXTRIN AND ACHROODEXTRIN IN THE STARCH.

It is well known that the consistency of common rice starch paste, gelatinized by means of heat or caustic alkalis, is slightly thinner than that of potato starch. Arthur Meyer explained this peculiarity by an assumption that common rice starch contains more or less soluble starch, but such is somewhat doubtful. The fact that the consistency of glutinous rice starch paste is equal to that of common rice starch, leads to the assumption that the essential constituents of glutinous rice starch are not dextrins; because if, other things remaining the same, glutinous rice starch contains a large amount of dextrins the consistency of its gelatinous paste ought to be thinner than that of the common rice starch paste. It can, therefore, be deduced that, even if dextrins are contained in glutinous rice starch, the quantity is not considerable. The author intended to show the absence of erythrodextrin and achroödextrin in the starch, taking advantage of the behavior of glutinous rice starch toward baryta water.

Bülow discovered that the so-called Lintner and Dull's amylodextrin and erythrodextrin are both precipitated by baryta water, while achroödextrin is precipitated only in an alcoholic medium. The limits of precipitation of several dextrins by baryta water were investigated by D. Moreau.

In accordance with Moreau's[1] method the author also determined the minimum quantities of baryta water with which all kinds of dextrins as well as starch paste are precipitated. For such testing 2 cc. each of a 1 per cent. solution of the samples were taken in test tubes with cork stoppers into which a measured amount of water and saturated baryta water (sp. gr. 1.027) was added and shaken, the volume of the mixture in each test tube being made 10 cc. After standing for 24 hours the clear supernatant solution was filtered and the filtrate examined by an iodine solution after acidifying with acetic acid. The results obtained were as in the following table:

			Iodine reaction of acidified filtrates					
Starch or dextrin solution, cc.	Water, cc.	Baryta water, cc.	Potato starch.	Common rice starch.	Glutinous rice starch.	Soluble potato starch.	Soluble glutinous rice starch.	Erythrodextrin.
2	7.6	0.4	.....	....	...	......	..	...
2	7.4	0.6	blue	blue	red	......	..	...
2	7.2	0.8	light blue	blue	red	blue	..	...
2	7.0	1.0	none	slightly blue	red	blue	red	...
2	6.8	1.2	none	none	pink	blue	red	...
2	6.6	1.4	none	none	none	reddish blue	red	red
2	6.4	1.6	none	none	none	reddish blue	red	red
2	6.2	1.8	none	none	none	light bluish violet	red	red
2	6.0	2.0	none	none	none	light violet	pink	red
2	5.8	2.2	none	none	none	light violet	pink	red
2	5.6	2.4	none	none	none	faint pink	pink	red
2	5.4	2.6	none	none	none	faint pink	light pink	red
2	5.0	3.0	none	none	none	none	none	red
2	4.0	4.0	none	none	none	none	none	pink
2	3.0	5.0	none	none	none	none	none	pink
2	2.0	6.0	none	none	none	none	none	pink

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[1] D. Moreau, *Wochenschrift für Brauerei*, **1905**, No. 344.

From these results the minimum quantity of the baryta solution, which precipitates dextrins or starches respectively after 24 hours, is calculated as follows:

Starch or dextrin.	Baryta solution.
Potato starch	1.0 cc.
Common rice starch	1.2 cc.
Glutinous rice starch	1.4 cc.
Soluble potato starch (Lintner's)	2.4 cc.
Soluble glutinous rice starch (Lintner's)	3.0 cc.
Erythrodextrin	above 6.0 cc.

Thus it will be seen that the glutinous rice starch closely resembles common starch as regards its behavior toward baryta water, while the soluble-glutinous-rice-starch, which was prepared by Lintner's method and which is colored red by iodine, resembles the soluble potato starch rather than the erythrodextrin.

In studying the effect of soluble starch or erythrodextrin upon the quantity of baryta water when one of either is added in small quantity respective samples of starches in question, it was expected that the minimum quantity of baryta water to be used would be greater than that starch sample alone would require. The accuracy of this expectation is to be found in the results obtained and tabularly arranged as follows:

Carbohydrate solution.	Solution taken cc.	Minimum quantity of baryta water to precipitate the carbohydrate, cc.
1 per cent. potato starch solution, 100 cc.	2.0	1.6
1 per cent. soluble starch solution, 1.0 cc.	...	...
1 per cent. glutinous rice starch solution, 100 cc.	2.0	1.6
1 per cent. erythrodextrin solution, 1.0 cc.	...	...
1 per cent. glutinous rice starch solution, 100 cc.	2.0	1.8
1 per cent. erythrodextrin solution, 2.0 cc.	...	...
1 per cent. glutinous rice starch solution, 100 cc.	2.0	2.6
1 per cent. erythrodextrin solution, 5.0 cc.	...	...

From the above results it can safely be concluded that, if glutinous rice starch contains a large quantity of erythrodextrin, the amount of baryta water to be used for a thorough precipitation of carbohydrates must be much greater than in case of potato or common rice starch. It will, however, be seen above that its value is quite close to that obtained in case of common rice starch. These results, as well as the consideration relative to the consistency of the paste, point to the probability that erythrodextrin does not exist in the glutinous rice starch.

As the author has stated elsewhere, achroödextrin is not precipitated by baryta water, while other dextrins and starches are precipitated by this reagent. This affords a convenient means of separation of achroödextrin from other carbohydrates. The author determined the minimum quantity of achroödextrin which can be detected in potato starch in the way already mentioned. The result was so very satisfactory that even less than 0.5 gram of achroödextrin in 100 grams of sample could be readily detected.

An attempt was next made to ascertain whether achroödextrin exists in glutinous rice starch in the following way: About 10 grams of glutinous rice starch were boiled with 100 cc. of water; after cooling, 400 cc. of saturated baryta water were added. After 48 hours the mixture deposited a white precipitate, leaving a clear supernatant solution. When the necessary quantity of 96 per cent. alcohol was added to the solution for precipitation of achroödextrin not even turbidity was noticed. This result shows that the glutinous rice starch does not contain achroödextrin.

ISOLATION OF THE HYDROLYZED PRODUCTS OF GLUTINOUS RICE STARCH.

It was found necessary to examine the products formed by the action of malt-diastase on glutinous rice starch. The saccharification was carried on at 55° C. with the diastase prepared from barley malt until the iodine reaction could no longer be observed. Dextrin was separated from this conversion product and purified by repeated precipitation with alcohol. The dextrin thus prepared was a white, gummy substance, soluble in water and not precipitated by baryta water. It gave no color with iodine and had very little action upon Fehling's solution. Its specific rotatory power $[\alpha]_D$ 3.95 was found to be 201.2. These facts show that the substance is achroödextrin.

From the conversion products, the author also obtained a sugar having an opticity of $[\alpha]_D$ 3.95–137.2 and a reducing power of K —64.3. When the sugar solution was treated with phenylhydrazine acetate, an osazone was formed which separated from the cold solution in the crystalline form, appearing as beautiful, long, flat plates under the microscope. After inversion, the sugar solution produced the characteristic glucosazone with phenylhydrazine acetate. It is therefore evident that the sugar is maltose. Thus, the conversion products by the action of malt diastase on glutinous rice starch are identical with those of common starch.

It is also worth mentioning that as the hydrolyzing action of the diastase on the glutinous rice starch paste proceeds, the red coloration by iodine becomes lighter and lighter and at the same time the reducing property of the product on copper oxide increases rapidly, and finally iodine ceases to give any more red color. Atkinson's statement that the presence of some peculiar albuminoid is responsible for the red coloration by iodine appears then to be incorrect. His view may also be refuted by the fact that the glutinous rice starch gives a bright red coloration with iodine solution even after it has been purified by treating with acid and alkali, in fact a still brighter red color than when albuminoid impurities were present. The author also examined the conversion products of glutinous-rice-starch using the koji-diastase and found that they consisted of glucose, maltose and dextrin. Glutinous-rice-starch was also hydrolyzed by a mineral acid to glucose.

RATIO OF DEXTRIN TO SUGAR IN THE CONVERSION PRODUCTS.

Several experiments have been carried out for the purpose of comparing the amounts of maltose and dextrin produced by the action of diastase on different kinds of starch.

Five grams, calculated as dried substance of each sample of starches obtained from different sources, were mixed with 20 cc. of water and then 60 cc. of boiling water added. The starch solution was heated upon the water bath to insure a thorough gelatinization of the starch, and after cooling was digested with 20 cc. of the malt extract (20 grams of malt in 100 cc. of water) at 55° C. Control experiments were made in each case with malt extract alone, and the corrected values for the starch conversions were obtained by subtracting from the total value the values found in the check solutions:

ONE HOUR'S SACCHARIFICATION.

Starch.	Sample taken. Grams.	Calculated as dried matter. Grams.	Solid in saccharified solution calculated from the density. Grams.	Composition of conversion products. Grams.		$[\alpha]_D$ 3.96 observed.	$[\alpha]_D$ 3.96[1] calculated.
				Maltose.	Dextrin.		
Glutinous rice starch.	5.45	5.00	4.98	3.70	1.38	155.0°	155.37°
Potato starch........	5.59	5.00	5.01	4.55	0.44	142.5	143.35
Soluble starch.......	5.86	5.00	5.00	4.58	0.43	144.3	143.49
Common rice starch..	5.80	5.00	4.87	3.99	0.92	149.9	149.80
THIRTY MINUTES' SACCHARIFICATION.							
Glutinous rice starch.	5.45	5.0	4.92	3.28	1.82	162.0	161.23
Potato starch........	5.59	5.0	5.05	4.00	1.08	150.9	151.60
Soluble starch.......	5.86	5.0	5.02	4.21	0.86	149.2	148.86

In these experiments, the coloration of glutinous rice starch by iodine disappeared most rapidly.

These figures distinctly show that the proportionality of the conversion products of glutinous rice starch differs entirely from those obtained from the other starches, the former containing the greatest amount of dextrin and the least of maltose.

This result also shows that Shimoyama's statement that glutinous rice starch contains a great amount of Nageli's amylodextrin is erroneous, because the amylodextrin ought to be, according to Brown and Morris,[2] hydrolyzed by malt-diastase completely to maltose.

The author obtained an impure amylodextrin by the continued action of 10 per cent. hydrochloric acid on ungelatinized potato starch for about eleven months, and examined the behavior of this substance with baryta water. The result was that Nageli's amylodextrin precipitated difficultly with baryta water. This fact shows also the non-existence of amylodextrin in glutinous rice starch which latter is readily precipitated by baryta water.

The author has also made a comparative study on the action of koji-diastase upon different kinds of starch; the results were that the iodine coloration of glutinous rice starch vanished most rapidly, while the amount of dextrin contained in the conversion products of glutinous rice starch was greater than that of the similar products of the other starches.

This peculiarity is to be attributed to the characteristic nature of glutinous-rice-starch, and it seems probable that the glutinous-rice-starch contains a greater amount of amylopectin or some analogous constituent, from which is produced a dextrin, more slowly hydrolyzed by diastase than the common starch.

CONCLUSION.

The starch of glutinous rice is characterized by a red coloration with iodine. The microscopic characteristics of the starch granules and the hydrolyzed products do not appear to differ in any way from those of common rice starch. The starch of glutinous rice does not contain amylodextrin (Nageli's), erythrodextrin, and special albuminoids, which were by some investigators considered as the cause of the red coloration by iodine.

The author proposes the suggestion that the red coloration of that peculiar starch by iodine is probably to be attributed to the characteristic nature of the starch itself, which is capable of dissolving only a very minute amount of iodine, but not to the presence of other dextrins or albuminoids as propounded by other investigators. Moreover, the glutinous-rice-starch contains none of the common starch which is colored blue by iodine.

Another remarkable fact is that the glutinous-rice-starch is rapidly hydrolyzed by diastase to dextrin with the production of a less amount of maltose than in the case of potato or common rice starch. The author considers that the glutinous-rice-starch contains a greater amount of amylopectin or some analogous constituent, which produces a dextrin hydrolyzed more slowly by diastase than the ordinary starch.

It is very probable that there are many other cereals in nature, containing a similar variety of starch. The author found that glutinous millet starch behaves like glutinous-rice-starch. A similar starch has also been observed in "mochi-kibi," "morokoshi" and a variety of "kaoliang."

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THE EFFECT OF SULFUROUS ACID ON FERMENTATION ORGANISMS.[1]

By W. V. CRUESS.

Received April 18, 1912.

The effect of sulfurous acid on fermentation and on the quality and composition of wine depends to a very great extent upon its action on the organisms naturally occurring on the grapes. The natural fermentation of grape must is a mixed one brought about by wild yeasts, wine yeasts, and to a smaller degree by molds and bacteria. Several enologists[2] have claimed that the proper addition of SO_2 to must results in a selection of the ellipsoideus, or true wine yeast, and an elimination of other organisms so far as their activity during fermentation is concerned. This gives a cleaner fermentation and a sounder wine than would result from the same must untreated with SO_2. During the vintage of 1911, laboratory and winery tests were made to observe the effect of sulfurous acid on the microörganisms occurring on California grapes.

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[1] Factors employed were: $[\alpha]_D$ 138° for maltose, $[\alpha]_D$ 202° for dextrose.

[2] Brown and Morris, *J. Soc. Chem.*, **1889**, 449.

[1] This work was undertaken at the suggestion and under the general direction of Prof. F. T. Bioletti, Univ. Calif., College of Agriculture.

[2] F. T. Bioletti, *Bulletin* **213**, Univ. Calif. Expt. Sta.; A. Bouffard, *Progres Agricole et Viticole*, **34**, 221–6, 394–8; **31**, 18–21; J. Ventre, *Ibid.*, **42**, 262–71; Chancrin, *Le Vin*, pp. 33–4.

The following table is given to indicate the relative susceptibility to SO_2 of pure cultures of various organisms under the conditions of experiments carried out in the laboratory. The active cells in several flasks, each containing 500 cc. of must inoculated with some one of the organisms listed in the table, were counted by dilution in must agar agar. The must was then divided into 100 cc. portions in small bottles. To these 50, 100, 200 and 400 mg. per liter of SO_2 respectively in the form of $K_2S_2O_5$ were added. The cultures were then allowed to stand at room temperature (20° C.), for thirty-six hours when counts of the active cells were again made by dilution on must agar. In taking the samples it was necessary to shake the flasks in order to avoid any loss of cells due to settling out. A comparison of the active cells before and after exposure to SO_2 should give an idea of the relative susceptibility of the various organsims tested to SO_2.

Table I.—Relative Resistance of Various Pure Cultures to SO_2.

Organism.	SO_2 in mg. per liter.	Original No. of cells per cc.	Cells per cc. after 36 hours exposure to SO_2.
Burgundy wine yeast..............	50	20,000	640,000
	100	20,000	2,000,000
	200	20,000	310,000
	400	20,000	36,000
Apiculatus yeast from California grapes........................	50	150,000	200,000
	100	150,000	75,000
	200	150,000	56,000
	400	150,000	0
Penicillium from California grapes....	50	120,000	40,000
	100	120,000	0
	200	120,000	0
	400	120,000	0
Aspergillus Niger from California grapes........................	50	450,000	120,000
	100	450,000	20,000
	200	450,000	30,000
	400	450,000	0
Wild yeast (pastorianus type) from California grapes................	50	620,000	580,000
	100	620,000	6,000
	200	620,000	190
	400	620,000	0
Vinegar bacteria from California grapes........................	50	310,000	14,000
	100	310,000	300
	200	310,000	2
	400	310,000	0

An examination of the above table shows that the ellipsoideus yeast, represented by the Burgundy wine yeast, is far more resistant to the inhibiting effect of sulfurous acid than the other microörganisms tested. Its numbers were not diminished by any of the amounts of SO_2 used and only with the very large dose of 400 mg. per liter was its increase prevented.

The apiculatus was able to increase slightly in the presence of 50 mg. of total SO_2 per liter, but 100 mg. per liter greatly reduced its numbers, and after exposure to 400 mg. per liter none of the cells of this yeast were able to develop on nutrient agar.

The ordinary green mold, Penicillium is seen to be very susceptible to sulfurous acid, 50 mg. per liter of SO_2 diminishing the number of active cells from 120,000 per cc. to 40,000 per cc. and 100 mg. or over per litre completely inhibiting its growth under the conditions of the experiment.

The Aspergillus was considerably more resistant than the Penicillium since it took 400 mg. per liter of sulfurous acid to render all the cells incapable of developing. It is to be noted, however, that it did not increase in numbers during the exposure to any of the amounts used, indicating a decided inhibiting effect, even with such a small dose as 50 mg. SO_2 per liter.

The wild yeast of the pastorianus type was even more sensitive than the apiculatus yeast and was prevented from increasing by a dose of 50 mg. per liter of SO_2, 100 and 200 mg. of SO_2 per liter reduced the number of active cells and 400 mg. per liter rendered all of the cells incapable of growth when transferred to agar plates. Thus this type of wild yeast (very common on California grapes) is seen to be very susceptible to the inhibiting effect of SO_2.

The resistance of the vinegar bacteria culture used was very low, as 50 mg. of SO_2 per liter reduced the number of active cells 95.5 per cent., 100 mg. 99.9 per cent. and 200 mg. per liter rendered the must practically free from vinegar bacteria, capable of growth. None of the bacteria could develop after exposure to 400 mg. per liter of sulfurous acid.

The practical value of these differences in susceptibility to SO_2 is in cases where it is desired to ferment a must with the addition of pure yeast, or where a fermentation as free as possible from the active molds, apiculatus, and various wild yeasts is wanted. Müller-Thurgau[1] has shown that the apiculatus yeast is particularly harmful to the fermentation of ellipsoideus yeast. This is because it develops very rapidly, exhausts the nutriment that should go to the ellipsoideus yeast, and at the same time gives products that are injurious to the growth of the wine yeast. The apiculatus can be eliminated by doses of SO_2 that do not impair the vitality of the wine yeast. The green mold probably does very little harm during fermentation but it is especially troublesome when grapes are shipped a long distance to the winery, due to the fact that it attacks broken berries, giving a moldy taste and odor to the grapes. This difficulty can be obviated by crushing the grapes and hauling in tank cars in which the crushed grapes have been sulfited to prevent the development of the Penicillium. The aspergillus mold and the vinegar bacteria do little harm during fermentation and amounts of SO_2 that will remove the apiculatus and wild yeast will prevent the growth of the aspergillus and vinegar bacteria.

Tests made on fresh must and crushed grapes indicate that the ellipsoideus yeast occurring naturally on the grapes is more resistant to sulfurous acid than the other organisms associated with it. The following experiment was made on must from Palomino grapes that were especially moldy and broken, so that the results represent extreme conditions. The organisms in the fresh must were counted by dilution on nutrient agar. The must was then divided in 500 cc. portions among a series of quart jars and sulfited by the addition of $K_2S_2O_5$ to give the amounts of total SO_2 indicated. After three hours exposure to the sul-

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[1] *Lafar Technical Mycology*, [2] **2**, 436–42.

furous acid, counts were again made on the active cells.

TABLE II.—EFFECT OF SO_2 ON ORGANISMS IN WHITE MUST (LABORATORY TEST.)

No. of flask.	Mg. SO_2 per liter added.	Mold cells per cc.	Apiculatus cells per cc.	Ellipsoideus cells per cc.
Original must no SO_2	00	97,625	7,341,400	58,575
1	32	13,310	189,030	182,995
2	79	19,360	21,380	33,880
3	127	14,651	14,651	43,953
4	190	7,600	00	58,400
5	253	4,800	00	73,600

The results demonstrate that very small amounts of sulfurous acid inhibit the increase of molds and apiculatus occurring naturally on the Palomino grapes in question. A moderate dose of 190 mg. per liter rendered all of the apiculatus cells exposed to it incapable of development when transferred to nutrient agar agar. The mold spores were more resistant, but were reduced in numbers in all cases. This indicates that they could do but little harm, since the ellipsoideus yeast would soon outgrow them and make the growth of the mold impossible by the exhaustion of the oxygen and the formation of alcohol. This conclusion is justified by the fact that the ellipsoideus yeast was not reduced in numbers by the amounts of SO_2 used above.

A test on a large vat of crushed grapes of the Zinfandel variety gave results similar to those on the Palomino must. The counts were made on average samples of the crushed grapes taken from the vat.

TABLE III.—EFFECT OF SO_2 ON ORGANISMS IN MUST FROM RED WINE GRAPES.

Sample.	Mold cells per cc.	Apiculatus cells per cc.	Wild yeast not apiculatus per cc.	Ellipsoideus yeast cells per cc.
Before sulfiting	1,600,000	2,830,000	30,000	120,000
One hour after sulfiting	None	None	None	560,000
After adding pure wine yeast	None	None	None	2,500,000

The molds and wild yeasts are seen to have been rendered incapable of developing after one hour's exposure to 120 mg. of SO_2 per liter. On the other hand the ellipsoideus yeast was apparently unaffected by the treatment, for it actually increased in numbers during this period. The addition of the pure Burgundy wine yeast greatly increased the number of wine yeast cells in the liquid. On sound grapes the numbers of ellipsoideus cells naturally present would be far less than indicated above, as these Zinfandel grapes had become moldy and broken during shipment to the winery. Thus in a normal must, that had been properly sulfited, the addition of the above amount of yeast (representing 1 per cent. of vigorously fermenting must) would insure a fermentation due almost entirely to the added yeast.

Sulfurous acid, usually in the form of potassium metabisulfite, is often employed for the defecation of white must to remove suspended solids. The effect of this practice on the organisms in the must is shown by the following tests:

TABLE IV.—EFFECT OF DEFECATION WITH SO_2 ON ORGANISMS IN MUST. Thompson seedless grapes; laboratory test.

Sample.	Mold cells per cc.	Yeast cells per cc.	Per cent. elimination of molds.	Per cent. elimination of yeast.
Original must	6,800	6,300	...	...
After 48 hrs. exposure to SO_2	None	11	100	99.84

TABLE V.—EFFECT OF DEFECATION ON ORGANISMS IN GREEN HUNGARIAN MUST. CELLAR TEST.

Sample.	Mold cells per cc.	Wild yeast cells per cc.	Ellipsoideus cells per cc.	Per cent. mold eliminated.	Per cent. wild yeast eliminated.	Per cent. ellipsoideus yeast eliminated.
Original must	29,262	8,603,000	29,262	...	...	...
After 32 hrs. defecation with 250 mg. per liter SO_2	256	none	493	99.12	100	98.32

TABLE VI.—PALOMINO MUST. CELLAR TEST.

Sample.	Mold cells per cc.	Apiculatus cells per cc.	Ellipsoideus cells per cc.	Per cent. mold eliminated.	Per cent. apiculatus eliminated.	Per cent. ellipsoideus eliminated.
Original must	112,658	1,565,500	529,133	...	..	...
After 3 hrs. defecation	35,937	226,270	585,640	68.1	85.6	...
After 8 hrs. defecation	44	660	13,800	99.96	99.6	97.91
After 20 hrs. defecation	10	None	16,280	99.99	100	96.92

The results demonstrate that defecation by the use of sulfurous acid is very effective in delaying fermentation by removing or inhibiting the growth of fermentation organisms. This permits of removal of suspended matter by sedimentation. Here, as in Table I, the molds are found to be more susceptible to SO_2 than the ellipsoideus yeast. The apiculatus is seen to be even less resistant than the mold. After defecation the clear must should be drawn off and fermented by the addition of a pure culture of selected wine yeast. This will give a fermentation practically free from injurious wild yeasts and molds.

The following experiment illustrates the effect of defecation by the use of SO_2 as applied to apple must on a laboratory scale. A count was made on the fresh juice by dilution on nutrient agar. The must was then divided among several flasks in 150 cc. portions. The quantities of SO_2 indicated were added and after 72 hours, counts were again made on the active cells.

TABLE VII.—EFFECT OF DEFECATION BY USE OF SO_2 ON APPLE MUST OF NEWTOWN PIPPIN APPLES GROWN IN CALIFORNIA.

Flask.	Period of defecation.	SO_2 in mg. per liter.	Mold cells per cc.	Wild yeast cells per cc.	Ellipsoideus cells per cc.
1	0 hrs.	00	100,000	Large number[1]	Very few[1]
2	72	00	50,000	5,000,000	5,000,000
3	72	100	00	00	2,700
4	72	200	00	00	300
5	72	300	00	00	00
6	72	400	00	00	00

TABLE VIII.—COUNTS OF CELLS IN SEDIMENT OF TABLE VII.

Flask.	Period of defecation.	SO_2 in mg. per liter.	Mold cells per cc.	Wild yeast cells per cc.	Ellipsoideus cells per cc.
3	72 hrs.	100	09	00	150,000
6	72 hrs.	400	00	00	1,200

The counts in Table VII were made from the super natant liquid and in Table VIII from the sediment. The

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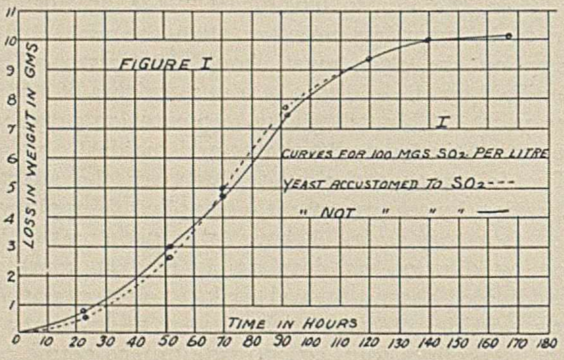
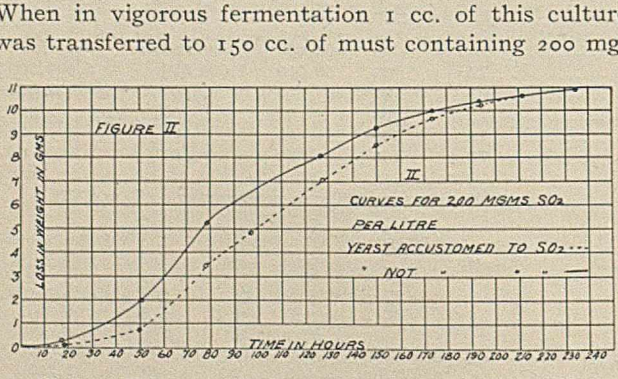
[1] The large number of mold cells present in must prevented a count of yeast colonies.

figures indicate that defecation by the use of sulfurous acid would be beneficial in the treatment of apple must, since it would result in the elimination of molds and wild yeasts and permit of fermenting the cider by the addition of pure selected cider yeast, after drawing off the defecated liquid. By comparing the results of Tables VII and VIII it is seen that the elimination of the ellipsoideus cells is largely due to settling out, whereas the effect on the molds and wild yeasts is due to the direct action of the sulfurous acid, since the number of ellipsoideus cells is greater in the sediment than in the supernatant liquid and the numbers of molds and wild yeasts are 00 in both cases.

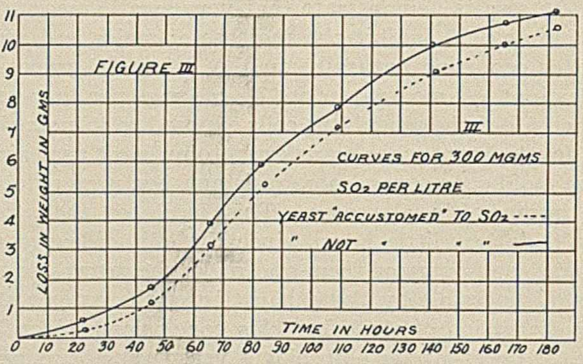
Some investigators have thought that the yeast that survives a given dose of sulfurous acid becomes more resistant to its effect. Taking this view, the ellipsoideus yeast that developed after sulfiting in the above tests would be a yeast accustomed to SO_2. To observe whether such an effect is produced a number of tests were made.

Burgundy wine yeast was grown in the presence of 100 mg. of sulfurous acid per liter. When in active fermentation 1 cc. of this culture was transferred to 150 cc. of must containing 100 mg. per liter of SO_2. A similar amount of must containing 100 mg. per liter of SO_2 was inoculated with 1 cc. of a vigorous culture of Burgundy wine yeast, grown in must to which no sulfurous acid had been added. The flasks were incubated at 32° C. and the rates of fermentation, as indicated by loss in weight, observed. The yeast, supposedly accustomed to SO_2, was then transferred to must containing 200 mg. per liter of sulfurous acid. When in vigorous fermentation 1 cc. of this culture was transferred to 150 cc. of must containing 200 mg. per liter of SO_2. A check flask containing 200 mg. per liter of SO_2 was inoculated with 1 cc. of a culture of Burgundy yeast unaccustomed to SO_2. The rates of fermentation were observed in each case. The above process was repeated in every respect with 300 mg. per liter of SO_2. The results of the tests are given in the accompanying curves.





At 100 mg. per liter the "yeast accustomed to SO_2" and the normal yeast gave practically the same kind of a fermentation. At 200 mg. per liter the yeast "accustomed to sulfurous acid" started more slowly than the other but finished in the same time. This indicates an increased susceptibility to SO_2, but not any decrease in fermentative activity. At 300 mg. the yeast "trained" to SO_2 showed a slower start of fermentation and a slower fermentation throughout. It is to be noted that the curve for the "accustomed" yeast in Fig. III does not cut the curve of the normal yeast during the fermentation period of the latter, although if the test had been carried far enough it would probably have done so. The curves, as they stand, show that the yeast unaccustomed to sulfurous acid had finished fermenting, whereas the other had not, at the end of the test. This indicates an increased susceptibility to SO_2 as well as a decrease in vitality, due no doubt to the long exposure to sulfurous acid. A number of similar laboratory tests of a qualitative nature bring out the same general features as indicated in the above tests, namely, that wine yeast (as typified by the Burgundy yeast) does not become accustomed to the action of sulfurous acid upon prolonged exposure to SO_2 in must, but tends to become more susceptible to it.



A test was made on the change of susceptibility to sulfurous acid of Burgundy wine yeast used at a winery during a vintage of six weeks. This yeast had been grown in must sulfited to remove the injurious organisms and theoretically should have become thoroughly accustomed to the effect of SO_2. The must in which it grew usually contained about 200 mg. per liter of sulfurous acid added in the form of $K_2S_2O_5$. This must was renewed at least once in every 24–72 hours so that the yeast was kept in a vigorous condition.

A series of flasks each containing 300 cc. of sterile must was inoculated with 1 per cent. of vigorously fermenting liquid from the yeast apparatus. The amounts of SO_2 indicated in the table were added in the form of $K_2S_2O_5$. A similar series with corresponding amounts of sulfurous acid was inoculated with the same variety of yeast, but yeast which had not been grown in the presence of SO_2. The rates of fermentation were observed in each flask.

TABLE IX.—SERIES I, YEAST NOT ACCUSTOMED TO SO_2.[1]

Date.	Hours.	Balling of flask A_1 100 mg. SO_2 per liter.	Balling of flask B_1 150 mg. SO_2 per liter.	Balling of flask C_1 200 mg. SO_2 per liter.
10/19/11 3 P.M.......	00	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/20/11 8 A.M.......	17	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/21/11 8 A.M.......	41	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/22/11 8 A.M.......	65	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/23/11 8 A.M.......	89	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/23/11 6 P.M.......	99	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/24/11 8 A.M.......	113	24.9	$25^1/_4$	$25^1/_4$
10/25/11 10 A.M......	139	24	$25^1/_4$	$25^1/_4$
10/26/11 10 A.M......	163	18	25	25
10/27/11 10 A.M......	187	13.5	20	21
10/28/11 2 P.M.......	215	6	10.5	14
10/29/11 9 A.M.......	234	3.5	7	8.5
10/30/11 9 A.M.......	258	0.5	4	5
10/31/11 10 A.M......	283	0	0.75	1
11/1/11 10 A.M.......	307	0	0	0

[1] Slow start of fermentation was due to fact that no incubator was available at winery so that the temperature was too low for rapid start of fermentation.

TABLE X.—SERIES, II YEAST "ACCUSTOMED" TO SO_2.

Date.	Hours.	Balling of flask A_2 100 mg. SO_2 per liter.	Balling of flask B_2 150 mg. SO_2 per liter.	Balling of flask C_2 200 mg. SO_2 per liter.
10/19/11 3 P.M.......	0	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/20/11 8 A.M.......	17	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/21/11 8 A.M.......	41	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/22/11 8 A.M.......	65	$25^1/_4$	$25^1/_4$	$25^1/_4$
10/23/11 8 A.M.......	89	$25^1/_4$	$25/^1{}_4$	$25^1/_4$
10/24/11 8 A.M.......	113	25	$25^1/_4$	$25^1/_4$
10/25/11 10 A.M......	139	24	$25^1/_4$	$25^1/_4$
10/26/11 10 A.M......	163	16	$25^1/_4$	$25^1/_4$
10/27/11 10 A.M......	187	11.5	$25^1/_4$	$25^1/_4$
10/28/11 2 P.M.......	215	5	$25^1/_4$	$25^1/_4$
10/29/11 9 A.M.......	234	2.5	$25^1/_4$	$25^1/_4$
10/30/11 9 A.M.......	258	0	$25^1/_4$	$25^1/_4$

The results are decidedly in favor of the yeast unaccustomed to sulfurous acid. Flasks B_2 and C_2 of the series with the "accustomed" yeast did not ferment, whereas the corresponding flasks A_1 and B_1 in the other series fermented out dry. A_2, however, fermented just as rapidly as A_1. This indicates that the yeast grown in the presence of SO_2 in the pure yeast apparatus had become more susceptible to the inhibiting action of SO_2, but where fermentation took place its rate of fermentation had not become reduced.

SUMMARY.

From the observations given it is seen that sulfurous acid may be used to advantage in inhibiting the growth of wild yeast molds, and vinegar bacteria, such as occur on California grapes and at the same time permit the vigorous development of the true wine yeast Saccharomyces ellipsoideus, naturally on the grapes, or added as starter.

Wine yeast can not be trained to become more resistant to SO_2 in appreciable quantities. Therefore, the present idea of going through a troublesome process of "accustoming" wine yeast to SO_2 does not seem to be based on the proper principles. A better way, no doubt, would be to sulfite the must to be fermented in order to eliminate molds, wild yeasts, etc., and then ferment it with a starter of pure wine yeast (or if it is apple juice, with pure cider yeast) that has been grown in musts free from sulfurous acid.

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CONCERNING THE SUGAR CONTENT OF WATERMELONS.

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Received January 24, 1912.

The literature on the sugar content of watermelons is comparatively meagre. Wiley[1] has examined the sugar content of melons, and for the average reducing sugar content of watermelons has reported it as 4.33 per cent. of the meat-juice and 2.47 per cent. of the rind-juice. He reported the sucrose content as 1.92 per cent. of the meat-juice and 0.34 per cent. of the rind-juice. The ash value was given as 0.31 per cent. of the juice from the meat and 0.38 per cent. of the juice from the rind. Kremla,[2] by six different determinations, found the reducing sugar content to be 4.19 grams sugar per 100 cc. of the juice. Nardini[3] reported the following results from the Italian Experiment Station: Invert sugar, 4.94 per cent.; sucrose, 0.765 per cent.; ash, 0.168 per cent. Jaffa,[4] from the California Experiment Station, reported the ash content of the total melon as 1.41 per cent.

At the time our investigation was started we had access to melons that seemed sweeter than the usual melons found on the market. Since other chemists had made no statements showing that the melons they had examined were other than the average market melons, it seemed desirable to investigate these apparently sweeter melons and determine their sugar content. The melons were the usual melons grown in the vicinity of Bloomington, Indiana; they had very thin rinds and were less desirable melons, owing to the ease with which they were broken during shipment to market.

In the course of the investigation we studied the ratio of juice to pulp and rind; some work was done on the ash content of the juice, but the main work had to do with the sugars present in the strained juice. We were interested in the alcohol and acetic acid, respectively, that could be produced by the fermentation of the juice, and some results of that phase of the investigation are given. In order to carry on the work, about a dozen medium-sized melons were procured near the end of the season and were preserved by cutting the melon with a silver knife and scraping the juice and pulp by means of a watch glass—as long as any red meat remained attached to the rind. The juicy pulp was filtered in some cases through paper, but this became a very tedious process, owing to the tenacious silt, so the major part of the juice was simply strained through a well-washed cheesecloth and collected in quart bottles and liter flasks. These were plugged with cotton and immediately sterilized in a bacteriological autoclave at a pressure of 16 to 18 pounds for 30 minutes.

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[1] Wiley, U. S. Dept. of Agriculture, *Report*, **1886**, 345.

[2] Kremla, *Chemie der menschlichen Nahrungs- und Genüssmittel*, edit. 4, 1904, **1**, 1496; **2**, 921.

[3] Nardini, *Ibid.*, **1**, 1496.

[4] Jaffa, *Ibid.*

The various vessels were then removed, capped with sealing-wax and allowed to stand in a dark cupboard. With scarcely any exceptions the juice remained perfectly sterile until needed. In the bottom of each bottle was a small precipitate (white in the filtered sample, reddish brown in the strained sample) of coagulated material. This was very likely of a protein nature but it was not investigated. A few samples of the juice that had been neutralized before heating were slightly brown in color after the sterilization.

Eleven different juices, not counting several modifications of a single juice in a few instances, were carried through the various analytical processes employed.

No. 1 was the natural juice, acid in reaction, strained and filtered.

No. 2A was the strained juice of a melon that had been cracked, apparently very shortly before arrival at the laboratory.

No. 2B and 2C were from the same melon, which was quite ripe and in good condition. The juice 2B was strained and neutralized with sodium hydroxide solution. After heating, this juice was dark in color. The juice 2C, already acid in reaction, was strained and filtered through paper. This juice yielded no residue after sterilization.

No. 3 was the natural juice taken from an average melon.

No. 4A was also the juice from a melon quite the average of the lot.

No. 4 and 4N were taken from the same melon. The former was allowed to remain naturally acid, while the latter was neutralized before sterilization. The melon was ripe.

No. 5 was the juice from an average melon strained and left acid in reaction.

No. 6 was the juice from a melon which was slightly green. This juice yielded no residue on heating.

No. 7 and No. 8 were the juices from the two poorest melons—strained only.

No. 9A and No. 9B were duplicated from the same melon which was perhaps the best in the lot. The 9A juice was left acid. Juice 9B was filtered and the filtrate, also left acid in reaction, was clearer than No. 9A.

No. 10 and No. 10A were juices from two different average melons. In each case the acid juice was strained.

No. 11 and No. 11A were from the same melon. Both samples were strained: the former was allowed to remain acid in reaction while the latter juice was made neutral.

In the respective juices, the solids were determined by means of the Brix hydrometer (column II) with the filtered juice at the ordinary temperature. The results include the temperature correction. The solids in terms of cane sugar were sought in a portion of the juice by means of the immersion refractometer. The values depending on the refraction of the mixture (column III) were obtained by use of freshly-opened filtered juice. Temperature corrections are included in the results. Portions of the juices examined with the hydrometer and refractometer were defecated and again examined with the refractometer. In the defecation, 100 cc. of the juice were placed in a 200 cc. graduated flask. Several drops of basic lead acetate solution were added, the flask being carefully shaken after the addition of each drop of the reagent. When a yellowish white precipitate settled out, leaving a water-clear solution, three to five drops of glacial acetic acid were added. A good excess of lead acetate gave harmful results, so it was avoided. The defecated juice was diluted to the mark and filtered. By this method the filtrates were always well clarified. The total solids in terms of cane sugar, obtained by the use of the Zeiss immersion refractometer on the defecated juice, are shown in column IV.

TOTAL SOLIDS IN TERMS OF PER CENT CANE SUGAR.

I.	II.	III.	IV.
Sample 1	9.02	9.05	9.62
2C	9.64	9.51	8.10
2B	9.57	9.58	10.16
2A	9.62	9.90	10.10
3	9.23	9.75	11.76
4A	10.26	10.49	10.96
4	9.42	10.25	10.68
5	8.42	6.72	7.76
6	9.52	9.50	8.42
4N	9.82	10.28	10.76
9A	8.63	8.74	9.48
9B	9.07	9.02	9.56

The results in columns III and IV are based on Wagner's "Tabellen für Zeiss Eintauschen Refractometer" and include corrections for the instrument and the temperature employed.

SUCROSE.

The determination of the sucrose was brought about by means of the polariscope both before and after inversion of the defecated juice. The per cent. sucrose (column II) was calculated from the Clerget formula:

$$\text{Per cent. sucrose} = \frac{100\ (\text{Direct - Invert reading})}{142.66 - \frac{T}{2}}$$

In column III is given the per cent. sucrose found by the Fehling titration method (sucrose equivalent to the reducing sugars resulting from inversion, minus the reducing sugars found present prior to inversion). Column IV shows the same data expressed in terms of grams sucrose per 100 cc. of juice.

The method employed in the inversion of the sucrose was as follows: 50 cc. of the defecated juice which had been freed from lead salts were placed in a 100 cc. graduated flask; 25 cc. of water were added and then, while constantly rotating the flask, 5 cc. 38.8 per cent. HCl were slowly added. The flask was placed in a water bath already heated to 70° C. and the juice heated to 68–70° C. in approximately three minutes. The heating at this temperature was continued for about seven minutes. The flask was then removed from the bath and cooled to 20°–21° C. and diluted to 100 cc. Readings were taken with a decimeter tube and the readings were multiplied by 2 and calculated by the general formula given earlier in this paper.

I.	II.	III.	IV.
Sample 1	0.9972	0.820	0.892
2C	0.732	0.840	0.916
2B	0.973	1.141	1.468
2A	0.729	0.811	0.898
3	too dark	0.993	1.084
4A	0.920	1.149	1.230
4	1.119	1.102	1.204
5	1.599	1.550	1.789
6	1.416	1.404	1.533
4N	too dark	0.847	0.928
9A	1.639	1.617	2.011
9B	1.543	1.613	1.873
10A	0.757	...	0.905
10	1.101	...	1.434
11A	1.592	...	1.846
11	0.7669	...	0.988
8	0.733	...	1.066
7	0.720	...	0.990

REDUCING SUGARS.

The defecated juices obtained in the previous determinations were allowed to act on Fehling's solution in the usual way. Five cc. each of the alkali and copper solution were measured by a pipette to an Erlenmeyer flask, diluted with 40 cc. water brought to boiling and then allowed to react with the defecated juice. No indicator was used. The various sugar solutions gave the following results expressed in grams reducing sugar per 100 cc. of juice:

Sample 1	5.678
2C	5.510
2B	5.514
2A	5.969
3	4.343
4 A	4.313
4	5.037
5	5.163
6	5.485
4N	4.580
7	5.687
8	4.504
9A	4.846
9B	4.692

ACETIC ACID AND ALCOHOL.

After obtaining the foregoing sugar data it seemed desirable to ascertain the amount of alcohol and acetic acid, respectively, that could be obtained by the fermentation of the respective sugar solutions. These fermentations were carried out at 34°–35° C., and after distillation the alcohol and acetic acid recovered from each fermentation mixture were estimated by means of the Zeiss immersion refractometer. All results include corrections for the temperature and the instrument and are based on Wagner's "Tabellen." Owing to the rush of other work at the time this work was in progress we could not check the alcohol determinations by the specific gravity method nor the acetic acid by the titration method. The refractometer results are given for what they are worth. Column II shows the per cent. alcohol by weight in a given volume of liquid that was recoverable from the same volume of the corresponding juice. Column III shows the per cent. acetic acid by weight of a solution resulting from the fermentation of a similar quantity of the corresponding melon juice. In the alcohol distillations the usual precautions regarding the constant volume of the distilling mixture and the presence of calcium carbonate were observed. In the acetic acid distillations the same precautions regarding constant volume and the presence of phosphoric acid were used:

I.	II.	III.
Sample 1	2.45	1.86
2C	2.95	1.98
2B	1.87	2.18
2A	2.36	1.69
3	2.70	1.27
4	1.03	1.91
4A	2.70	1.69
4N	2.06	1.69
5	1.84	1.74
6	2.12	1.87
9A	3.06	lost
9B	2.85	lost
10A	2.73	lost
11	2.29	1.69
11A	2.39	1.54

In working up the melons our main efforts were directed in preserving the juice and incidentally we became interested in finding the ratio of pulp and rind to juice. The pulp and rind were weighed just after pressing, and the following results were obtained on a few of the average melons:

Sample.	Juice, Per cent.	Rind, Per cent.	Pulp, Per cent.	Total melon weight (grams).
3	41.2	49.7	9.1	6250
4	42.9	45.1	12.0	7250
5	42.5	47.1	10.5	7590
7	42.9	50.9	7.2	6000
8	51.5	41.4	7.1	4820

Although the above figures are only approximate it seems that a melon reasonably ripe and having a comparatively thin rind is about 40 per cent. juice. (Number 8 was an exceptional melon.)

PENTOSES.

With regard to the pentose content of the juice the investigations indicated that only a small amount of pentoses were present. Of Sample 2C, 50 cc. were boiled with HCl in the usual way, distilled and the distillate converted into the phloroglucid which was weighed. The latter corresponded to only 0.00236 gram pentose in the sample taken. No further work was done with the small amount of pentoses present.

ASH CONTENT.

The ash of three samples of the juice was investigated. The residue, on evaporation of the juice, was sulphated by the addition of 10 cc. conc. H_2SO_4 to the residue from 100 cc. of the juice. This sulphated juice was taken up in water, the insoluble portion again sulphated, extracted with water and the insoluble part weighed after ignition. The united extracts were evaporated and weighed:

Sample of juice.	Per cent. soluble ash.	Per cent. insoluble ash.
1	0.2328	0.038
2C	0.2019	0.02+
3	0.2103	0.030

CONCLUSIONS.

1. The melons examined were about 43 per cent. juice, 47 per cent. rind and 10 per cent. pulp.
2. The ash content was near 0.25 per cent. of the juice; of the ash, about one-eighth was insoluble.
3. On fermentation, the sugar present yielded an alcoholic solution containing about 2.5 per cent. alcohol by weight.

4. There could be obtained from the fermented melon juice an acetic acid solution that was about 1.75 per cent. pure acid.

5. The reducing sugars, by the Fehling titration method, were found to run near 5.5 per cent. of the juice. By the polariscope they were found in a smaller quantity usually. We are unable to explain the fact that the two methods do not run closer together. It would seem that the lead acetate defecation did not take out all the substances in the juice that might reduce Fehling's solution.

6. Usually more than 1.00 per cent. of the juice was sucrose.

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THE DETERMINATION OF BENZALDEHYDE IN MARASCHINO CHERRIES AND MARASCHINO LIQUEUR.

By A. G. Woodman and Lewis Davis.

Received April 9, 1912.

Comparatively recent investigations by food authorities into the composition of Maraschino cherries, and the possibility of distinguishing the genuine product from artificial imitations, have made desirable a method for the determination of small amounts of benzaldehyde, a common ingredient of food products of this nature.

For this purpose the method of determining benzaldehyde as the phenylhydrazone, originally proposed by Fischer[1] and adapted to the examination of almond extracts by Denis and Dunbar,[2] suggested itself. It was evident almost from the beginning, however, that this method, although satisfactory for the comparatively large amounts (0.1 gram) of benzaldehyde present in almond extracts, is not suitable for quantities as small as five milligrams, as found in Maraschino cherries. This is clearly shown in Table I, which gives the results obtained by the Denis and Dunbar method on known amounts of redistilled benzaldehyde dissolved in 95 per cent. alcohol. Blank determinations to correct for the effect of the reagent were made at the same time. The precipitate obtained in each case in the blank determination was of a gummy, resinous character, as was true also of the determinations involving the smaller amounts of benzaldehyde.

Table I.—Results Obtained by the Denis abd Dunbar Method.

Mg. benzaldehyde taken.	Mg. ppt. obtained.	Equivalent mg. benzaldehyde.	Per cent. of theory.	Mg. ppt. in blanks.
29.3	53.7	27.4	93.61	3.1
4.965	9.7	5.248	105.7	3.0
4.965	8.8	4.761	95.9	3.0
4.740	9.1	4.922	104.0	3.9
9.480	16.3	8.818	93.09	3.9

As shown in the table, the lowest value for the blanks was three milligrams, or almost 30 per cent. of the total weight of precipitate when five milligrams of benzaldehyde were present. The results differ quite widely, some being above and some below the theoretical value.

Further study of the method as applied to small amounts of benzaldehyde showed that the precipitation was markedly affected by several distinct factors. A high percentage of alcohol retarded or even prevented the precipitation, while too little alcohol tended to make the precipitates gummy instead of crystalline. The best results were obtained when the alcohol amounted to about ten per cent. by volume. It was found also that the weight obtained in the blank determinations was proportional to the length of time that the solutions stood after adding the reagent and before filtering, being reduced from 3.0 milligrams to 0.3 milligram for half an hour's standing. The character of the precipitate varied also with the length of time that the solution stood, being much lighter in color for the shorter time. The results obtained with known amounts of benzaldehyde by precipitating and allowing the solution to stand for half an hour were, however, too low, showing incomplete precipitation. It was found possible, however, to secure complete precipitation in ten minutes by shaking the solution in a stoppered flask after the addition of the reagent. About 95 to 97 per cent. of the theoretical values were obtained with five milligrams of benzaldehyde, while the weight of the blank did not exceed 0.5 milligram for 10 cc. of reagent. Some of the results obtained under these varying conditions are shown in Table II.

Table II.—Effect of Varying Conditions on the Precipitation of Benzaldehyde.

Mgs. benzaldehyde taken.	Mgs. ppt. (corrected).	Equivalent benzaldehyde.	Per cent. of theory.	Conditions of precipitation.
7.097	12.10	6.546	92.26	20 per cent. alcohol.
7.097	12.00	6.492	91.49	20 per cent. alcohol.
7.097	12.00	6.492	91.49	30 per cent. alcohol.
7.097	11.70	6.330	89.21	30 per cent. alcohol.
5.359	11.70	6.330	118.1	1 per cent. alcohol.
5.359	11.40	6.167	115.1	1 per cent. alcohol.
6.780	11.80	6.384	94.17	10 per cent. alcohol and 30 mg. acetaldehyde.
6.780	11.60	6.276	92.43	10 per cent. alcohol and 30 mg. acetaldehyde.
5.707	9.70	5.248	91.96	10 per cent. alcohol shaken 5 minutes with reagent.
5.707	9.20	4.977	87.22	10 per cent. alcohol stood over night before adding reagent.
6.690	10.60	5.735	85.72	
6.690	10.80	5.842	87.34	10 per cent. alcohol, total volume 200 cc.
6.700	10.80	5.842	87.20	
6.700	10.80	5.842	87.20	

To summarize these results briefly: The amount of alcohol present during the precipitation should be between 8 and 12 per cent. by volume. With 20 per cent. or more, the precipitation is incomplete, as might be predicted from considerations of solubility, no precipitation taking place at all with 50 per cent. of alcohol present. Too small an amount of alcohol tends to cause decomposition of the reagent, with consequent too high values for both the blanks and the benzaldehyde determinations. The presence of acetaldehyde has practically no effect on the precipitation, which is borne out by the fact that when acetaldehyde was present the blank determinations gave an increase of only 0.1 milligram over the 0.5 milligram usually obtained. Since the other alde-

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[1] *Z. anal. Chem.*, **25**, 230 (1885).

[2] This Journal, **1909**, 256.

hydes of this series are closely related to acetaldehyde in their chemical properties, it may fairly be assumed that the presence of aliphatic aldehydes, which are the ones most likely to be present in liqueurs like Maraschino, exercises no deleterious effect. On account of the relative solubility of benzaldehydephenylhydrazone, the volume of solution for precipitation should not exceed 110 cc.

From the above considerations and based on the experience gained in more than one hundred determinations on known amounts of benzaldehyde, the following procedure is recommended for its determination in Maraschino cherries and Maraschino liqueur.

Dilute 100 cc. of the liquor from Maraschino cherries, or 50 cc. of Maraschino liqueur to 140 cc. in a 500 cc. flask and distil 110 cc. Determine approximately the alcohol in the distillate, filtered if necessary, by the pycnometer or immersion refractometer. Transfer 100 cc. of the distillate to a 300 cc. Erlenmeyer flask and add alcohol or water, as may be necessary, so that the solution shall contain approximately ten per cent. of alcohol by volume. Add 100 cc. of the reagent prepared as directed below, stopper tightly with a rubber stopper, and shake vigorously for ten minutes. Remove any precipitate adhering to the stopper, and filter on a tared Gooch crucible, washing with cold water, and finally with about ten cc. of ten per cent. alcohol. Dry in a vacuum desiccator for 20–24 hours at about 20 cm. pressure, or, if preferred, in a vacuum oven at 70°–80° C. for three hours. The precipitate should be kept from strong light as far as possible. A blank determination must be run at the same time, deducting the weight obtained from that of the precipitate. With our reagent this blank has been usually 0.0005 gram. The corrected weight of the precipitate, multiplied by 0.5411, gives the weight of benzaldehyde.

Reagent.—Mix 3 cc. of glacial acetic acid with 40 cc. of water, add 2 cc. of phenylhydrazine, shake thoroughly, and filter the emulsion through several thicknesses of filter paper. The clear filtrate should be used immediately, as standing over five minutes gives a turbid reagent.

The phenylhydrazine should be chemically pure, free as far as possible from dark color and turbidity. Frequent agitation of the precipitate during filtration through a rotary motion of the flask prevents it from sticking to the sides. The determination of the benzaldehyde in the distillate should be carried out without delay to prevent loss by oxidation.

TABLE III.—BENZALDEHYDE IN 10 PER CENT. ALCOHOL.

Mg. benzaldehyde taken.	Mg. ppt. obtained (corrected).	Equivalent benzaldehyde.	Per cent. of theory.
5.359	9.5	5.140	95.90
6.363	11.5	6.212	97.77
6.595	11.7	6.330	95.98
48.30	86.8	46.96	97.23
81.80	146.7	79.38	97.03
5.408	9.5	5.140	94.99
8.230	14.6	7.900	95.98
9.930	17.6	9.521	95.90
81.12	144.8	78.34	96.58
81.12	145.0	78.45	96.72

The method can be applied to the determination of benzaldehyde in almond extracts, using 10 cc. of the extract diluted to 100 cc. with water, and 15 cc. of the reagent.

Typical results on known amounts of benzaldehyde by this method are shown in Table III.

The first six of the results in the table were obtained by direct determination on solutions of pure benzaldehyde. The remaining ones were distilled as directed in the procedure. Experimental evidence has shown that these dilute solutions of benzaldehyde can be distilled without material oxidation. Distilling in a current of carbon dioxide was tried but found to offer no advantage. The presence of considerable amounts of reducing sugars and sulphurous acid did not appreciably affect the distillation or determination.

The benzaldehyde content of some of the "Maraschino Cherries" and "Maraschino" liqueur on the market is shown in the following table:

TABLE IV.—BENZALDEHYDE CONTENT OF COMMERCIAL SAMPLES OF CHERRIES.

Brand.	Alcohol by volume.	Corrected wt. of precipitate.	Benzaldehyde. Mg. in 100 cc.
"Rosebuds"	0.0	8.70[1]	5.177
"Touraine"	0.0	53.00[1]	31.54
"Magnolia"	0.0	128.60[1]	76.54
Dandicolle & Gaudin	2.09	38.30	22.79
"Regina"	1.73	31.70	18.87
"Dupont"	4.97	53.90	32.07
"Bigarreaux"	4.27	20.40	14.29
Dalidet & Co.	7.96	14.30	8.509
Ginter Co.	0.0	16.00	10.58
"Percer"	6.19	60.60	36.07
Middleby Co.	0.0	6.900	4.106
MARASCHINO.			
G. Luxardo	32.60	...	3.57
Richelieux	25.94	...	17.02
Marie Brizard & Roger	28.97	...	0.0
Cusenier (cherry liqueur)	32.63	...	12.01
Cusenier (Maraschino)	19.00	...	0.0
Nuyens et Cie	24.78	...	1.78
H. Shufeldt & Co., Peoria, Ill.	30.60	...	41.3

[1] In the case of some samples which contained extract of syringa, the precipitate was colored orange-red, but was calculated as benzaldehyde.

Genuine Maraschino, apparently, has a very low content of benzaldehyde. Consequently, Maraschino cherries, which show a relatively large amount of benzaldehyde, are in all probability artificially flavored. Determinations of benzaldehyde on unflavored cherries have shown that more benzaldehyde would come from the cherries, themselves, than from genuine Maraschino added as a flavoring agent. However, the former does not exceed 3–4 milligrams per 100 grams of cherries. In general, then, it might be said that in a sample of cherries flavored with genuine Maraschino liqueur, the benzaldehyde, expressed in milligrams per 100 cc. of the liqueur, should not be more than two or three times the alcohol content, expressed in per cent. of volume. Samples containing practically no alcohol and above 20 mg. of benzaldehyde are evidently entirely artificial.

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COMMERCIAL CINNAMON AND CASSIA.

By Harry E. Sindall.

Received May 14, 1912.

The varieties of cinnamon and cassia on the market are rather numerous, and differ from each other considerably in flavor, strength, ash, volatile oil, alcohol extract, etc. Considering these differences it seems of interest to tabulate the composition of some of the more important varieties as shown by average samples of large lots ground in the commercial way. Among the commonest used are broken China, Ceylon chips, broken Batavia, Saigon and Seychelle cassia. In addition, some data are given on some cinnamons and cassias not so well known. Broken China is Cassia cinnamon,[1] sometimes known as China cassia or Canton cassia, and is cultivated in the southeastern provinces of the Chinese Empire and exported by the way of Calcutta. It occurs in quills usually shorter than those of Saigon. The bark is aromatic, and somewhat astringent. It is imported in large rattan bales, and used extensively in commerce. Ceylon cinnamon is collected from *Cinnamomum zeylaniuum*,[1] indigenous to and cultivated in the island of Ceylon. It comes in closely rolled double quills, composed of numerous thin layers of the inner bark of the shoots. The odor is delicately aromatic, and very distinct from either Cassia or Saigon bark. Ceylon chips consist of the small refuse of the whole bark, and apparently the great amount of dirt present is due to the fact that these pieces are collected off the ground for shipment. Ceylon chips are imported in large and heavy bales packed by a press. Its use in commerce is very limited on account of its dirty condition. Ceylon cinnamon contains from 0.5 to 1 per cent. volatile oil. Batavia cassia is the bark of *Cinnamomum Burmanni*.[1] It occurs in double quills, the larger sometimes enclosing the smaller quills, 5–8 cm. long, outer surface light or reddish brown, nearly smooth, inner surface dark brown with occasional depressed areas, odor and taste aromatic and distinctly mucilaginous. Broken Batavia consists of quills broken in small pieces, and is imported very clean in ordinary bagging and used extensively in commerce. Saigon cassia is obtained from *Cinnamomum Loureirii*,[1] and is cultivated in Cochin China, and parts of China, and exported from Saigon in bundles about 30–40 cm. long, 20 cm. wide, and 10 cm. thick, weighing about 1.5–2 kg., and consisting of pieces varying in size and color from small brownish black single quills to large thick grayish-brown transversely curved pieces. The odor is aromatic, taste mucilaginous, aromatic and pungent. It is used very extensively in commerce, is imported in wooden boxes covered with rattan, and is usually clean. Seychelle cassia comes from the islands of that name in the Indian Ocean. It is a very thick bark, mild in flavor and odor, and exceedingly clean. It is imported in ordinary bagging.

Table I gives the average, maximum, and minimum of total ash and acid insoluble ash, by years, of samples from large lots. The A. O. A. C. methods of analysis were used.

Table I.—Percentages.

Variety.	Samples.	Total ash.			Ash insoluble in HCl.		
Year 1908.		Max.	Min.	Av.	Max.	Min.	Av.
Broken China.......	(24)	7.47	3.12	4.79	4.17	0.69	2.02
Ceylon chips........	(4)	7.60	7.38	7.47	3.80	3.02	3.59
Broken Batavia....	(5)	5.00	4.31	4.68	1.71	1.13	1.40
Saigon.............	(9)	4.52	3.63	4.25	1.52	0.58	1.09
Seychelle..........	(4)	5.91	3.63	4.70	1.70	0.05	0.90
Year 1909.							
Broken China.......	(15)	4.26	3.37	3.77	1.53	0.94	1.20
Ceylon chips........	(4)	13.41	7.83	10.49	8.16	3.25	5.57
Broken Batavia....	(2)	3.96	3.63	3.79	0.19	0.16	0.18
Saigon.............	(2)	4.36	4.22	4.28	1.71	0.78	1.24
Seychelle..........	(6)	4.90	3.42	4.40	0.27	0.03	0.11
Year 1910.							
Broken China......	(2)	3.97	3.71	3.84	1.27	1.24	1.25
Ceylon chips........	(4)	8.39	5.88	7.15	4.18	0.51	2.32
Broken Batavia....	(4)	3.90	3.57	3.78	0.34	0.25	0.29
Year 1911.							
Broken China.......	(14)	3.72	2.78	3.27	1.00	0.50	0.76
Broken Batavia....	(7)	5.04	3.57	4.32	0.86	0.21	0.48
Saigon.............	(6)	4.80	3.71	4.21	0.79	0.43	0.66
Seychelle..........	(4)	4.80	3.57	4.10	0.61	0.28	0.38

As the table shows, prior to 1909, the quality of broken China imported made it a difficult problem for the spice grinders to conform with the maximum total ash and acid insoluble ash standards of six and two per cent., respectively, given in Circular No. 19, Office of the Secretary of Agriculture, because the bales were often full of pebbles and dirt. However, after the Food Inspection Officials had rejected an importation, broken China changed for the better, and unless very cheap material is bought the spice grinder has very little trouble with this variety today.

Table II shows analyses of samples of other varieties ground in small lots in the laboratory. The flavors of these samples vary from the mild Seychelle cassia to the strong Saigon. The barks with the exception of the Seychelles and Batavias are dark in color, but vary in thickness and shape. The volatile ether extract on which the strength of the flavor is supposed to depend varies remarkably as also does the crude fiber.

Table II.—Percentages.

Variety.	Total ash.	Water soluble ash.	Ash insoluble in HCl.	Volatile ether ext.	Non-volatile ether ext.	Alcohol ext.	Crude fiber.
Seychelle bark (*a*)......	4.08	2.54	0.29	0.66	1.87	9.16	49.49
Seychelle bark (*b*)......	5.49	2.73	0.07	0.70	1.99	9.72	44.66
Ordinary broken China.	3.96	0.91	1.24	0.90	2.91	3.76	24.84
No. 1 broken Saigon....	3.77	1.25	0.05	3.39	4.13	7.80	25.29
Extra No. 1 Batavia...	2.92	0.71	0.09	2.45	2.95	9.07	13.33
Pakhoi rolls...........	2.62	0.82	0.33	1.16	2.58	8.86	21.07
Coarse Corintjie........	3.14	1.09	0.48	2.23	3.52	5.24	28.16
Regular No. 1 Corintjie.	5.97	2.08	0.13	1.33	4.45	6.78	19.04
China rolls............	2.85	0.64	0.15	1.64	3.32	7.14	24.73
Good short stock Batavia	4.10	1.67	0.19	2.49	4.10	9.38	14.08
Kwangsi rolls 3rd......	3.39	1.45	0.21	2.71	4.45	6.78	18.61

Table III gives analyses of twelve samples of ground cinnamon purchased in retail packages and representing the general character of the cinnamon offered to the consumer in the eastern market.

These samples are blends of the different varieties, and with a few exceptions comply with the standards of Circular No. 19. It would appear that by using ordinary caution in buying and blending, no difficulty should be experienced in complying with the standards of Circular No. 19 in regard to total and acid insoluble ash. It must be understood that the spice grinder

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[1] Kraemer's "Botany and Pharmacognosy," 2nd Ed., pp. 513–16.

TABLE III.—PERCENTAGES.

Samples.	Total ash.	Water sol. ash.	Ash insol. in HCl.	Volatile ether ext.	Non-volatile ether ext.	Alcohol ext.	Crude fiber.
1........	6.90	1.34	2.64	1.44	2.85	10.68	36.88
2........	3.37	0.92	0.90	1.83	3.89	6.28	28.88
3........	6.88	0.78	2.80	1.68	3.80	6.28	31.14
4........	9.35	0.86	6.11	1.81	3.40	6.80	29.10
5........	3.44	1.28	0.43	0.67	1.88	7.76	23.40
6........	3.50	0.85	1.03	1.58	3.80	8.08	25.06
7........	3.53	1.19	0.49	0.93	2.01	7.66	24.30
8........	3.88	1.32	0.31	1.03	2.88	6.74	26.96
9........	4.75	1.07	1.54	1.40	3.01	7.76	23.34
10........	2.52	0.09	0.15	0.79	1.92	8.46	27.16
11........	3.50	1.08	0.45	0.72	1.42	6.04	23.74
12........	4.15	1.34	0.64	0.63	1.91	7.88	26.49

does not practice blending to work in dirty material, but because blending is necessary to obtain the desired flavor that is demanded by the trade.

LABORATORY WEIKEL & SMITH SPICE CO.,
PHILADELPHIA, PA.

THE RIPENING OF HOPS.

By C. E. BRADLEY AND H. V. TARTAR.

Received April 22, 1912.

The changes which take place in the chemical composition of the hop cone during the ripening period are of interest both from the scientific and from the technical standpoint. Although the composition of the bitter principles of the hop has been known for a long time, their chemical constitution is a perplexing subject which has in recent times engaged the attention of a number of investigators. From their studies, it appears that some of the constituents of the hop cone are closely related in chemical composition, and it is quite possible that changes take place during the ripening period in which one constituent passes over into the form of another. If this does occur, a study of the composition of the hop cone at different stages of ripeness might be valuable in throwing light on the chemical constitution of the different bitter principles.

From the technical standpoint, it is important that hops should be picked at the degree of ripeness when they possess the maximum brewing value. Recent investigations show that the major part of the actual brewing value of hops lies in the content of soft bitter resins, and hence the amount of these constituents in the hop cone at different stages of ripeness is of prime importance. At present, many brewers, regardless of intrinsic value, insist that hops should be picked somewhat green while others prefer to have the cones fully ripened. As a result, the hop growers who desire to produce a product of high quality are at a loss to know just when to gather their crops.

Because of the nature of the literature on the chemical composition of the hop, it may be well to state, by way of explanation, that investigators are agreed that the principal constituents of the hop cone are: a volatile oil, a hard resin commonly designated as the "gamma" resin, two soft bitter resins designated as the "alpha" and "beta" resins, a wax, and a tannin. The constituents designated as resins are not true resins, but owing to the common use of the term in this connection, the authors have continued its use. The recent work of Siller[1] indicates that the gamma resin may be composed of two different substances, but the work is hardly conclusive and we believe needs further study.

EXPERIMENTAL PART.

In August, 1910, a study was begun at this laboratory of the composition of the hop cone at different stages of the ripening period. The samples were gathered approximately five days apart, the first being picked August 11th, the last September 26th, and all taken from the yard of the Seavy Hop Company, near Corvallis, Oregon. In collecting, representative cones of various sizes were taken from the upper and outer portion of the vines, which was well exposed to the sun. On August 11th, two samples were secured, one being of the smaller and the other of the larger and more fully developed cones.

Very soon after the samples were gathered they were spread out and allowed to dry in the shade at room temperature. When the drying operation was complete, the hops were bagged, great care being taken not to crush the cones and to avoid loss of the lupulin through sifting.

In the analytical work, the method of the authors[2] for the determination of the hard, total, and soft (bitter) resins was employed. The separation of the alpha and beta bitter resins was carried out according to the method outlined by Siller.[3] Chapman's[4] method was used for the determination of tannin. Moisture was estimated by drying *in vacuo* over sulfuric acid at room temperature. The determination of the wax was made incident to securing the solutions

COMPOSITION OF HOP CONES AT DIFFERENT STAGES OF THE RIPENING PERIOD.

Sample No.	Date of picking.	Moisture percentages.	Dry matter percentages.	Composition of Dry Matter (Percentages). Wax.	Total resins.	Total soft bitter resins.	Alpha resin.	Beta resin.	Gamma resin.	Tannin.
1	Aug. 11 (cones smaller size).	8.07	91.93	0.52	10.39	8.44	1.88	6.56	1.95	3.48
2	Aug. 11 (cones larger size). .	7.32	92.68	0.57	12.20	10.76	2.74	8.02	1.44	2.92
3	Aug 16...................	7.71	92.29	0.37	14.07	12.56	3.53	9.03	1.51	2.98
4	Aug. 21...................	10.67	89.33	0.55	15.00	13.76	3.84	9.92	1.24	2.59
5	Aug. 26...................	10.12	89.88	0.34	16.24	14.51	3.92	10.59	1.73	2.88
6	Aug. 31...................	9.31	90.69	0.46	16.48	15.17	4.82	10.35	1.31	3.06
7	Sept. 5...................	8.60	91.40	0.35	18.39	16.79	6.27	10.52	1.60	2.81
8	Sept. 11...................	9.42	90.58	0.32	20.48	18.24	7.07	11.17	2.24	3.36
9	Sept. 19...................	8.87	91.13	0.38	20.57	18.41	8.47	9.94	2.16	3.28
10	Sept. 26...................	7.30	92.70	0.33	20.67	19.41	8.40	11.01	1.26	2.76

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[1] *Ztg. Untersuch. Nahrung-Genuss.*, **18**, 241.

[2] THIS JOURNAL, **4**, 209 (1912).

[3] *Ztg. Untersuch. Nahrung-Genuss.*, **18**, 241.

[4] *J. Inst. Brew.*, **13**, 646 (1907); **15**, 360 (1909).

necessary to the determination of the total resins. The extract obtained from extracting the hops with ether was taken up with alcohol, and the wax, insoluble in this solvent, was collected on a tared filter, washed with alcohol, dried at room temperature and weighed. Owing to the exceedingly small amount of volatile oil present and the consequent difficulty of making a quantitative estimation, the determination of this constituent was omitted.

The results of the analyses are given in the preceding table. In order to afford an accurate comparison, the amounts of wax, tannin, and the different resins have been calculated to dry matter.

The results show that there is a continuous increase in the amount of soft bitter resins throughout the ripening period. The riper the hop, the richer it is in these substances and if high soft bitter resin content is a criterion of brewing value, the fully ripened hop is much to be preferred. The ratio of the amount of alpha bitter resin to the amount of beta bitter resin is of interest. On August 11th, the ratio was 1 : 3.48, while on September 26th, it was 1 : 1.30. Between the first picking and the last, the amount of alpha bitter resin increased 450.5 per cent., while the beta bitter resin increased but 167.8 per cent. There seems to be no marked change during the ripening period in the amount of gamma resin, wax and tannin. From the analytical data, there is also no evidence that one constituent changes to the form of another during the process of ripening.

Agricultural Experiment Station,
Corvallis, Oregon.

ANALYSES OF SOME FATS OF THE AMERICAN BUFFALO (BISON).

By Albert H. Schmidt.

Received March 1, 1912.

During the month of December, 1905, there was sold in the Union Stock Yards a mixed car lot of stock, consisting of some cattle, a few so-called Cattaloes—a cross between cattle and buffalo—and one pure bred specimen of the buffalo, or American bison. I obtained five different kinds of the fats of this particular animal and analyzed them.

Having gone over all the available literature on fats and oils and found no reference to previous analyses of buffalo fats, I believe it may be of interest to place on record the analyses of various fats of an animal that is now almost extinct on our continent.

For comparison, I also obtained samples of the corresponding fats from a lot of native steers ranging in age from two to four years. These fats as well as the buffalo fats were rendered in the laboratory.

The one striking point is the difference in the kidney fats of the cattle as compared with the buffalo. This is no doubt due to the difference in size of the kidneys of the buffalo, as compared with cattle. The buffalo kidney is about one-half the size of the cattle kidney and is surrounded by a compact and comparatively small amount of fatty tissue, whereas the cattle kidney is large, and in native cattle is surrounded by a large mass of fatty tissue which is much softer and less firm than the fatty tissue of this particular buffalo.

Analyses of Buffalo Fats.

Name of fat.	Sp. gr. at 15°.	Free fatty acids.	Titer.	Iodine No.[1]	Saponification No.
Caul fat........	0.9263	0.90%	50.1° C.	33.23	200.6
Kidney fat......	0.9346	1.65%	52.2° C.	29.45	199.3
Ruffle fat.......	0.9364	1.90%	51.0° C.	32.50	199.4
Paunch fat......	0.9244	1.50%	47.4° C.	34.92	204.2
Chip fat........	0.9344	1.25%	49.6° C.	35.16	199.5

Analyses of Fats of Native Steers, Two to Four Years Old.

Name of fat.	Sp. gr. at 15°.	Free fatty acids.	Titer.	Iodine No.[1]	Saponification No.
Caul fat.........	0.937	0.30%	48.8° C.	36.10	203.0
Kidney fat.......	0.933	0.60%	42.85° C.	48.86	196.0
Ruffle fat........	0.932	0.25%	48.6° C.	36.13	199.0
Paunch fat.......	0.934	0.20%	43.8° C.	46.04	201.3
Chip fat.........	0.937	0.25%	43.4° C.	47.20	196.8

This anatomical difference in size of the buffalo kidney as compared with its close relative, the cattle, is not readily explained. In its wild state the buffalo was often without water for three or four days when roaming over our semi-arid plains. What bearing this may have on the size of the kidneys of animals living under such conditions is open to question.

The hindquarters of the buffalo are far lighter than those of cattle and, therefore, it is logical to assume that the organs in the posterior part of the buffalo would be smaller than the corresponding organs of cattle.

I am not able to account for the high percentage of free fatty acid in the buffalo fats, as they were rendered when comparatively fresh and in the same manner as the cattle fats. I had no record of the age of this buffalo bull at the time of slaughter, but was told that it was about seven or eight years old.

Laboratory of Sulzberger & Sons Company,
Chicago.

THE DETERMINATION OF EUCALYPTOL (CINEOL) IN ESSENTIAL OILS.[2]

By Francis D. Dodge.

Received May 15, 1912.

The methods so far suggested for the determination of eucalyptol in essential oils have proved rather unsatisfactory, for, although eucalyptol possesses to an unusual degree the capacity of forming molecular compounds with a variety of other substances, these compounds are not, in general, easily purified, nor stable enough to be utilized for analytical purposes.

The hydrochloride, hydrobromide, phosphate, arsenate, oxalate and ferrocyanide have been described, as well as the compounds with iodol beta-naphthol, and resorcinol, but the attempts to make any of these the basis of an assay method have not been very successful. After much fruitless experiment along this line, I was compelled to abandon the compounds of eucalyptol, and endeavored to utilize another property, namely, its stability to cold permanganate solution.

Eucalyptol, being a saturated cyclic compound, of considerable stability to alkaline reagents, is practi-

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[1] Iodine numbers determined by Wijs' method.

[2] Read before N. Y. Sec. Am. Chem. Soc., April 8, 1910.

cally unaffected by cold permanganate, whereas all terpenes and unsaturated compounds are oxidized, more or less readily, to soluble products.

The unattacked eucalyptol can be measured, and its purity confirmed by physical tests.

The assay may be conducted as follows: 10 cc. of the oil (eucalyptus or cajeput) are run into a 500 cc. flask having a narrow neck, and 5–6 per cent. $KMnO_4$ solution added in small portions, with shaking, keeping the flask in ice water, until the reagent is no longer reduced. The amount required will vary from 100 cc. for rich oils to 400 cc. for inferior ones. When an excess of permanganate has been added, the flask is kept cold, with occasional shaking, for 12–18 hours. The precipitated manganic oxide is then dissolved by sufficient sulphurous acid (or sodium bisulphite and hydrochloric acid) and the flask filled with water, allowing the unoxidized oil to collect in the neck. After settling, the oil is transferred by a capillary pipette, to a graduated tube, washed with a little alkali to remove traces of sulphurous acid, and the volume read off.

All reagents should be perfectly clear, or filtered if necessary.

The eucalyptol thus obtained should show:

Sp. gr. at 15°, 0.929–0.930.

Opt. rotation, ±0°.

Soluble in $3^1/_2$ volumes 60 per cent. alcohol at 25°.

This method has been used for several years with very satisfactory results. Examples:

	S. G.	O. R.	Per cent. E. by vol.	S. G. of E.
Oil eucalyptus........	0.928 @ 15°	+0.05°	85	0.929
	0.923 @ 15°	+0.55°	81	0.929
	0.915 @ 15°	—3.15°	52	0.929
	0.908 @ 25°	+0.50°	68	0.929
	0.905 @ 25°	—6.0°	66	0.930
	0.098 @ 25°	—4.16°	74	0.928
Oil cajeput...........	0.913 @ 25°	—2.10°	60	0.929
	0.916 @ 25°	—1.45°	61	0.927
	0.914	—1.96°	56	...

Check assays on known mixtures of eucalyptol, terpenes, and terpineol, have shown the reliability of the method for technical work.

The isolation of the eucalyptol in a pure state is a great advantage, as any stable compounds which might be present are immediately manifested by their effect on the physical constants. Thus:

+ Camphor (stable to $KMnO_4$) increases S. G. and shows + O. R.

Inactive camphor (stable to $KMnO_4$) increases S. G.

Fenchone (stable to $KMnO_4$) increases S. G. and shows + O. R.

Paraffins or petroleum products increased, diminish S. G. and solubility.

Borneol (oxidized to camphor).

Menthol (oxidized to menthone).

Menthone (slowly oxidized) diminishes S. G. and shows O. R.

Bornyl acetate (stable) increases S. G. and shows O. R.

The method as outlined is, I believe, the only direct method among those applicable to constituents of the essential oils, *i. e.*, one in which the compound to be estimated is isolated in a pure and determinable shape.

LABORATORY DODGE & OLCOTT CO.,
BAYONNE, N. J.

RECENT ANALYSES OF THE SARATOGA MINERAL WATERS.

By LESLIE RUSSELL MILFORD.

Received February 21, 1912.

GENERAL.

This group of mineral springs is recognized as one of New York State's unique natural resources, and their discovery dates back to 1767 when, according to tradition, the Indians brought Sir William Johnson to the High Rock Spring to be treated for gout.

The general belief is that the wells and springs in this region have a common source far down in the earth and situated along a geological fault, the strata at the west being many feet above those corresponding in the east.

The minerals are held in solution by the great amount of carbon dioxide which saturates the waters along the mineral stratum. This stratum is supposed to be the remains of an extinct volcano or the remnant of a Silurian Ocean. It was through this geological fault that the springs found their way to the surface flowing by their own gas pressure.

The popularity of these springs soon became known, and a water resort of great therapeutic value, resembling, in quality, the famous French Vichy, was given to the public.

The springs and wells at Saratoga may be divided into three groups: Geysers Park, Congress Park, and High Rock Park, each of which contains its supply of mineral waters.

About fifteen years ago it was discovered that the carbon dioxide with which these mineral waters were charged could be profitably separated from the waters and sold. A large industry soon became established in Saratoga, companies being formed, generally called "gas companies," for the promotion of the industry. At first these gas companies extracted the carbon dioxide from what were called "dry wells" or "pockets" and also from the mineral water as it naturally issued from the ground. But later it was discovered that by pumping with more powerful and modern machinery a far larger amount of mineral water could be forced from the ground and consequently more gas extracted.

This pumping soon began to have a marked effect on the other springs, causing a diminution in flow and alteration of the minerals in solution. A great amount of litigation was soon begun between the spring owners and the gas companies, the spring owners showing that pumping affected the flow of their springs and the "gas companies" asserting a property in the flow of the mineral waters from the springs on or under their lands. The result of this agitation over the effect of pumping caused an "anti-pumping law" to be passed by the legislature in 1908. The passage of this act was followed by more lawsuits extending over a period of many months. The need of unified ownership in the springs became apparent and the legislature in 1909 passed an act appointing the Commissioners of the State Reservation at Saratoga Springs, who at once began their duties of preserving the springs and restoring them to their former natural condition.

To aid them in their work special investigations were undertaken by the Division of Laboratories of the State Department of Health at the request of the Saratoga Reservation Commission.

The analyses, and their explanations which follow, represent the work which has been recently completed and a part of the series of the analyses which are to be made.

The writer personally collected and sealed the samples in 5-gallon demijohns so that the analyses are known to be from true samples of the mineral water as it came from the source.

An important feature to note with this work is that the State Hygienic Laboratory is only forty miles from the Reservation at Saratoga so that a great amount of field work was easily carried on in connection with the laboratory examinations. Also a quick

CONSTITUENTS AS ACTUALLY DETERMINED.

	Hathorn Spring No. 1.			Coesa (Carlsbad) Spring.			Hathorn Spring No. 2.	Hathorn Spring No. 3.
	1.	2.	3.	4.	5.	6.	7.	8.
Formula.			Results in milligrams per liter.					
SiO_2	21.58	19.60	13.85	8.60	13.50	7.70	8.15	8.50
SO_4	trace	5.60	21.42	3.77	2.80	27.00	12.60	6.60
HCO_3	4354.14	3585.60	2219.00	4746.34	4244.50	3912.50	5677.90	5581.60
NO_3	*a*	none	none	*a*	none	none	none	trace
NO_2	*a*	none	trace	*a*	none	none	none	none
PO_4	0.05	none	none	*a*	none	none	none	none
AsO_4	*a*	none	none	*a*	none	none	none	none
BO_2	trace	small amount	trace	trace	small amount	trace	trace	trace
Cl	5370.03	3685.50	2293.00	5150.45	4419.60	4180.00	7044.75	5775.70
Br	20.31	26.90	2.05	*a*	40.30	40.90	29.84	16.10
I	2.82	1.50	0.60	*a*	1.60	1.90	3.81	1.26
Fe	5.95	*a*	18.70	10.08	*a*	16.10	4.50	14.30
Fe and Al	7.14	9.80	19.40	*a*	13.10	16.90	16.30	17.30
Al_2O_3	2.24	*a*	1.40	*a*	*a*	1.50	8.50	7.60
Mn	*a*	*a*	none	*a*	*a*	3.60	trace	none
Ca	1008.71	650.70	499.80	733.65	628.60	781.90	974.85	1057.80
Mg	826.73	228.80	90.00	332.90	298.80	288.40	472.40	412.30
Ba	17.54	5.50	12.31	15.93	10.10	4.70	25.30	13.70
Sr	trace	trace	trace	trace	trace	1.70	6.10	2.70
K	85.90	197.20	471.40	304.53	237.80	242.20	442.80	365.50
Na	3455.29	2430.70	1280.10	3525.55	3014.50	2556.90	4369.00	3621.90
Li	20.16	0.50	3.70	15.18	5.30	12.20	11.60	12.80
NH_4	*a*	10.70	6.00	*a*	13.40	5.53	18.10	13.30
Oxygen to form Fe_2O_3	....	....	......		5.70			
F	trace	......	......					
HYPOTHETICAL FORM OF COMBINATION.								
NH_4Cl	*a*	31.80	17.90	*a*	39.67	16.46	53.90	39.60
LiCl	*b* 150.28	3.00	22.40	*b* 113.89	31.80	74.20	70.50	76.10
KCl	164.11	350.70	898.80	574.05	415.60	422.10	815.60	676.40
NaCl	8720.45	5762.40	3253.80	8324.11	6873.50	6444.70	10825.90	8957.30
KBr	*c* 20.36	40.00	3.00	*a*	60.00	60.00	43.75	25.00
KI	*d* 2.02	1.90	0.40	*a*	2.10	2.50	5.00	1.65
Na_2SO_4	*e* trace	8.20	31.70	*e* 5.47	4.10	39.90	18.64	9.80
$NaNO_3$	*a*	none	none	*a*	none	none	none	trace
$NaNO_2$	*a*	none	trace	*a*	none	none	none	trace
$NaBO_2$	trace	trace	trace	trace	trace	trace	trace	trace
$NaHCO_3$	73.32	586.40	276.10	898.61	1126.70	68.19	362.10	331.80
$Ba(HCO_3)_2$	29.70	10.40	23.30	30.10	19.10	8.90	47.80	25.90
$Sr(HCO_3)_2$	trace	trace	trace	trace	trace	4.00	14.60	6.40
$Mg(HCO_3)_2$	3017.52	1377.80	556.40	2020.71	1798.90	1750.70	2867.40	2502.60
$Ca(HCO_3)_2$	2918.05	2635.30	2024.20	2971.30	2545.80	3166.70	3948.10	4281.40
$Fe(HCO_3)_2$	19.29	31.10	29.60	32.15	*a*	25.50	37.70	22.50
Mn_3O_4	*a*	none	none	*a*	*a*	5.00	trace	none
Al_2O_3	1.24	*a*	1.40	*a*	(18.80)	1.50	8.50	7.60
Fe_2O_3	....	....	......	......	....	....	....	....
SiO_2	21.55	19.60	13.85	8.60	13.50	7.70	8.15	8.50
Total solids	15154.82	10858.60	6152.85	14978.99	12949.70	12098.05	18764.59	16640.75
Residue on evaporation	12663.61	*a*	6030.00	*a*	*a*	10570.00	16220.00	13830.00
Temperature	*a*	*a*	10.5° C.	*a*	*a*	11° C.	10.5° C.	10.4° C.
Organic matter	trace	....	......	......	....	....	....	....
Density	1.0115	....	......	......	....	....	....	....
NaBr	26.23	....	......	......	....	....	....	....
NaI	2.39	....	......	......	....	....	....	....
NaF	trace	....	......	......	....	....	....	....
Na_3PO_4	0.10	....	......	......	....	....	....	....
K_2SO_4	trace	....	......	6.84	....	....	....	....
$LiHCO_3$	194.74	....	......	147.40	....	....	....	....

a, Not given.
b, Equivalent of $LiHCO_3$ reported.
c, Equivalent of NaBr reported.
d, Equivalent of NaI reported.
e, Equivalent of K_2SO_4 reported.

1, C. F. Chandler, *The American Chemist*, **2,** No. 6, (1871).
2 and 5, "Mineral Waters of the U. S.," Dept. of Agriculture, *Bulletin* No. **91.**
3, 6, 7 and 8, Files of New York State Department of Health, January, 1912.
4, Analysis by E. E. Smith, Ph.D., M.D., August, 1901.

delivery of the samples for mineral analysis is to be had.

The methods given in *Bulletin* **91**, Bureau of Chemistry,[1] except for the determination of lithium, were followed. For lithium a new method was adopted which is described by the author in another paper.

The waters of the Hathorn Spring No. 1 and the Coesa Spring (formerly known as the Carlsbad) have been analyzed by other chemists and the results of the analyses have been published in the literature, but for the sake of comparison these older analyses have been inserted beside the new ones. Where the results have been combined in a different way than was adopted by the Bureau of Chemistry and followed by the New York State Department of Health, the writer has computed them to a comparable equivalent. The hypothetical forms of combination have been computed as milligrams per liter.

From the data we can see that great changes have taken place in the springs from time to time. The water of the Hathorn Spring No. 1 when analyzed by Prof. Chandler forty years ago was over twice as strongly mineralized as it is now. It was also less mineralized when the sample was taken last July than it was when analyzed by the Bureau of Chemistry of the U. S. Department of Agriculture.

The water of the Coesa Spring contained less minerals in solution when the sample was taken in November, 1911, than it did when analyzed by Dr. Smith or the U. S. Department of Agriculture.

The amount of lithium found in the last analyses is higher than that reported in the results published in *Bulletin* **91**, because of a new method employed which now gives more complete results.

The Hathorn Spring No. 1 is situated in the village of Saratoga, while the Coesa is situated at the Geysers.

These two waters have an abundant supply of gas and are suitably mineralized.

The Hathorn Spring No. 2 and Hathorn Spring No. 3 have never been analyzed by other analysts, so that no data for comparison are available. These two springs are situated in the Geysers district about 300 feet apart and were found in the early part of 1910 by drilling. Hathorn No. 2 is the most highly mineralized spring in Saratoga and its waters are pronounced by eminent physicians to be of great therapeutic value. Hathorn No. 3 is of the same general nature as Hathorn No. 2. As seen from the analyses these springs contain the important constituents—magnesium, sodium, lithium and carbon dioxide.

ANALYSES OF THE GAS.

The supply of carbon dioxide being great, it was thought advisable to analyze the gas from some of the important springs where the sample could be easily collected.

SARATOGA SPRING WATERS.

The gas was collected in a five gallon demijohn by first filling it with the charged water, issuing from the spring, then inverting and displacing the water by the gas from the spring. The apparatus of Hempel was used for measuring the sample, then it was estimated by the ordinary absorbents in the absorption pipettes.[1] Hydrogen sulphide was determined by passing the gas through a measured amount of standard arsenious acid solution and titrating back with iodine, using starch as an indicator.[2]

Gas from Coesa (Carlsbad) Spring.

Sample of gas taken July 14, 1911:

Sample for analysis corrected	100 cc.	
Carbon dioxide	97.5	
Oxygen	0.0	
Combustible	0.0	
Nitrogen and non-combustible	2.5	
Hydrogen sulphide	0.0	When three liters of the gas were tested.

Gas from Hathorn Spring No. 3.

Sample of gas taken July 13, 1911:

Sample for analysis corrected	100 cc.	
Carbon dioxide	98.1	
Oxygen	0.0	
Combustible	0.0	
Nitrogen and non-combustible	1.90	
Hydrogen sulphide	0.0	When three liters of the gas were tested.

No samples of gas were taken from Hathorn Springs Nos. 1 and 2.

BACTERIOLOGICAL EXAMINATIONS.

The waters of these springs have been examined bacteriologically from time to time, and the results showed at the time these samples were taken that the bacterial count was very low; no organism of the *B. coli* type was isolated. This proves that the springs are of a high sanitary purity.

In the near future other analyses will be made, and the results will be published from time to time.

The writer wishes to express his gratitude to the State Department of Health and the Saratoga Reservation Commission for the permission to use their data and information.

State Hygienic Laboratory,
State Department of Health,
Albany, N. Y.

DETERMINATION OF LITHIUM.

By Leslie Russell Milford.

Received February 21, 1912.

In the work with the first samples of the Saratoga mineral waters, which the writer has been analyzing, the determination of lithium was found to be difficult and the results obtained were not satisfactory because of the fact that parallel determinations would not check and too small volumes of water had to be used.

The waters of these springs are highly mineralized, the chlorides ranging from 100 to 11,000 parts per million. Therefore, a great deal of trouble was experienced in volatilizing the ammonium salts when working with large volumes of water. Mechanical loss, due to decrepitation and splitting apart of the crystals, was a constant source of error. On the other hand, if one took a small volume of water the chlorides could be dried and the ammonium salts driven off more easily, but the possibility of multiplying errors would be great because of the relative small amounts of lithium present.

The need of an improvement or change of the method given on page 29, *Bulletin* **91**, of the Bureau of

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[1] "Mineral Waters of the United States," U. S. Dept. of Agriculture, Bureau of Chemistry, *Bulletin* **91**, 1907.

[1] Hempel-Dennis, "Methods of Gas Analysis," 1906.

[2] Sutton, "Volumetric Analysis" (Mohr's method), 1901.

Chemistry[1] became apparent. By consulting the literature and various solubility tables[2] and studying the methods of Gooch,[3] Treadwell,[4] Kennicut,[5] Frenkel,[6] and Rammelsberg,[7] the following procedure was adopted whereby a larger volume of water could be used and a residue obtained which would give, when treated, a lithium salt containing only a spectroscopic trace of sodium and potassium.

Method.—Two hundred to five hundred cc. of the water are evaporated to dryness in a large platinum dish with the occasional addition of small amounts of concentrated hydrochloric acid. After all of the water has been evaporated to dryness the dish and contents are heated at 120° C. for about 30 minutes to dehydrate the silica. The residue is then treated with a little dilute hydrochloric acid, just enough to moisten the contents of the dish. Then about 25 cc. of 95 per cent. alcohol are added and the residue is rubbed up with a small pestle until all lumps and crystals are crushed. The alcoholic extract is then poured on an 11 cm. quantitative filter and the filtrate caught in another platinum dish. The residue is washed with 95 per cent. alcohol until it shows no lithium line when examined in the spectroscope. The alcoholic filtrate and washings are united and evaporated on the water bath. When all of the alcohol has evaporated some dilute hydrochloric acid is added to the contents of the dish, and the whole evaporated to dryness and then the residue rubbed up with absolute instead of 95 per cent. alcohol. The filtrate is caught as before in a platinum dish and the residue on the filtrate washed with absolute alcohol until no lithium line is seen when tested from time to time with the spectroscope. The alcohol is evaporated and the dry residue taken up with a little dilute hydrochloric acid. Calcium hydrate is added until the solution is alkaline. The magnesium is precipitated as the hydrate and the solution is filtered. To the filtrate add ammonium hydrate and ammonium oxalate to precipitate the calcium. This is allowed to stand twelve hours or over night when it is filtered off. The calcium oxalate precipitate must be thoroughly washed (usually about 100 cc. of water is sufficient) as lithium is held relatively fast by the precipitate and does not wash out easily. When the residue no longer shows lithium, as verified by the spectroscope, the solution is evaporated to dryness and the excess of ammonium salts driven off by first heating the dish on a radiator, then over the free flame. The residue in the dish is taken up with a little dilute hydrochloric acid, heated and ammonia and ammonium oxalate are again added to precipitate any calcium which might be present. In any case the solution is filtered from any calcium or magnesium that precipitates on concentrating the solution. The filtrate is evaporated to dryness and all ammonium salts are driven off by heating in platinum to a little below redness. The residue is again taken up with water, filtered, and washed (using as little wash water as possible), then evaporated to dryness and heated in platinum to a little below redness to drive off any ammonium salts. All of the calcium and practically all the magnesium have now been removed, and there is left a residue containing lithium chloride with traces of sodium and potassium chlorides. If we have iodides and bromides present, this residue will contain small amounts of these substances because they are more soluble than the chlorides. In order to insure a residue consisting of chlorides only we treat the contents of the dish with a little dilute hydrochloric acid and chlorine water, evaporate to dryness, and gently ignite. By this we have replaced the iodine and bromine with chlorine.

The residue is now taken up with a little water and treated with a few drops of dilute hydrochloric acid and transferred to a large platinum dish.

About 30 cc. of amyl alcohol are added and the contents of the dish brought to boiling with constant rapid stirring when heating to minimize the bumping caused by the escape of the water. When all of the water has evaporated, the dish is placed on the steam bath and a drop of dilute hydrochloric acid added to reconvert small amounts of lithium hydrate to the chloride. The evaporation is continued until the volume reaches about 15 cc. The amyl alcohol is then filtered into a platinum dish and evaporated to dryness. Water and a few drops of dilute sulphuric acid are now added and the contents of the dish again evaporated to dryness. The excess of sulfuric acid is removed by heating the dish over a radiator and then over the direct flame to dull redness. The dish is cooled, the contents dissolved in water and a few drops of ammonium hydrate are added to precipitate the last trace of magnesium which is invariably present at this stage. Filter, wash with boiling water, evaporate to dryness, free from ammonium salts, and repeat previous process till no more magnesium precipitates on addition of ammonium hydrate. Finally filter into a weighed platinum dish, evaporate to dryness, burn, cool in a desiccator, and weigh as lithium sulfate. From this result we subtract 0.0017 gram to correct for the solubility of the sodium and potassium chlorides in amyl alcohol, their presence having been verified by the spectroscope.

The contents of the filters containing the NaCl, KCl, etc., which were taken out by the 95 per cent. alcohol and absolute alcohol together with the contents of the platinum dish and filter from which the amyl alcohol has been driven off, are all dissolved in water, united, freed from other salts and made up to a definite volume. By using aliquot portions we can determine sodium and potassium by Gooch's method. Or the usual procedure, using a small portion of the silica filtrate, can be followed.

Advantages Given by this Modification: (1) Waters high in chlorides can be handled with ease with no danger of loss of lithium by decrepitation.

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[1] and [3] "Mineral Waters of the United States," U. S. Dept. of Agriculture, Bureau of Chemistry, *Bulletin* **91**, 1906.

[2] Atherton Seidell, "Solubilities of Inorganic and Organic Substances," 1907.

[4] and [7] Treadwell-Hall, "Analytical Chemistry," 1911.

[5] Chamot-Redfield, "Analysis of Water for Household and Municipal Purposes," 1911.

[6] M. Frenkel, D.Sc., "Extract from the Records of Medical Hydrology and Climatology," Paris, Dec., 1903.

(2) Large volumes of water can be used, thus reducing the error when computing to milligrams per liter.

(3) The results can be found to check and can be obtained much more quickly by having a residue free from an excess of sodium and potassium chlorides.

(4) The method involves the use of calcium hydrate instead of barium hydrate for the precipitation of magnesium. This procedure does not introduce another substance which has to be removed by ammonia and ammonium oxalate because we have our calcium in common and have a precipitate of calcium oxalate which is less soluble and more easily washed than barium oxalate.

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A NEW VOLUMETRIC METHOD FOR TIN.

By Willbur W. Patrick and G. C. Wilsnack.

Numerous methods for the determination of tin have been tried out in this laboratory with various degrees of success. Gravimetric methods giving results of the required accuracy are too lengthy and tedious for ordinary use in laboratories where it is required to complete a large number of determinations in a short time. Shorter schemes, such as weighing the combined oxides of antimony and tin, determining antimony in a separate sample, and calculating tin by difference, cannot be used for alloys containing lead, copper, or numerous other metals which are to be found in some commercial alloys, unless the amount of these impurities contaminating the oxides be determined and taken into consideration.

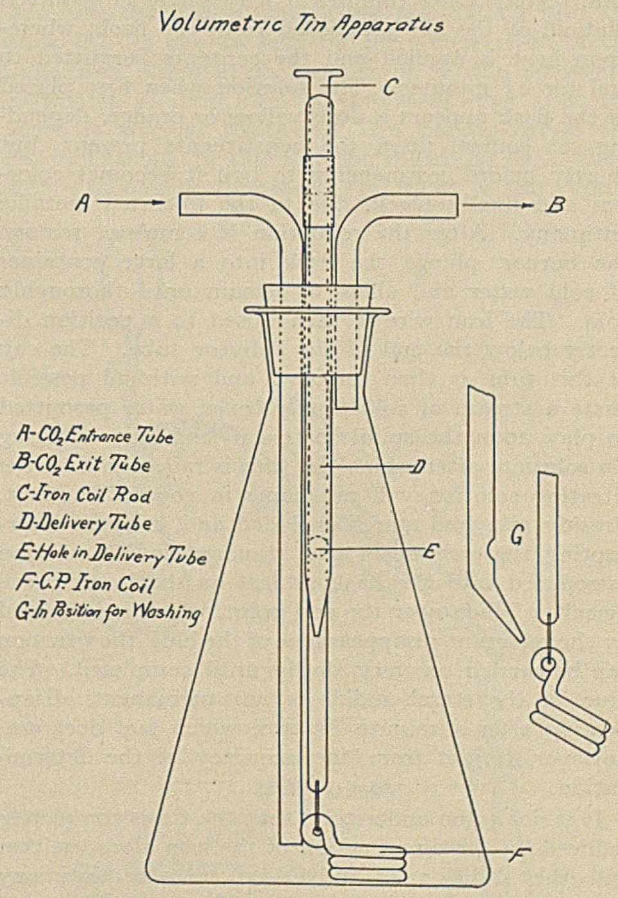
The volumetric methods proved to be rather unsatisfactory, especially if the titrating solution was standardized against a standard reducing solution in preference to C. P. tin. The authors found that determinations on quantities as small as 5% were unreliable, and that on high percentages it was almost impossible to obtain consistently accurate results even if the oxidizing solution was standardized against an equivalent amount of metal treated in an exactly similar manner.

Endeavoring to overcome these difficulties, the following method was finally adopted. The results obtained are consistent and correct to within 0.2 per cent. on amounts of 50 per cent. or over and considerably more accurate on smaller percentages. As large percentages of copper, lead, nickel, and perhaps other metals not experimented with, interfere, it has been found expedient to modify the method somewhat in the presence of these elements. Both determinations will be described.

REGULAR METHOD.

The following scheme of analysis is available where no more than 5 per cent. of either lead or copper is present in the alloy. Where the percentages of these elements exceed this limit a modification of the method is necessary.

Place an amount of sample corresponding to 0.5 gram or less of tin in a 500 cc. Jena Erlenmeyer flask and add 0.15 gram C. P. metallic antimony if as much or more is not already present in the alloy. If the sample contains less than this amount it is necessary to make up the deficiency. Add 10 cc. of concentrated sulphuric acid and heat to effect solution. Remove from the hot plate and cool. Dilute the cold sulphuric acid solution with 10 cc. of water, add 60 cc. of concentrated hydrochloric acid, and then 40 cc. more of water. Prepare a four-hole rubber stopper that fits the neck of the flask. Through one hole pass a glass tube bent at right angles reaching to the bottom of the flask and through the hole diagonally opposite insert another tube bent in a similar manner but extending only a short distance below the bottom of the stopper. Through the third hole pass a long thin glass rod fitted with a 2″ piece of platinum wire. This rod should fit rather snugly without, however, giving any difficulty to the operator in raising or lowering it during the determination. The platinum wire is now bent into the shape of a hook and a piece of very nearly C. P. iron wire attached. Swedish iron in plates of $^1/_8$″ thickness cut into strips of $^1/_8$″ in width and four inches in length, curled up in the form of a spiral, will suit the purpose well. Through the fourth hole pass a $^1/_2$″ tube 4″ long and drawn out at the lower end to an opening small enough to enable the operator to introduce iodine solution in sufficiently small quantities to obtain the starch iodide reaction within one drop of titrating solution. The tapered end is bent slightly in the di-



rection of the submerged wire for the purpose of conducting a stream of water to free the iron from adhering tin solution after it has been withdrawn from the liquid. This delivery tube should also be provided with a 1/4" hole about 3/4" above the lower opening to afford a means of escape for the carbon dioxide gas which is being rapidly introduced during the titration. A carbon dioxide generator is connected to the long tube while a piece of rubber tubing connects the short tube opposite to a 100 cc. pipette which dips into a reservoir of water. This automatically prevents any air from entering the system when a partial vacuum is formed in the flask during the determination, which cannot be taken care of by the entering carbon dioxide gas. Having attached the iron to the platinum wire, the rubber stopper is firmly placed in position in the neck of the flask and the rod lowered so that the spiral of wire rests on the bottom of the flask. The generator and water seal are attached as previously described, a cap is placed over the opening of the large delivery tube and a rapid stream of carbon dioxide gas passed through the system. After a few minutes it may safely be assumed that all of the air is expelled from the flask, whereupon heat is applied and the contents permitted to boil for 25 minutes. The solution when first placed in the flask appears a deep yellow or orange, depending, of course, upon the constituents present, but shortly before commencing to boil it becomes colorless and finally black, due to the liberated metallic antimony. After the reduction is complete, remove the burner, plunge the flask into a large container of cold water and allow to remain until thoroughly cold. The iron wire is then raised to a position directly below the end of the delivery tube. The cap of this tube is then removed and with all possible haste a stream of cold *freshly boiled* water permitted to play upon the spiral to free it from any adhering tin solution, after which the wire is raised so that the titrating solution will not come in contact with it. Freshly prepared starch is added and, without interrupting the passage of gas, standard iodine solution introduced into the flask as fast as the burette will permit. When near the end point, which is indicated by the reluctant disappearance of the blue, the titration can be carried on very slowly until completed. The blue of the starch iodide is not permanent, disappearing after a minute or two, which fact does not, however, detract from the accuracy of the determination.

It is not to be understood that the tin is completely reduced by the direct action of the iron alone, neither will the addition of pulverized metallic antimony bring about the desired result. However, this metal as deposited is in a state where its chemical activity is at a maximum, thus enabling it to fully complete the reduction.

Standardize the sodium thiosulphate, which serves to determine the strength of the iodine solution, very carefully against a bichromate or permanganate solution of known strength. It is essential that the utmost accuracy be employed in the above standardization, since 0.1 cc. more or less of a $N/10$ oxidizing solution makes a considerable difference in the ultimate tin value of the iodine. It has been found advisable in finding the normality of a freshly prepared iodine solution to check the theoretical standardization against C. P. tin.

MODIFIED METHOD.

A modified method is used when 5 per cent. or more of copper or lead, or any other interfering element, is present in the specimen to be analyzed.

Place 0.5 to 1 gram of sample in a small casserole and add if necessary 0.15 gram of antimony as in the regular method. Cover the sample with 8–10 cc. of concentrated nitric acid and evaporate to dryness. It is advisable in order to facilitate the subsequent filtration to bake strongly for about 15 minutes. Cool and add 20 cc. of 1–1 nitric acid, and, after breaking up the lumps with a stirring rod, filter and wash several times with hot water. If the baking has been conducted properly no traces of oxides will be discernible in the filtrate. The precipitate with the filter paper is then placed in a 500 cc. Jena Erlenmeyer flask and treated with 20 cc. of concentrated sulphuric acid and 2 grams of potassium sulphate. Place the flask on a piece of asbestos over a medium hot burner and heat carefully till the first violent reaction is over, after which the heat can be increased. Towards the end of the oxidizing operation, while the liquid is still black however from the free carbon present, the flask and contents should be cooled and the sides of the container washed down with a stream of water. The particles adhering so firmly to the wall of the flask that the water does not loosen them should be brought back into the main solution with the aid of a "policeman." The removal of the carbon should by no means be hastened by the addition of an oxidizing agent, since this will cause the antimony to assume the pentavalent form, which must be avoided. The addition of the water will now have a tendency to again cause frothing when the heat is applied, making it necessary to conduct this operation very carefully. From 2–2 1/2 hours are usually required, depending upon the intensity of heat employed, to rid the solution completely of the carbon. Cool, introduce the required amount of water, but add only 45 cc. of hydrochloric acid instead of 60 cc. as in the regular method.

If very large percentages of antimony are present, enough to obscure the end point obtained with the starch solution, it is well to treat in the usual manner up to the point where the metallic antimony separates out. The solution should then be rapidly cooled, filtered with suction and washed with hot water. About 0.10 gram of metallic antimony, which has previously been dissolved in a few cc. of sulphuric acid, is then added, the solution returned to the original container, and the reduction continued. The concentration of the solution after this operation should not be changed to any great extent, the additional acid introduced off-setting in a large measure the water used for washing. Antimony present up to 25 per cent. will not obscure the end point, provided a good light and white background are available.

The accompanying table gives a few results obtained on mixtures containing various amounts of copper, lead and nickel as noted. These figures are fairly representative of the results which may be obtained by the methods described in the preceding pages.

	Approximate amount.					
Method.	Copper. Gram.	Lead. Gram.	Nickel. Gram.	Tin taken. Gram.	Tin found. Gram.	Error. Mg.
Regular......	..	..	..	0.4040	0.4038	0.2
Regular......	..	..	..	0.0568	0.0575	0.7
Regular......	0.03	..	..	0.4470	0.4478	0.8
Regular......	0.05	0.05	..	0.1143	0.1153	1.0
Modified......	0.25	0.30	..	0.4060	0.4065	0.5
Modified......	0.03	0.66	0.03	0.1764	0.1763	0.1
Modified......	..	0.30	0.05	0.4272	0.4261	1.1
Modified......	0.15	0.80	..	0.0216	0.0214	0.2
Modified......	0.08	0.80	..	0.1000	0.1000	0.0
Modified......	0.50	..	..	0.4530	0.4526	0.4

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A NEW APPARATUS FOR THE VOLUMETRIC DETERMINATION OF CARBON DIOXIDE.

By HOWARD W. BRUBAKER.

Received April 13, 1912.

In THIS JOURNAL for March, 1912, appeared an account, by L. T. Bowser, of a volumetric method for the determination of carbon dioxide. In this method the carbon dioxide is liberated and then absorbed in a solution of potassium hydroxide. This solution is washed into a 100 cc. graduated flask, water added to the mark and an aliquot titrated, using phenolphthalein as the indicator to the disappearance of the red color, then methyl orange, the second part of the titration indicating the amount of carbon dioxide in the solution.

The writer had occasion to try out the method to see whether it could be used by a class of comparatively inexperienced students of chemistry. As a result of a little experience with the method some objectionable features were found with the apparatus used by Mr. Bowser which make it impracticable for use by students. Probably the most objectionable feature is the necessity of washing out the potassium hydroxide from the tall absorbing cylinder into a measuring flask. This process requires skilled manipulation, especially since it is necessary to wash the cylinder thoroughly and yet keep the whole volume of liquid and wash water down to 100 cc., which seems advisable, in order that a sufficiently large fractional portion of the solution may be titrated without using a very large volume.

Another objection lies in the fact that at the end of the decomposition of the carbonate when an attempt is made to distil over some of the liquid, in order to drive the last portion of carbon dioxide into the absorbing cylinder, there is a tendency for the potassium hydroxide solution to suck back into the condensing apparatus. In order to overcome these objections and to make the method applicable for the use of inexperienced students the writer devised the apparatus shown in the accompanying figure.

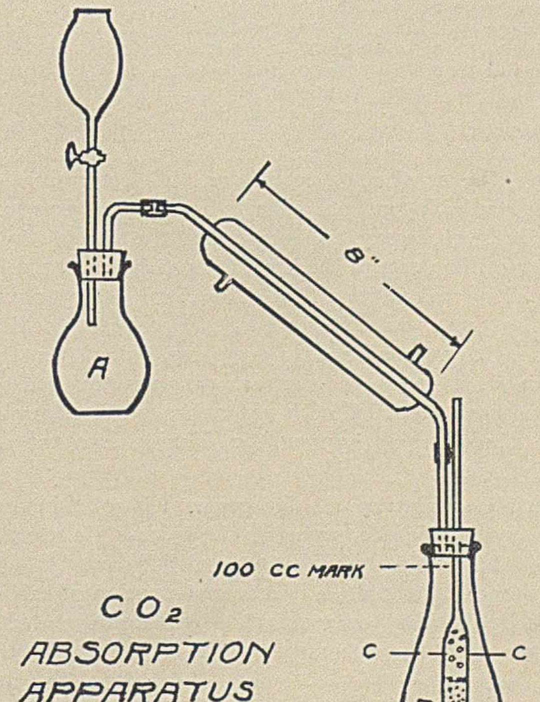
B is a standardized Erlenmeyer flask holding 100 cc. when filled to the mark.

C is a 10 cc. pipette half filled with glass beads, having a coil of copper wire at the bottom to prevent any of the beads from becoming wedged into the tapering part of the tube.

Eight cc. of the potassium hydroxide solution (50 grams KOH in 100 cc. water) are placed in the flask B which is then connected with the condenser as shown in the figure.

One gram of the material to be analyzed is placed in the flask A with about 50 cc. of water. The hydrochloric acid is run in from the funnel, drop by drop, until sufficient has been added to decompose the sample.

The carbon dioxide distils into the flask B, forcing the potassium hydroxide solution up into the pipette until it stands near the top of the broad portion where the bubbles break. There is left a thin layer of potassium hydroxide covering the bottom of the flask. The carbon dioxide which is not absorbed by this layer of potassium hydroxide passes up through the liquid in the pipette and is completely absorbed. After adding the hydrochloric acid the liquid in the distilling flask is heated and finally boiled for five minutes, the steam condensing and falling into the flask B. As can be seen by the construction of the apparatus, there is no backing up of the potassium hydroxide solution into the condenser even when the flame is entirely removed. This boiling drives the residual carbon dioxide into the absorbing flask where it is completely absorbed. If there is any doubt as to the last portion of carbon dioxide in the flask B having been absorbed, the flask is shaken for a minute or two after disconnecting it and while holding a finger over the opening of the glass tube.



After distilling steam over for five minutes the writer has always found the carbon dioxide to have been completely absorbed.

The stopper with the pipette is now partly withdrawn from the flask B, the pipette rinsed out several times into the flask and water added to the 100 cc. mark. After mixing, a 25 cc. portion is taken for titration. The advantages of this apparatus are as follows:

1. Ease of construction.
2. Ease of manipulation.
3. It permits of distilling over as much of the liquid as desired, to drive out the residue of carbon dioxide, without experiencing any annoyance due to sucking back of the potassium hydroxide solution into the condenser.
4. It eliminates the necessity of transferring the alkaline solution to another vessel before making it up to a definite volume, thus also keeping it away from contact with the carbon dioxide of the air.

The following table shows some results obtained with the apparatus here described.

SAMPLE.	CO_2 FOUND.	PER CENT.
Na_2CO_3	By direct titration	39.40
Na_2CO_3	By distillation and titration:	
Na_2CO_3	1st run	39.40
Na_2CO_3	2nd run	39.45
Baking powder No. 1	Available CO_2, 1st distillation	8.10
Baking powder No. 1	Available CO_2, 2nd distillation	8.02
Baking powder No. 1	Available CO_2, 3rd distillation	8.10
Baking powder No. 1	Total CO_2, 1st distillation	11.01
Baking powder No. 1	Total CO_2, 2nd distillation	10.91
Baking powder No. 2	Available CO_2, 1st distillation	8.76
Baking powder No. 2	Available CO_2, 2nd distillation	8.62
Baking powder No. 3	Available CO_2, 1st distillation	10.74
Baking powder No. 3	Available CO_2, 2nd distillation	10.91
Limestone	Gravimetric method	40.25
Limestone	Volumetric, 1st titration	40.23
Limestone	Volumetric, 2nd titration	40.40

When the method is used for the determination of the available carbon dioxide in baking powders, where it is necessary to decompose the sample with water, frothing occurs during the heating of the solution. This makes it difficult to distil over enough water to drive out the last of the carbon dioxide. In order to overcome this difficulty, when the distillation was carried as far as was practicable, the distilling flask was filled with water through the dropping funnel, thus forcing any carbon dioxide into the absorbing flask.

By using a solution of 25-30 per cent. alcohol instead of pure water, for decomposing the baking powder, it was found possible to prevent excessive frothing.[1] One could then clear the flask of the last portion of carbon dioxide by distilling over a little of the liquid and thus do away with the necessity of filling the flask with water.

It is necessary to determine the carbon dioxide in the potassium hydroxide solution used as the absorbing reagent and to apply the correction in each titration.

In the writer's experience with the volumetric method for carbon dioxide the greatest source of error is in the titration. The end point with phenolphthalein must be approached with care as the disappearance of the red color is rather slow.

ITHACA, NEW YORK.

A MODIFICATION OF THE SWEENEY METHOD FOR CRUDE FIBER.

By CORNELIA KENNEDY.

Received May 6, 1912.

The method for the determination of crude fiber as recently modified by M. O. Sweeney[1] does not prove entirely satisfactory for all kinds of feed stuffs, especially those which are rich in protein. In his method an ether extracted sample of feed is first boiled for 30 minutes with 1.25 per cent. sulphuric acid. This acid solution is neutralized with 10 per cent. sodium hydroxide and 200 cc. of a boiling 2.65 per cent. sodium hydroxide solution added and boiled for 30 minutes. The sample is then filtered, washed, dried, weighed, incinerated and reweighed.

The acid dissolves certain nitrogenous bodies, pentosans, gums, etc., and when the alkali solution is added a heavy precipitation of some of these materials is caused. This precipitate is weighed with the crude fiber and consequently materially increases the percentage amount of fiber.

The following modification of the Sweeney method does away with this difficulty and gives results which check, within the limits of error, with the official method.

As in the above method the prepared sample is first boiled with 200 cc. of a 1.25 per cent. sulphuric acid. Neutralization is done away with, by making the alkali solution of such strength that it both neutralizes the acid and leaves the 400 cc. of 1.25 per cent. sodium hydroxide; 200 cc. of a boiling 3.52 per cent. sodium hydroxide are therefore added, and the whole boiled 30 minutes. The solution and fiber are then thrown onto a linen filter (which works more rapidly than a gooch because of the nature of the solution) and washed free of alkali. (Suction may be used to

	Official method.		Sweeney's method.			Sweeney's modified.		
	Per cent.	Average.	Per cent.	Average.	Increase over official method.	Per cent.	Average.	Increase over official method.
Bran	12.04		14.21			12.47		
	11.49	11.76	14.06	14.13	2.37	12.20	12.33	0.57
	0.55		0.15			0.27		
Sucreen	14.33		15.92			14.67		
food	13.92	14.12	15.58	15.75	1.63	14.43	14.55	0.43
	0.41		0.34			0.24		
Sugar and	6.90		7.44			7.12		
flax feed	6.89	6.90	7.44	7.44	0.54	7.08	7.10	0.20
	0.01		0.00			0.04		
Oil meal	7.87		10.20			8.81		
	7.86	7.87	10.08	10.14	2.27	8.80	8.81	0.03
	0.01		0.12			0.01		
Bran	11.37		12.95			11.81		
	11.11	11.24	12.94	12.95	1.71	11.69	11.75	0.51
	0.26		0.01			0.12		

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[1] For this improvement of the method, the writer is indebted to Prof. G. W. Cavanaugh of Cornell University.

[1] U. S. Dept. Agr., Bur. of Chem., *Bull.* **137**, 157.

cause a more rapid filtration.) The fiber is then thoroughly washed with boiling 1.25 per cent. sulphuric acid, which will remove the material precipitated by the addition of the alkali, washed free of acid, removed from the linen filter to a crucible, dried, weighed, incinerated and reweighed.

The Sweeney method has a great advantage over the official method by doing away with a filtration and thus saving time. This advantage is preserved in the modification of the Sweeney method.

The preceding table shows the results of all three methods on 5 different samples of feeds.

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STUDIES ON SOIL HUMUS.

By Sherman Leavitt.

Received January 30, 1912.

Humus is recognized as one of the most valuable constituents of a soil and yet little is known as to its composition. Fifty or sixty years ago, chemists thought they had shown humus to have a definite chemical composition with percentages of carbon, hydrogen, nitrogen and oxygen constant. According to their theory, humus was a salt of humic acid (also considered a definite chemical compound) which, upon oxidation, yielded simpler hypothetical organic acids called crenic and apocrenic. Although, as far as the writer knows, they had little or no experimental proof, many of these theories have been held to by some until quite recently.

In spite of all the work which has been done during the past fifty years, but little is known about humus. It is the belief of the writer that most chemists who have worked on the subject within the last fifteen years will agree that it is far from being a definite compound, and, in fact, that it is as variable in composition, if indeed not more so, as the different soils of which it is a component part.

Why does soil *A* accumulate humus matter readily while soil *B*, under similar conditions of treatment, etc., apparently makes no appreciable and permanent improvement?

We are working at this problem along two general lines: First, under field conditions; second, under laboratory control.

This article will be confined mainly to the second class, as definite results from the field cannot be obtained under many years.

In the laboratory, large samples of soils that are under field experimentation are being used. These were procured from car-load lots, thoroughly mixed, so that the samples are quite representative of the types under investigation. These samples represent four distinct type soils in different sections of Tennessee and were chosen for the reason that each one was the poorest soil of that particular type. It was thought of interest to include a Florida Everglade soil, rich in humus, for comparison in the chemical work.

As most of the humus matter in Tennessee soils is present in the first six inches of soil, the laboratory work on humus has been confined to this layer.

At the beginning of this work it was deemed advisable to remove completely, under the same conditions of extraction, the humus matter from a large quantity of each one of these soils. Under similar conditions of preparation, the humus matter obtained from each one of these soils ought to be at least approximately comparable. Any appreciable difference in the approximate composition of the several samples of humus might have great significance and might point to some quite different behavior of the humification process in the several soils. This may be taken as the key-note of the following investigation:

A number of quantitative chemical methods for the determination of percentage of humus in soils were subjected to examination for their respective values. The investigation earlier reported[1] brought out some valuable points, notably that the humus matter from different soils could be absolutely different both in appearance and in behavior toward reagents. Several of the methods in use for the determination were found unreliable on Tennessee soils for the reason that they failed to show all of the organic matter in the ammonia solutions.

In this later investigation, dealing more specifically with the properties of the several humus samples, a description of the method of procedure in the preparation of the samples of humus will be given. During the work, it was deemed advisable to modify the method of removing clay from the samples, the reasons for which will be given.

Method A.—Five hundred grams of the air-dried soil were extracted with 1 per cent. hydrochloric acid, according to the Official Method, washed free from acid and then extracted three days with 4 per cent. ammonia, allowed to settle and the supernatant liquid drawn off. Fresh 4 per cent. ammonia was added and the process repeated. The soil was extracted three times with successive portions of 4 per cent. ammonia, about two liters of solution being used for each extraction. The last extraction contained very little coloring matter. The extractions were all evaporated to dryness in a large porcelain dish on the hot water bath, baked for some hours, and cooled. The residue was then extracted with about two liters of 4 per cent. ammonia, washed by decantation and filtered. A large proportion of the flocculated clay was retained on the filter paper, which was thoroughly washed with 4 per cent. ammonia. The process of evaporation, baking, extraction, washing and filtering, was repeated a number of times until the filtrate appeared absolutely clear. This was then evaporated to dryness in a large beaker to drive off the excess of ammonia; dissolved in hot, distilled water; filtered and washed into a 500 cc. graduated flask; cooled and 1 cc. of strong ammonia added to prevent fermentation; then made up to the mark. The solution was thoroughly mixed and allowed to stand for two months to give finely divided clay, still in suspension, a chance

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[1] "Soil Humus as Determined by Different Methods," This Journal, 2, 269.

to settle out. The supernatant solution was pipetted off for analysis and the amount of humus and ash present determined in 10 cc. portions.

All of the preliminary work was carried on with the humus prepared as above until the supply was exhausted. Fearing a possible hydrolysis of some of the organic compounds might have taken place during the many evaporations to dryness and baking of the humus matter, it seemed wise in making up new samples of humus to modify the method of removing clay so as to reduce the chance of hydrolysis to as low a figure as possible.

Since this change was decided upon, the Illinois Experiment Station has published Stewart's doctoral thesis as *Bulletin* 145 of that Station. Among the general conclusions reached, the author says: "The evaporation on the water bath of the ammoniacal solution, in the preparation of the *matiere noire* in quantity for analysis, causes a hydrolysis of the organic phosphorus compounds." This would seem to confirm the fear of possible hydrolysis of some of the organic compounds other than organic phosphorus compounds.

The modified method of removing clay decided upon depends almost entirely on long settling of the solution for the removal of most of the clay, instead of baking on the steam bath, as in Method A. It was also deemed advisable to make all concentrations and evaporations at not over 60° C., final concentrations to be made in a partial vacuum, taking care never to allow the solution to become more concentrated than 700 cc. During the greater part of the evaporation, the volume of the solution was kept at approximately two liters and was not brought below one liter until the final concentration, the excess of ammonia by that time being expelled. Fortunately, this slow evaporation with constant additions of cold fresh solution to the evaporating solution tends to flocculate the clay left in suspension.

Method B.—Twenty-two hundred and seventy grams (approximately 5 pounds) of soil were extracted as under Method A, proportionately larger amounts of acid and 4 per cent. ammonia being used. Reverse filtration through fine mesh linen and the siphon were used as much as possible to avoid handling the great bulk of clay. This solution was transferred to large, deep, tightly-stoppered jars and allowed to stand undisturbed for about three months, until the supernatant liquid was quite clear. The solution was then siphoned off and filtered, first through coarse filter paper and then through S & S special hardened and toughened filter paper No. 575, suction being used toward the end of the operation. The paper, with removed clay, was thoroughly washed with 4 per cent. ammonia to make sure that all organic matter was obtained. The residual clay gave no indication of occluded organic matter on being baked on the bath and extracted with ammonia according to Mooers and Hampton's method.[1] The evaporation and concentration of the filtrate and washings were carried on between 50° and 60° C., as described in the above paragraph. When the filtrate and washings were concentrated to about 700 cc., they were filtered into a liter graduated flask and the paper thoroughly washed with warm water. The whole solution was now cooled and made up to the mark and 1 cc. of chloroform added as a preservative. The flask was placed aside to stand several months before use, to allow additional finely divided clay an opportunity to deposit. The filtrations at best were mostly slow and troublesome, especially the earlier ones. In order to obtain humus satisfactorily by this method, at least six months were required for the proper preparation of samples.

An investigation of this kind is, for many reasons, extremely difficult. As we have already seen, the preparation of samples for comparison is a tedious process, requiring abundant time and patience. The resulting samples are complex in structure and practically nothing is known of them.

As a preliminary investigation of the subject, a study was made of the effect of different mineral elements, such as calcium and iron, on humus in water solution. Some of the richest soils in Tennessee are of the red type, high in iron and very retentive of humus matter.

For this reason it seemed advisable to study the effect of iron in its different states of oxidation, as *ic* and *ous* iron on the removal of humus matter from water solution. Humus prepared from both good and poor soils was used. Some interesting results were obtained which, however, will need further confirmation. As a matter of interest, these results have been inserted and will be discussed briefly. The writer, however, does not wish to lay stress on the results or the conclusions drawn until they are borne out by more extensive work.

TABLE I.

Character of soil.	Laboratory number.	Humus in soil.	Humus by ferric iron.	Humus by ferrous iron.	Humus by calcium chloride.
		Per cent.	Per cent.	Per cent.	Per cent.
Good.........	916	1.46	60.39	65.06	41.10
Good.........	819	1.29	66.67	64.34	45.74
Good.........	1206	5.11	61.65	73.19	42.67
Good.........	1267	1.66	65.82	57.14	49.74
Poor.........	1266	0.39	69.63	83.22	53.57
Poor.........	844	0.52	48.07	39.65	42.31
Poor.........	867	0.87	22.96	44.82	18.40
Poor.........	1096	0.93	46.61	85.92	64.22
Poor.........	1101	0.90	28.15	66.81	40.76

In connection with the above work, it is interesting to note that the analysis of the humus ash of a Florida soil, which had 9.56% of humus, showed an ash content of 21.4 per cent. ferric oxide.

Ferrous iron precipitated more humus matter than ferric iron from the same humus samples, in two-thirds of the soils experimented with. Out of nine soils, four of which were classified as good, having from 1.30 per cent. to over 5.00 per cent. of humus, and five soils ranked as poor, having less than 1.00 per cent. of humus, with one exception ferric iron precipitated 20 per cent. more from the humus of the good soils than from the humus of the poor soils.

Calcium, in the form of chloride, was found to pre-

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[1] *J. Am. Chem. Soc.*, **30**, No. 5 (1908).

cipitate less humus matter from good soils than either form of iron.

In all of the above cases, organic matter was left in solution. This could be removed as a copper salt more or less completely, when the solution was slightly acid and after the removal of any interfering element, such as excess of iron. This result is quite similar to the writer's finding in the first paper on the subject,[1] where it was noted that a precipitate of organic matter with copper was always obtained after a precipitation of humus matter with hydrochloric acid. It would seem possible that hydrochloric acid and ferric iron precipitate approximately the same substances.

TABLE II.

Most of the results given are averages of from three to five determinations.

	Percentages on original soil.						Percentages on basis of humus.			
									Furfural determination calculated to	
Location of soil.	Humus in original soil.	Nitrogen in original soil.	Nitrogen in 1% hydrochloric acid extract.	Total nitrogen dissolved by 1% acid.	Weight of humus used for determination, ash not included.	Weight of ash not counted as humus.	Proteids or like proteids pptd. by $(NH_4)_2SO_4$.	Starch-like bodies calculated to starch.	Per cent. pentoses.	Per cent. pentosans.
Cookeville, Tenn	0.93	0.0730	0.0020	2.74	0.369	0.065	70.4	10.40	3.83	3.37
Crossville, Tenn.	0.90	0.0737	0.0014	1.90	0.238	0.013	33.6	8.37	4.14	3.64
Jackson, Tenn.	0.39	0.0560	Nitrogen present; partly lost.	Over 2.00	0.112	0.012	75.0	10.80	Present[2]	Present[2]
Gallatin, Tenn.	1.66	0.1350	0.0042	3.11	0.392	0.016	57.9	10.60	4.22	3.72
Florida Everglades, Fla.	9.56	1.750	0.0345	1.97	2.392	0.067	61.4	4.47	1.99	1.74

In all the samples examined, strong evidence was found of a carbohydrate body in amounts varying from 4.5 per cent. to 10.8 per cent., calculated as starch. This body is very similar to starch, although it gives no reaction with iodine.

Dilute, boiling, hydrochloric acid, according to the Sachsee method, hydrolyzed it to reducing sugars which were determined by Allihn's method, and for convenience calculated to starch. On treating the humus with diastase, with subsequent acid hydrolysis, we obtained practically the same results as by the direct acid hydrolysis. The original solutions of humus gave no reactions with Allihn's solution either before or after inversion with cold hydrochloric acid.

From the acid hydrolysis solution on a sample of humus obtained from a Florida Everglades soil, a crystallizable sugar was obtained which reduced Allihn's solution. Some of the mother liquor had no optical rotation and was easily fermentable. The solution, after fermentation, gave reactions for ethyl alcohol and acetic acid, and also continued to reduce Allihn's solution.

This crystallizable sugar, on account of its ease of fermentation, we classify as a hexose sugar, although it has not as yet been completely identified. Schreiner and Shorey[3] have recently obtained a pentose sugar by hydrolysis of a gummy mass precipitated by alcohol from a caustic soda extract of a soil high in pentosans. This result is very similar to the one obtained in this laboratory.

Pentosans were obtained, by the Official Method, from all samples of humus examined in this laboratory. This result is also fully in accord with the findings of Schreiner and Shorey,[1] who obtained pentosans in all ten soils examined by them. Our results varied from 1.74 per cent. in the case of the Florida soil (all percentages on the basis of humus and not on original soil) to 3.72 per cent. on the Gallatin soil; in terms of pentoses, the figures would be 1.99 per cent. to 4.22 per cent., respectively.

In the preparation of the samples of humus under method B, the 1 per cent. hydrochloric acid extracts of the original soils were saved as completely as could conveniently be done. These were evaporated to dryness and, with some difficulty, determinations of nitrogen were made upon the total large residues. The determination on the Jackson soil was partly lost. It is interesting to note that in every case an appreciable amount of nitrogen was obtained in the 1 per cent. hydrochloric acid extract of the original soil. This, the writer believes, is contrary to the generally accepted opinion that there is no nitrogen in the 1 per cent. acid extract. This nitrogen is probably due to amino acids,[2] which are somewhat soluble in dilute mineral acids.

We must keep in mind the fact that these nitrogen determinations, as given in Table II, are all too low as a result of the inevitable loss in handling the large bulks of soil and extract. In the Tennessee soils under examination, a variation of from 1.9 per cent. to 3.1 per cent. of the total nitrogen in the soil was found to be soluble in 1 per cent. hydrochloric acid. This quite appreciable portion of the whole nitrogen is probably present as amino acids. It is not included as humus nitrogen.

In this paper the writer has tried to emphasize the following facts:

INVESTIGATION.

a. Two methods were used for the removal of clay in the preparation of large amounts of humus:

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[1] "Soil Humus as Determined by Different Methods," THIS JOURNAL, **2**, 269.

[2] Had enough solution for only a qualitative analysis.

[3] *Experiment Station Record*, **23**, No. 1, 11.

[1] *Experiment Station Record*, **23**, No. 1, 11.

[2] The writer is indebted to Professor W. R. Orndorff for this suggestion.

1. Mooers and Hampton's method.

2. Mechanical separation, without evaporation, to dryness.

b. Preliminary indications were obtained of the relative behavior of ferric iron, ferrous iron and calcium in the retention of humus from water solution.

c. Protein or like-proteins were present in humus examined.

d. A starch-like body was present which can be hydrolyzed by acids and also acted upon by diastase with subsequent acid hydrolysis. Both of these processes gave reducing sugars, in comparable amounts, in all samples of humus examined.

e. One of these reducing sugars was obtained in a crystalline form but has not, as yet, been fully identified. This was obtained from the humus of a Florida soil.

f. Pentosans were present in appreciable amounts in all samples of humus examined.

g. Nitrogen, probably present as amino acids, was found in the 1 per cent. hydrochloric acid extract in all soils examined by the Official Method for the determination of humus.

The work was done at the Agricultural Experiment Station of the University of Tennessee, Knoxville, during the years 1909 and 1910.

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AN EXAMINATION OF CITY STREET SWEEPINGS.[1]

By J. J. Skinner and J. H. Beattie.

Received April 19, 1912.

The value of street sweepings is a matter that is of interest to officials of all the large cities. The débris which is collected from the streets of cities is commonly used as fertilizing material, being sold to near-by gardeners, truckers, and farmers, its rather low cost making it particularly attractive. The main object of the city official is to dispose of the material; in some cases it is burned and in others it is hauled to a dumping ground and used as filling material.

There is some variation in the character of the material collected from the streets of different cities, depending on the nature of the industries, the kind of paving material used, and the character of traffic on its streets, yet on the whole the collections from sweepings are very similar and consist chiefly of manure from animals, leaves, dirt, and trash, such as paper, fruit skins, particles of coal, etc. It is possible that the sweepings contain finer particles of the paving substance and some oily material dropped from vehicles. This is especially true at the present time, when the use of power vehicles for pleasure and business is so extensive. The effect of the sweepings on crops, especially when used continually year after year on the same fields, is one of much interest and has caused considerable speculation.

This article deals with an investigation of the street sweepings of one of the larger cities. The material has been studied from the point of view of its organic and inorganic constituents and through cultural tests, where its effects on plant growth was observed.

CHEMICAL EXAMINATION FOR MINERAL SALTS.

Three samples of the sweepings were examined: sample No. 1 consisted of the débris secured by hand sweeping with a brush, sample No. 2 was that secured by sweeping with a machine, and sample No. 3 was the decomposed débris from a dump pile which had been accumulating for some length of time. There was no apparent physical difference between Samples No. 1 and No. 2, both being composed mostly of the raw horse manure. Sample No. 3 consisted principally of well-decomposed horse manure. The chemical analysis of the three samples is given in Table I, the results being stated in per cents. of dry material. The analyses were made by Mr. J. G. Smith, of the Laboratory of Physical and Chemical Investigations:

Table I.—Analyses of Street Sweepings.

Number and description.	Nitrogen (N). Per cent.	Potash (K_2O). Per cent.	Phosphate (P_2O_5). Per cent.
1 Hand sweepings	1.34	0.71	1.03
2 Machine sweepings	0.86	0.55	0.55
3 Decomposed sweepings	0.60	0.56	0.60

This table shows each of the samples to contain appreciable amounts of nitrogen, potash, and phosphate, sample No. 1 being somewhat higher in each of these fertilizing constituents. Stable manure as determined from an average of a large number of samples[1] contains about 1.6 per cent. of nitrogen, 1.5 per cent. of potash, and about 1.00 per cent. of phosphoric acid, the figures being based on dry material. Comparing these amounts with that contained in ordinary horse manure from the stable, it will be seen that the content of nitrogen, potash and phosphate is higher in the latter. The lower result might be expected, as the sweepings are not all horse manure, but contain considerable foreign material, aside from the fact that they are frequently subjected to leaching by rain.

EFFECT ON GROWTH.

The efficiency of street sweepings and other manures of this nature as fertilizing material should not be judged merely by the percentage of mineral salts which they contain. The organic material itself has an important bearing on the question, as it may be of such a nature or contain constituents which cause it to have either a beneficial or harmful effect on soils.

Experiments were undertaken to test the effect of sweepings on crops, by growing plants in soil to which they had been added. In these experiments an especially constructed paraffine wire pot,[2] possessing certain advantages over the ordinary clay pot, was used.

To test the effect of sweepings on soil, wheat was grown in the paraffine wire pots for one month. The soil used in the test was a clay loam. The soil was divided into four portions. To three of these was added a sample of one of the three types of sweepings, while to the fourth good stable manure was added

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[1] From the Laboratory of Soil Fertility Investigations by permission of the Secretary of Agriculture.

[1] Storer, F. H., "Agriculture in Some of its Relation with Chemistry."

[2] For description of method, see *Circular* **18**, Bureau of Soils.

in order that a comparison might be made. These cultures were checked against the growth in untreated soils. The sweepings and manures were used at the rate of 5 tons per acre. The tests were conducted in a green-house, where the conditions of temperature and moisture could be controlled. When the plants had grown for 30 days, they were cut and the green weight recorded. Three pots were used for each treatment, six plants in each pot.

Table II.—Growth of Wheat in Soil Treated with Street Sweepings and Stable Manure.

Treatment.	Green weight. Grams.	Increase. Per cent.
Soil untreated	1.708	..
Soil + hand sweepings (Sample No. 1)	2.240	31
Soil + machine sweepings (Sample No. 2)	1.880	10
Soil + decomposed sweepings (Sample No. 3)	1.800	5
Soil + stable manure	2.500	46

The figures in this table show the sweepings to be beneficial, especially sample No. 1, but not as efficient as good stable manure.

Another test was made in which corn was grown in the soil treated with street sweepings and stable manure, the manurial treatments and general methods being the same as in the first experiment. Results which substantiate those obtained in the latter were secured. The green weight is given in the table below:

Table III.—Growth of Corn in Soil Treated with Street Sweepings and Stable Manure.

	Green weight. Grams.	Increase. Per cent.
Soil untreated	3.700	..
Soil + hand sweepings (Sample No. 1)	4.710	27
Soil + machine sweepings (Sample No. 2)	4.160	12
Soil + decomposed sweepings (Sample No. 3)	3.440	—8
Soil + stable manure	4.950	34

There was an increased growth with samples No. 1 and No. 2, but a decrease where sample No. 3 was used. Again the stable manure had a more beneficial effect than the best of the sweepings. The growth is shown in Fig. 1.

Another culture test was made, using a vegetable (radish) as the plant on which to test the effect of the street débris. The growth of plants in this experiment is shown in Fig. 2. Again the sweepings are beneficial, the plants in Pots Nos. 2, 3 and 4 being larger than in the untreated Pot No. 1. Pot No. 4, which contains the soil treated with decomposed sweepings, has smaller plants than any other except the check. It will be recalled that this treatment showed the least effect also in the case of wheat and corn. Pot No. 5, which is treated with stable manure, has produced the largest growth, which again shows that the sweepings are not as helpful as good stable manure.

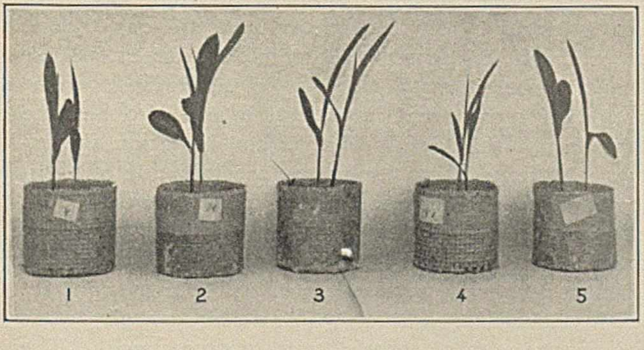

Fig. 1.—Effect of Street Sweepings and Stable Manure on Corn.

(1) Soil untreated; (2) soil + stable manure; (3) soil + sweepings No. 1; (4) soil + sweepings No. 3; (5) soil + sweepings No. 2.

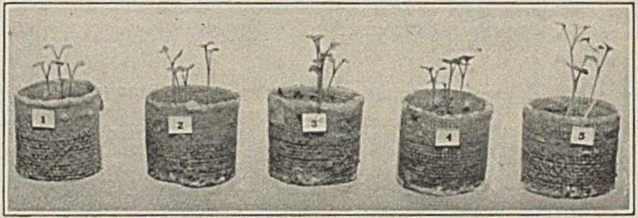

Fig. 2.—Effect of Street Sweepings and Stable Manure on Radishes.

(1) Soil untreated; (2) soil + sweepings No. 1; (3) soil + sweepings No. 2; (4) soil + sweepings No. 3; (5) soil + stable manure.

EXAMINATION FOR MINERAL OIL.

As was pointed out, the sweepings are apt to contain lubricating oils and fine particles from the decay of the paving materials, which may be a factor in determining their usefulness as a fertilizer material. In order to study this point the three samples were repeatedly extracted in an extraction apparatus with petroleum ether until the solvent was no longer colored. The fatty material was saponified with alcoholic potash and the amount of mineral oil extracted by petroleum ether determined. Sample No. 1 contained 1.7 per cent., sample No. 2 2 per cent., and sample No. 3 2 per cent. of the crude mineral oil. This high content of mineral oil suggests the possibility of the recovery of low-grade lubricating oil from city street sweepings, especially in those cities which have considerable automobile traffic.

EFFECT OF THE OIL ON GROWTH.

The effect of the oil extracted from the sweepings was tested with wheat plants. Young wheat seedlings were grown in distilled water and nutrient solution cultures. Fifty milligrams of oil from each sample were put in the culture bottle containing 250 cc. of solution. The oils from all of the samples were harmful to growth, the roots as well as the tops being affected. Oils from samples No. 1 and No. 2 reduced the growth of wheat 10 per cent. in the case of the distilled water cultures, and the oil from sample No. 3 reduced the growth 20 per cent. In the solution containing the nutrient salts, the oils used in the same amount, from sample No. 1 reduced growth 6 per cent., from sample No. 2 7 per cent., and from sample No. 3 11 per cent.

TEST OF SWEEPINGS AFTER OIL WAS EXTRACTED.

The sweepings from which the oils had been extracted were next tested as to their effect on growth. The petroleum ether was evaporated completely from the manure by allowing it to stand in the open for a week or more. The same kind of soil was used as in the previous experiments and the extracted sweepings were added to portions of the soil at the rate of 5 tons per acre. Treatments with stable manure, extracted with petroleum ether and also in its natural condition, were included in the test as a means of comparison with the samples of sweepings. The plants were grown in the paraffine pots for 30 days, then the green weights were taken. Three pots were used for each treatment. The growth is given in Table IV.:

TABLE IV.—EFFECT OF STREET SWEEPINGS, AFTER BEING EXTRACTED WITH PETROLEUM ETHER.

	Green weight of	
Treatment.	Wheat. Grams.	Radish. Grams.
Soil untreated	1.910	3.700
Soil + hand sweepings, extracted (Sample No. 1)	2.270	5.400
Soil + machine sweepings, extracted (Sample No. 2)	2.270	5.700
Soil + decomposed sweepings, extracted (Sample No. 3)	2.190	5.200
Soil + stable manure, extracted	2.260	5.800
Soil + stable manure, natural	2.270	5.700

An examination of the figures in the table shows that the sweepings and stable manure had about the same efficiency in causing increased growth; this is true with both the grain and the vegetable crop. The oil was also extracted from the sweepings by using ether as the solvent and the sweepings afterwards tested in soils. This test also showed that the sweepings were practically as good as the stable manure.

It will be recalled that the effect of the unextracted sweepings was not nearly so good as the effect produced by the stable manure. In other words, after the oil was removed from the street débris its action was practically the same as that of the stable manure. That the oil is the deleterious constituent of the sweepings is also borne out by the fact that the oil itself, when added to culture solutions in which plants were growing, markedly reduced their growth.

The application of street sweepings to soils will undoubtedly have a beneficial effect and be a factor in building up the land; the possible danger of a harmful effect from the oily substance which it contains must, however, be considered. If the oil could be economically extracted this danger would be averted. The oil in the débris for the first year or two may not have any effect, but a continuous application to a field year after year may eventually impair its productiveness, unless through drainage or other natural agencies the oily material is drained off or changed. In some localities this is probably the case, as the use of such material is still said to be effective, although it has been applied for a number of years. No very definite field information on this point is, however, at hand. In this connection attention must be called to the fact that the presence of an unusual amount of oil in such street sweepings has been the result of automobile traffic, and hence appears only in recent years as an appreciable factor in the use of street sweepings as fertilizer, and it is not improbable that the amount of oil will even further increase in the next few years.

Aside from the physiological action of the oily material here mentioned, there are probably other more strictly physical effects due to the coating of soil particles, thus interfering with normal moisture movements and solubility of the mineral soil constituents.

Vegetable or animal oils undergo changes in soils under the influence of soil organisms, but so little is known concerning the action of organisms on the strictly hydrocarbon oils that no statement concerning the possible disappearance or change of this oil in street sweepings can be made.

BUREAU OF SOILS,
WASHINGTON, D. C.

INORGANIC PHOSPHORUS IN PLANT SUBSTANCES—A METHOD OF ESTIMATION.

BY R. C. COLLISON.

Received May 15, 1912.

In the synthesis of organic phosphorus compounds by the plant and their storage in seeds as reserve food, the inorganic phosphates play an important part. The phosphorus used in this synthetic process is taken into the plant in inorganic form and used in the building up of complex organic phosphorus compounds such as lecithins, phospho- and nucleo-proteids and salts of phytic acid.

It is believed by some investigators that unmodified plant tissue and a large number of the seeds contain practically no phosphorus in inorganic combination. Since inorganic phosphate is the starting point in the synthesis of organic phosphorus compounds and as there exist in the plant enzymes which have the property of splitting off inorganic phosphorus from such compounds, it would seem probable that at least an appreciable quantity of phosphorus in inorganic form might be found in such plant tissues and seeds.

It is doubtful whether the failure to demonstrate the presence of appreciable quantities of inorganic phosphorus in seeds has been due to its absence in the plant substance under examination or to analytical methods, which may be questioned from a chemical and practical standpoint.

Methods of estimating inorganic phosphorus in plant substances usually begin with some means of acid extraction of the material, with subsequent separation of the phosphates from the extract. Some of the proposed methods may be questioned on the ground of mechanical imperfection and also because they do not take into sufficient consideration the influence of organic matter on the precipitation of phosphates with the common precipitating agents. This influence on precipitation was investigated, to some extent, by the author two years ago.[1]

Dilute acid extracts of plant substances contain, besides inorganic salts, also proteids, carbohydrates and, in the case of cereals, salts of phytic acid. The proteids and carbohydrates both inhibit the formation of ammonium-phosphomolybdate, and the salts of phytic acid especially have the property of suppressing the formation of this precipitate in a marked degree. The influence of phytin, especially, was investigated by the author two years ago. That it is no

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[1] *Bull.* **215**, Ohio Agr. Exp. Sta., April, 1910.

small factor contributing to the accuracy of the final results can be readily appreciated when the results below, which were secured at that time, are examined.

Commercial phytin was dissolved in 0.2 per cent. nitric acid and pure sodium phosphate, equivalent to 0.0420 gram magnesium pyrophosphate, added. Acid molybdate solution in excess was then added and the solutions digested at 60° C. for one hour. The volume of the solutions was about 200 cc.

TABLE I.[1]—INFLUENCE OF PHYTIN ON THE PRECIPITATION OF PHOSPHORUS.

Grams phytin.	Grams pyrophosphate recovered.
1.0	0.0000
0.5	0.0260
0.4	0.0329
0.3	0.0371
0.0	0.0420

Phytin is only one of the substances present in acid extracts of seeds, which may have a retarding or inhibiting influence on the precipitation of phosphorus. Large quantities of some salts of organic acids seem to have this tendency. Alkaline citrates, solutions of which seem to have the property of dissolving phytin, have tendencies in this direction.

These results, it is believed, indicate very clearly that failure to demonstrate the presence of inorganic phosphorus in some of the seeds may easily have been due to discrepancies in the analytical methods.

There is no absolute standard with which we can compare results by different methods. The only standard we have for comparison is one established by the addition of a known quantity of pure phosphate to a plant substance, together with the constancy of our analytical results. Complete recovery of the phosphorus added and a constant result for inorganic phosphorus without such addition constitutes the most reliable test we have at present of any given method.

The difficulties in precipitation above noted have been, to some extent, overcome by some previous work two years ago.[1] A brief description of the method published at that time is here given.

Ten grams of the substance are extracted with 300 cc. of 0.2 per cent. hydrochloric acid for three hours: 250 cc. of the filtered extract are precipitated with magnesia mixture and made strongly ammoniacal. After 12 hours the precipitate is filtered off and washed with ammonia and finally with alcohol. The dried paper with the precipitate is thoroughly shaken with a measured volume of acid alcohol, the mixture filtered, an aliquot of the filtrate evaporated and phosphorus determined in the residue.

This method avoids the necessity of precipitating phosphorus in the presence of proteids and salts of phytic acid. It has now been in use for two years in this laboratory and has given more satisfactory results than any method previously used.

In all the plant substances examined from time to time, appreciable quantities of inorganic phosphorus have been found by this method. A few results are here given for illustration:

TABLE II.—TOTAL AND INORGANIC PHOSPHORUS IN A FEW PLANT SUBSTANCES.

Substance.	Total phosphorus. Per cent.	Inorganic phosphorus. Per cent.
Oats, grain	0.397	0.060
Wheat, grain	0.394	0.036
Corn, grain	0.266	0.041
Soya beans	0.547	0.054
Cow peas	0.445	0.056
Rice polish	0.600	0.027
Alfalfa hay	0.230	0.136
Blue grass	0.256	0.158

With substances giving extracts low in organic material, as is the case with the rough feeds, such as the hays, and also with many other substances, the method gives very consistent results. With substances giving extracts high in organic material, this method may cause high results due to great difficulty in filtering the extracts, the prolonged standing probably causing decomposition of organic phosphorus compounds, and in other cases low results due to the influence of organic substances on precipitation of magnesium-ammonium-phosphate.

These difficulties are met with especially in the extracts of leguminous seeds, cereal grains and their byproducts, which are in general very difficult to filter.

With the purpose of eliminating these sources of objection a new method is proposed, which, although bearing some resemblance to the old method in its minor details, is quite different as regards extractive medium and method of precipitation.

While investigating the solubilities of inorganic and organic phosphorus compounds in connection with the acid water extraction method, the author found that cold acid alcohol (94 per cent. alcohol containing 0.2 per cent. of hydrochloric or nitric acid) has the property of dissolving the common phosphates, which are insoluble in neutral or slightly alkaline alcohol. Proteids in general, nucleinic acid from yeast, carbohydrates and salts of phytic acid appear for the most part to be insoluble. Taking these facts into consideration, an acid alcohol extraction of the material is proposed. Such an extraction would insure solution of inorganic phosphates, which could be filtered from the undissolved organic phosphorus compounds in the residue.

For the investigation of this proposed method of extraction and separation three plant substances were selected.

(1) Soya beans, on account of their high percentage of soluble protein and also because dilute acid water extracts of the ground beans, as well as the precipitated extracts, are extremely difficult to filter.

(2) Rice polish, on account of its rather high content of phytin.

(3) Corn germ meal, on account of its content of nuclein phosphorus.

The method of procedure and the new method in detail, as proposed, is as follows:

NEW METHOD OF ACID ALCOHOL EXTRACTION IN DETAIL.

A ten-gram sample of the substance, very finely ground, is placed in a 400 cc. Florence flask and covered with exactly 300 cc. of 94 to 96 per cent. phos-

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[1] *Bull.* **215**, Ohio Agr. Exp. Sta.

phorus-free alcohol, which contains 0.2 per cent. of hydrochloric acid (calculated from the per cent. HCl in the concentrated acid). The flask is shaken at intervals of five minutes for three hours. The extract so obtained is then filtered through dry double 11 cm. filters into dry flasks. No suction is necessary. An aliquot of 250 cc. of this filtrate is placed in a 400 cc. beaker and made just alkaline to litmus paper with ammonia. A slight excess of ammonia does no harm. The solutions are allowed to stand 8 to 12 hours or overnight and then filtered through double 11 cm. filters, care being taken to decant the clear liquid as long as possible. The precipitate is then transferred to the filter and washed with 94 to 96 per cent. alcohol, which has been made very slightly ammoniacal. In transferring the precipitate, some of the material may stick very tenaciously to the beaker. In this case, after cleaning the beaker fairly well, add 5 drops of hydrochloric acid to the beaker, rub out the latter with a rubber tipped rod, add 10 cc. of alcohol and then make just alkaline with ammonia and transfer this last portion to the filter. In this way the last traces of the precipitate can be easily removed. After washing several times, the inner filter with the precipitate is spread out and allowed to dry completely. It is then transferred to an Erlenmeyer flask containing exactly 100 cc. of 0.5 per cent. nitric acid in water (calculated from the per cent. HNO_3 in the concentrated acid). The flask is stoppered and the contents thoroughly shaken until the paper and precipitate are broken up. It is best to let stand for some hours. The material in the flask is then filtered through dry double 11 cm. filters into dry beakers and exactly 75 cc. of the filtrate precipitated with 50 cc. of official acid molybdate solution in the usual way. Ten grams ammonium nitrate and two hours digestion at 60° C. are usually sufficient. The final result represents the amount of inorganic phosphorus in 6.25 grams of the original sample.

It is advisable to reprecipitate the pyrophosphate, if the final solutions are highly colored, which is sometimes the case with some of the rough feeds, as the hays. In the case of substances which are relatively high in inorganic phosphorus, a smaller sample may be taken, 3 to 6 grams. In using this method with substances which are tenacious and gummy, and which do not break up readily in acid alcohol, as is true of dried fruits and other substances containing considerable sugar, the same may be worked up with sand and a definite quantity of water, 15 to 20 cc., is usually sufficient. This may be done in a mortar and the material washed out into the flask with acid alcohol, care being taken to use the correct volume, namely, 300 cc. minus the quantity of water used. This method deflocculates the most refractive substances in this regard. It is also very important to have the original material ground as fine as possible before extraction.

Three sets of determinations were made by this method on soya beans, rice polish and corn germ. In each case determinations were made with and without the addition of a known amount of pure phosphate, in an endeavor to recover the latter completely.

The first two sets of results were slightly low, due to insufficient time given for precipitation, since the filtered extracts were made ammoniacal and filtered immediately. Following the detailed method as stated, allowing the extracts after precipitation to stand the specified 12 hours, very consistent results were obtained as shown by the following table:

TABLE III.—RECOVERY OF ADDED PHOSPHORUS BY ACID-ALCOHOL EXTRACTION METHOD.

Substance.	Without phosphate.	With phosphate 0.0037 gram phosphorus.	Theoretical results.	Per cent. inorganic phosphorus.
Soya beans	0.0015	0.0053	0.0052	0.024
Rice polish	0.0012	0.0048	0.0048	0.019
Corn germ	0.0018	0.0053	0.0054	0.028

The figures are grams of phosphorus (element) and are averages of three determinations.

The first column of figures represents the quantity of inorganic phosphorus found in the material itself. Column 2 represents the amount found after the addition of pure phosphate in known quantity, and column 3 the results which should have been obtained after adding pure phosphate, assuming that the figures in column 1 are the correct ones for inorganic phosphorus. For example, the inorganic phosphorus in 6.25 grams of soya beans amounted to 0.0015 gram phosphorus. To every 6.25 grams of sample were added pure sodium phosphate equivalent to 0.0037 gram phosphorus. Thus, if the added phosphorus were completely recovered, the result should have been 0.0015 + 0.0037 = 0.0052 gram phosphorus for the theoretical.

These results check with the theoretical as closely as could be desired, indicating complete recovery of the phosphate.

In Table IV are given similar results on a more extended scale. The pyrophosphate was reprecipitated, the results being given in column 3.

TABLE IV.—INORGANIC PHOSPHORUS BY NEW METHOD, WITH AND WITHOUT PURE PHOSPHATE.

Substance.	Without phosphate.	With phosphate 0.0037 gram phosphorus.	With phosphate reprecipitated.	Theoretical results.	Per cent. inorganic phosphorus.
Cow peas	0.0014	0.0053	0.0051	0.0051	0.023
Oil meal	0.0017	0.0057	0.0053	0.0054	0.027
Corn meal	0.0016	0.0056	0.0051	0.0053	0.025
Wheat, grain	0.0008	0.0046	0.0044	0.0045	0.012
Wheat bran	0.0021	0.0063	0.0060	0.0058	0.034
Wheat germ	0.0025	0.0068	0.0064	0.0062	0.040
Clover hay	0.0043	0.0085	0.0082	0.0080	0.070
Timothy hay	0.0030	0.0068	0.0067	0.0067	0.047
Oats, grain	0.0026	0.0067	0.0064	0.0063	0.041
Cottonseed meal	0.0014	0.0055	0.0053	0.0051	0.023
Rice polish	0.0012	0.0050	0.0049	0.0049	0.019
Corn germ	0.0018	0.0055	0.0055	0.0055	0.029
Soya beans	0.0015	0.0053	0.0052	0.0052	0.024

The figures represent grams of phosphorus (element).

Here again the results agree with the theoretical in every case.

The extracts of substances which by the acid water extraction method filter with great difficulty, by the acid alcohol extraction method filter with great ease, as well as the solutions after precipitating by neutralization.

In order to make the comparison complete, a similar series of determinations was made by the acid water extraction method on the same substances, with and without phosphate added.

Table V.—Comparison of Acid Water and Acid Alcohol Extraction Methods. Results by Acid Water Method.

Substance.	Without phosphate.	With phosphate. 0.0081 gram phosphorus.	Theoretical results.	Per cent. inorganic phosphate, acid water extn.	Per cent. inorganic phosphorus, acid alcohol extraction.
Cow peas	0.0013	0.0068	0.0094	0.020	0.023
Oil meal		Unfilterable			0.027
Corn meal	0.0014	0.0092	0.0095	0.022	0.025
Wheat, grain	0.0006	0.0074	0.0087	0.009	0.012
Wheat bran	0.0037	0.0098	0.0118	0.059	0.034
Wheat germ	0.0022	0.0090	0.0103	0.035	0.040
Clover hay	0.0037	0.0088	0.0118	0.059	0.070
Timothy hay	0.0026	0.0105	0.0107	0.042	0.047
Oats, grain	0.0034	0.0110	0.0115	0.055	0.041
Cottonseed meal	0.0048	0.0124	0.0129	0.076	0.023
Rice polish	0.0016	0.0087	0.0097	0.025	0.025
Corn germ	0.0018	0.0097	0.0099	0.029	0.029
Soya beans	0.0010	0.0032	0.0047	0.015	0.024

The results in the first three columns are expressed in grams of phosphorus (element).

The inorganic phosphorus was recovered in five cases, namely, corn meal, timothy hay, oats, cottonseed meal and corn germ. It is interesting in this connection that all five are substances which do not give a large quantity of organic material on extraction. On the other hand, cow peas, wheat, wheat bran, wheat germ, clover hay, rice polish and soya beans are all plant substances which yield a large quantity of soluble organic matter on extraction, which has evidently had its effect in preventing complete precipitation, since the phosphate added was not entirely recovered in these substances.

Hydrolysis has possibly been a factor contributing to the variations in the results by the two methods, especially in the case of cottonseed meal and wheat bran. The higher results in these two substances may indicate the splitting off of inorganic phosphorus from organic compounds. This factor would have considerable bearing on results by the old method, in which extraction and precipitation is made in a water solution. On the other hand, in the new method this factor would not have special significance, since extraction and filtration are made in alcohol and the presence of strong alcohol practically throughout the process tends to prevent enzyme action and bacterial decomposition.

As a factor in causing low results may be mentioned the property of some organic bodies to combine with inorganic salts in water solution and also the property of such bodies of inhibiting the precipitation of phosphorus, either chemically or mechanically. Phytin, proteids and carbohydrates seem to have these properties, some in a marked degree.

The chief considerations which recommend the acid alcohol extraction method may be stated as follows:

(1) Alcohol extraction tends to prevent enzyme and bacterial decomposition of organic phosphorus compounds.

(2) Organic phosphorus compounds in general seem to be practically insoluble in the solvent.

(3) Filtration of the extracts of even the most difficultly filterable materials is very rapid.

(4) Recovery of the alcohol used is possible.

(5) A considerable saving of time over the old method is secured.

(6) Results on all the substances examined seem to be consistent and in all cases added inorganic phosphorus was completely recovered.

The author does not claim that the acid alcohol extraction method gives final and absolute results for inorganic phosphorus in vegetable substances, but hopes that it may be useful in more nearly approximating the truth.

Lack of time has prevented further work on some of the details of the method, such as the influence of a longer time of extraction or a slightly stronger acid, and the substitution of a second acid alcohol separation to take the place of the dilute nitric acid separation in the Erlenmeyer flask, details which might be of considerable interest.

It is also thought that this method might be adapted to the determination of inorganic phosphorus in animal tissues. Tissues dried by vacuum could be extracted by acid alcohol, either before or after ether extraction of fat and lipoid phosphorus, thus determining inorganic phosphorus on the same sample and rendering unnecessary the tedious and, in the case of fresh brain and blood, the somewhat unsatisfactory and difficult method of hot water extraction.

It is the hope of the author that some of these points will be more thoroughly investigated.

The author wishes to express thanks to Dr. E. B. Forbes for his courtesy in making this investigation possible.

Nutrition Laboratory,
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LABORATORY AND PLANT

DESIGN AND EQUIPMENT OF THE CHEMICAL ENGINEERING LABORATORY AT THE UNIVERSITY OF WASHINGTON.

By H. K. Benson.

Received April 3, 1912.

A description of the new chemistry building of the University of Washington was published some time ago (*J. Am. Chem. Soc.*, **32**, 967). Recently the space set aside for chemical engineering practice has been utilized in the design and equipment of a chemical engineering laboratory of which a brief description may be of interest.

The general plan is shown in the accompanying diagram (Plate I). The room is well lighted and completely fire-proof, since it has a concrete floor, brick walls, and wire-lath-cement ceiling. It is supplied with all the accessory equipment available in the building such as steam, gas, compressed air, etc., and with the installations named in the description of Plate I.

The function of the laboratory is to offer facilities for the acquirement of familiarity with fundamental processes in chemical manufacture such as distillation, extraction, filtration, desiccation, grinding and pulverization, mixing, calcination, fusion and steam digestion. At the same time it furnishes a workshop for industrial research problems which arise from local conditions.

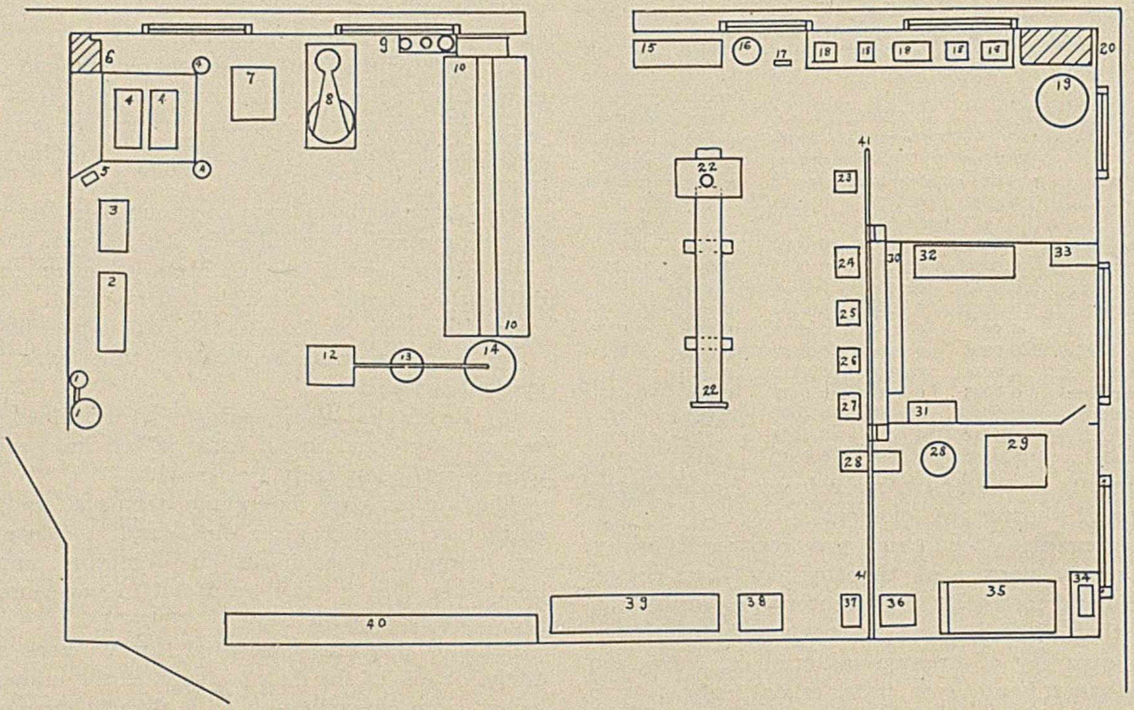


Plate I.

1. Continuous extraction apparatus.
2. Filter press.
3. Hydraulic press.
4. Wood distillation retort.
5. Drying oven.
6. Flue.
7. Steam superheater.
8. Steam still.
9. Alcohol still.
10. Work table.
12. Vacuum dryer.
13. Condenser.
14. Vacuum still.
15. Sulphurous acid plant.
16. Pulp digester.
17. Fan motor.
18. Heating furnace.
19. Seger furnace.
20. Flue.
22. Rotary cement kiln.
23. Case crusher.
24. Paste mill.
25. Pony mixer.
26. Braun disc. pulverizer.
27. Drug mill.
28. Vacum pump and equalizer.
29. Wood grinder.
30. Shelves.
31. Desk.
32. Balance table.
34. Testing table.
34. Drying closet.
35. Mixing table.
36. 14 H. P. motor.
37. Pebble mill.
38. Moist closet.
39. Storage rack.
40. Lockers.
41. Shafting.

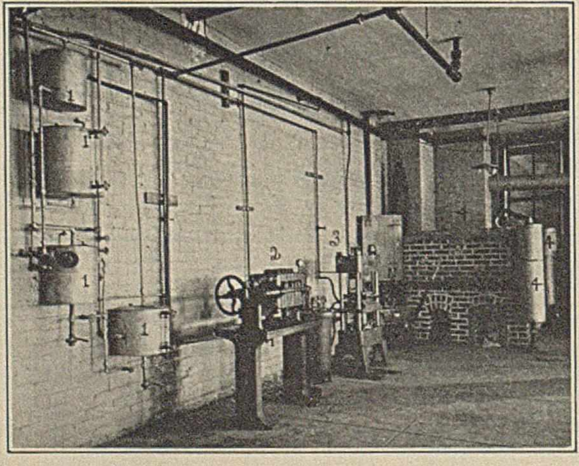


Plate II.

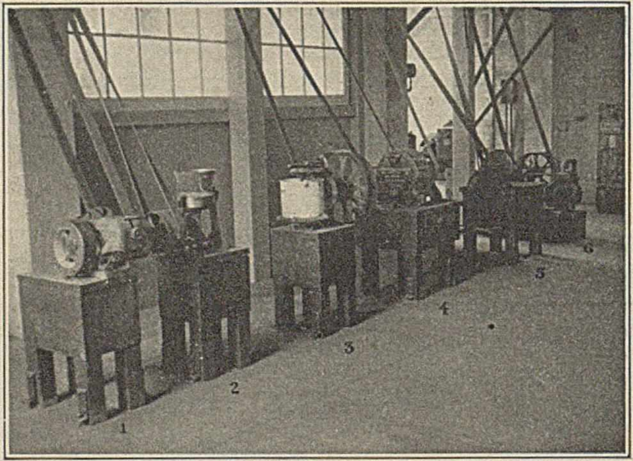
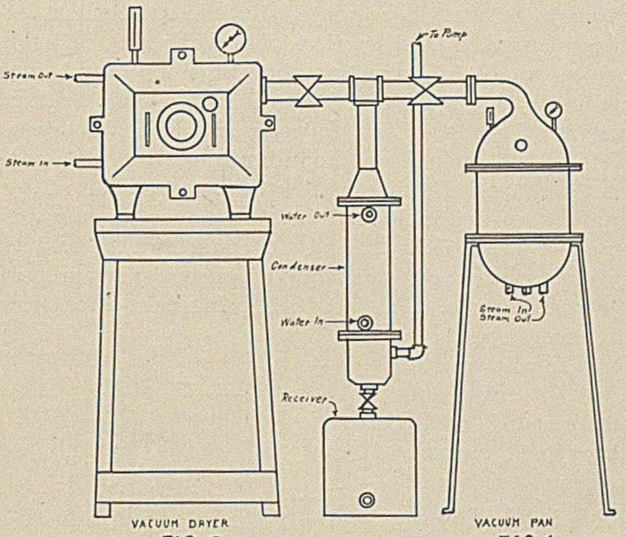


Plate III.

For distillation the laboratory is equipped with a steam still modeled after those used in the turpentine industry: with an electrically heated destructive distillation retort (Fig. 4, Plate II) and with a steam jacketed copper vacuum still (Fig. 1, Plate IV). In the latter the use of steam from a superheater enables a wide range of use in connection with the vacuum pump Fig. 6, Plate III). The extraction of oils by solvents is carried on by means of a continuous extraction apparatus (Fig 1, Plate II) or by pressure in a Boomer and Boschert type of hydraulic press (Fig. 3, Plate II). For filtration and clarification, the Sperry filter press (Fig. 2, Plate II) is used.

The effect of varying pressure on desiccation is illustrated by a Stokes vacuum drier (Fig. 2, Plate IV) which may be subjected to a twenty-four inch vacuum or a forty-pound air pressure. Grinding machines of various types have been selected. For rock materials, a case jaw crusher (Fig. 1, Plate III) is used and a number of ball and pebble mills in other laboratories are also available. For pigments the Day pony mixer (Fig. 3, Plate III) for mixing and a paste mill (Fig. 2, Plate III) for grinding with oil are employed.



VACUUM DRYER
FIG 2

VACUUM PAN
FIG 1

PLATE IV.

For the reduction of wood, roots, bark, etc., to powder form, a Mitts and Merril wood grinder and a Greenbaugh drug mill (Fig. 5, Plate III) have been installed.

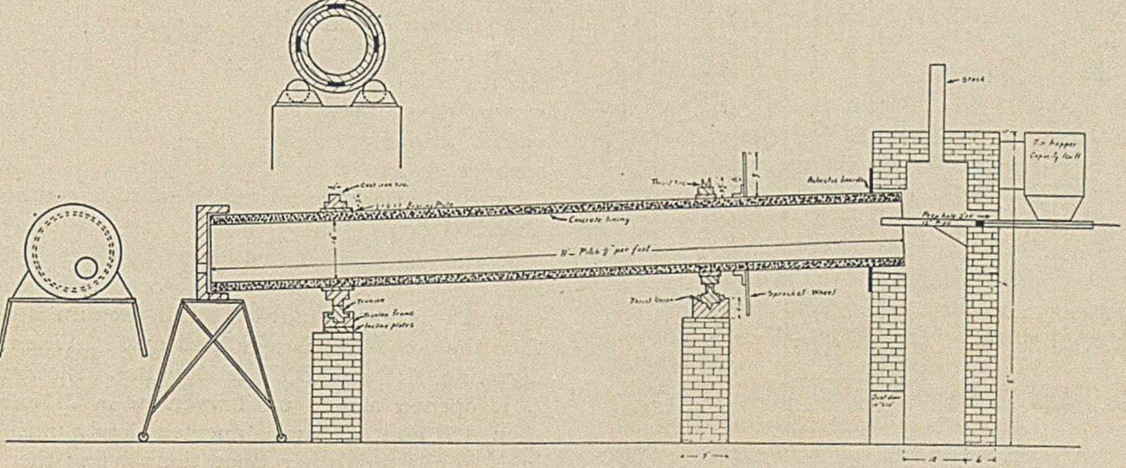


PLATE V.

In the testing of ceramic materials use is made of heating furnaces of the usual type. They are equipped with Case gas burners, a forced draft being supplied by a small motor-driven fan. This equipment also includes a Seger down draft furnace which utilizes preheated air in combustion.

The silicate industry is represented in the installation of cement testing apparatus consisting of moist closet, storage racks, mixing table, tensile strength machine, and in the design of a small rotary kiln equipped with an oil burner (Plate V). For experimental work with lime-silica combinations a small digester (Plate VI) capable of yielding 100 pounds steam pressure is employed. The latter apparatus is also available for experiments in wood pulp digestion in connection with a small sulphurous acid plant.

A work table for refining operations has been provided with outlets for steam, compressed air, vacuum, gas, water and superheated steam.

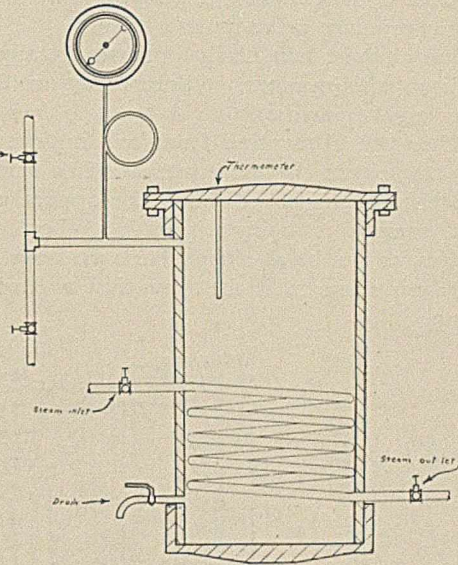


PLATE VI.

From this brief description in connection with diagrams and illustrations it will be seen that stress in chemical engineering education at the University of Washington is laid upon certain fundamental operations, all of which are closely related to the industries now established in the Pacific Northwest.

UNIVERSITY OF WASHINGTON,
SEATTLE.

A NEW APPARATUS FOR THE DETERMINATION OF CARBON DIOXIDE.

By E. W. GAITHER.

Received April 1, 1912.

The apparatus shown in Fig. 2 was designed primarily for the determination of CO_2 in soils by the well known double titration method. It has the advantage over other apparatus used for this determination, in that it does not have to be taken apart for any operation involved; it is very compact, being set up on a single ring stand, and occupies only about 10″ to 12″ desk space; there are no very delicate parts; the control of the major operations is centered in a single stopcock, and the adaptability of the absorption towers to a wide variety of work. It will stand a vacuum of 70 cm. and is adaptable for either atmospheric pressure or vacuum work.

One chemist can easily operate six apparatus, and by using this number, 36 determinations can be made in an eight-hour day.

After the absorption from one sample is complete the tower can be cut out, another sample started and the CO_2 removed from the apparatus while the first sample is being titrated. When desired, one apparatus can be at atmospheric pressure and another at 70 cm. vacuum at the same time and with the same pump.

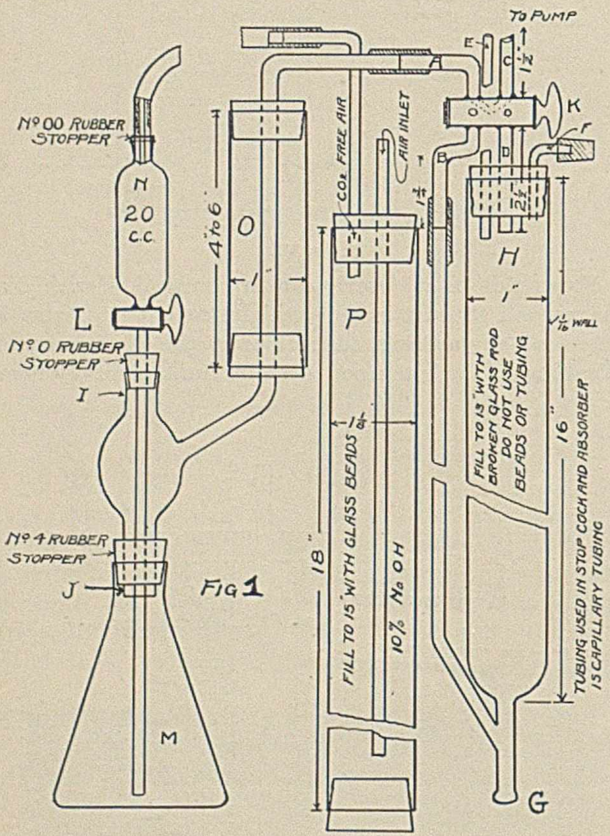


FIG 1

The entire apparatus can be washed out without taking apart any of the rubber connections. 200 cc. of distilled water will wash out the tower, so that one drop of N/10 HCl will more than neutralize the remaining NaOH, if the washing is done properly.

By using 50 cc. of 4 per cent. NaOH, the CO_2 evolved from 1 gram of $CaCO_3$ can be absorbed in 20 minutes, with bubbles passing into absorber at the rate of from 10 to 15 per second.

For ordinary substances that do not foam when boiled, condenser O[1] can be connected direct to flask M through the rubber stopper, thus eliminating the bulb.

OPERATION.

The apparatus is connected to the suction pipe and a stopcock or screw pinchcock is placed between the suction and absorber *H*. *G*, *B* and *D* are closed and *L* opened. *A* and *C* are connected by turning stopcock *K*. Flask *M*, containing the sample, is connected, the pump started, and the flow of air through *P* and *M* regulated by the pinchcock between absorber and suction; while the CO_2 is being driven out of *M*, introduce the absorbing liquid from a pipette through *E* and follow it with a little distilled water. Close *A*, *C* and *L*, pour acid into *N*, connect *N* to *P* and open *L* until equilibrium is reached; connect *A*,*B* and *D*,*C*, and after adjustments are made apply heat under *M* and boil for 20 or 30 minutes. Remove heat, close *B* and *D*, connecting *A* and *C*, cut off suction by means of pinchcock and prepare for next sample. While CO_2 is being exhausted from *M*, containing second sample, open *E* and *F*, draw out absorbed CO_2 through *G*, connect a funnel to *E* and pour in water until broken rod in *H* is covered, draw out through *G* and repeat the operation; when full, the second time, turn *K* to connect *B* and *D* and allow liquid to rise in *B′*. When 200 to 250 cc. of water have been passed through *H* connect *A* and *C*. Titrate all or an aliquot of the solution containing the absorbed gas.

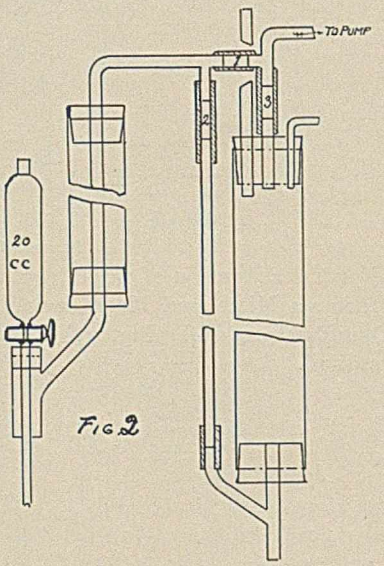


FIG 2

If the vacuum method[1] is to be used, *L* is closed and the pinchcock between absorber and suction is opened very slowly until the full vacuum is obtained, then the flow of air is regulated by *L*. When through digesting, *A*,*B* and *D*,*C* are closed and suction cut off, *L* is opened slowly until vacuum in *M* is relieved, then *A*,*B* and *D*,*C* are connected slowly until vacuum in *H* is relieved, other operations being the same as when working at atmospheric pressure.

PRECAUTIONS.

Do not connect *A*,*B* and *D*,*C* when there is a partial vacuum in *M*, or liquid will be drawn from *H* into *M*. Do not apply heat under *M* unless suction is previously applied and there is enough vacuum to prevent back pressure, or NaOH solution will be forced out of *P* through air inlet. Always open *F* when washing out apparatus or introducing an absorbing liquid. Do not connect *B* and *D* when *H* is full or the liquid will rise in *B′* and have to be washed out.

The apparatus can be flushed out by removing *M*

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[1] Inlet and outlet tubes for cooling this and the corresponding condenser in Fig. 2 are not shown in the drawings.

[1] By F. S. Marr, *J. Agr. Science*, **3**, Pt. 2, pp. 156–60.

and *N*, stoppering *J* and connecting *A*,*B* and *D*,*C*, forcing water through *I*.

Fig. 1 shows a home-made apparatus that gave very satisfactory service until stopcock *K* was designed to replace pinchcocks 1, 2 and 3.

Hydrogen may be substituted for air by connecting air inlet tube in *P* to a hydrogen generator.

Department of Chemistry,
Ohio Agricultural Experiment Station,
Wooster.

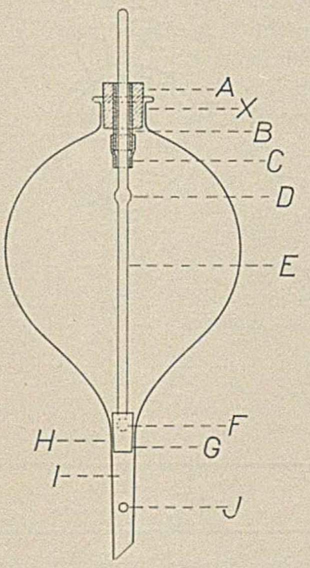
AUTOMATIC FILTER FEED.

By Thos. A. Mitchell.

Received April 18, 1912.

The accompanying diagram shows a device for automatically supplying solution to any laboratory filtering medium where a quantity of liquor, or wash water, is required to be filtered. The apparatus is especially serviceable where it is desired to filter over night.

The main body consists of a pear-shaped funnel of the separatory type, minus the glass stopcock. The neck X is of such size as will take a No. 3 rubber stopper. The outlet I is about 6 cm. long and 1 cm. inside diameter, being slightly enlarged at H to engage the No. 00 rubber stopper G which is attached, as shown, to the glass rod E at F. This glass rod should be of a diameter that will pass freely through the glass tube B 5 mm. in diameter. A nodule is formed by heating as indicated at D.



The upper portion consists of a No. 3 rubber stopper, A, a glass tube, B, 3 cm. long and 5 mm. inside diameter, and a piece of $^{3}/_{16}$″ pure rubber tubing, C, 15 mm. long.

The hole J should be about 4 mm. in diameter and determines the level of the liquor in the filtering apparatus below.

In use, the glass rod E, with stopper G attached, is passed through at X and the stopper G inserted at H. The liquor to be filtered is poured in through X, using the protruding glass rod as a guide for the solution, if it be so desired. After the solution has been added, the parts A-B-C, assembled as a unit, are slipped over the upper end of the glass rod and the rubber stopper A made tight at X.

By quickly lifting the glass rod the nodule D will enter the protruding rubber tube C resulting in an air-tight joint at C and a free passage at H. The amount of liquor passing through H is regulated by the volume of air which enters through the trap J. The hole J is not absolutely essential, but we find it does away with considerable upward suction of the liquor below, thus assuring a better washing of the residues in cases where that is the desired result.

With E-G in position the nodule D should be about 3 cm. below the tubing C.

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NOTE ON PROTECTORS FOR GLASS STOPCOCKS.[1]

By Walter O. Snelling.

Received May 2, 1912.

Probably every chemist has at some time or other suffered the inconvenience of having a glass cock drop out and break. It is not infrequent for such an accident to result in the loss of the entire apparatus, and at the best there is involved the loss of the time and expense required in sending the parts back to the maker.

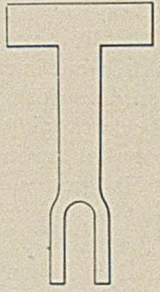
Fig 1

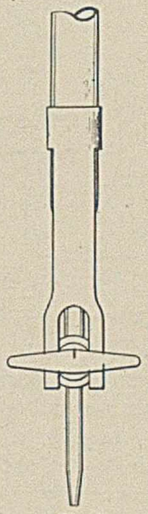
Fig 2

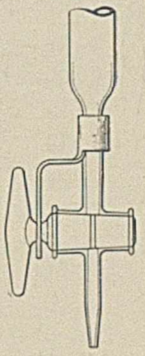
Fig 3

Some months ago Dr. Charles E. Munroe called my attention to a clip or holder which he had devised, and which was being used by him as an attachment for burets and similar glass apparatus containing stopcocks. The device is simple, easily made, and admirably answers its purpose. It consists of a piece of sheet hard-rubber, so shaped as to encircle some glass part of the apparatus, while a small 2-tined fork passes around the thinnest part of the movable portion of the cock, holding it so securely as to prevent it from dropping out, no matter in what position the apparatus is held, while at the same time allowing perfect freedom of motion of the stopcock, and also enabling the cock to be removed when desired. In Fig. 1 is shown the blank, as cut from sheet rubber, for one form of the Munroe holder, and Fig. 2 shows this form attached to a buret. Ordinary hard rubber sheets of about $^{3}/_{64}$″ thickness is the most convenient material from which to make the blanks. After the blank has been cut it is placed in boiling water for a few minutes to soften, when it may be bent in any desired form, and upon becoming cold will retain whatever form has been thus given it.

Fig. 3 represents another form of the Munroe clip, and one which has also been found to give very satisfactory results. This form is placed permanently upon the apparatus by the blank being bent into

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

shape while attached to the buret, both being placed in hot water. The form shown in Fig. 2 can be put on or be taken off the buret at any time, by simply sliding the sleeve along the buret until the tines of the fork are free from the stopcock, and then sliding it down along the tube until it is free.

After I had used the Munroe clip for some time, and had become familiar with the security it affords against the accidental breakage of stopcocks, it occurred to me that for new apparatus, a glass stopcock could be easily constructed which would be quite free from the danger of the cock slipping out. In the preparation of glass stopcocks the cock is always cut off from a longer piece of glass, and it should be a simple and easy matter to leave the glass a little longer than is now usually done, and then after grinding the cock a small groove could be cut in this extended portion. By wrapping a rubber band around in this groove, or attaching a small rubber ring, complete security would be afforded against the accidental loss of the cock. I had some stopcocks prepared as shown in Fig. 4, fitted with a small rubber ring as indicated (partly in section) in Fig. 5. The device affords absolute security against accidental loss of the cock, while at the same time it is nearly invisible, is not in the way of the operator, and can be instantly removed when required. It further serves to keep the cock in place, preventing the loss of fluid which sometimes results from a cock becoming slightly displaced.

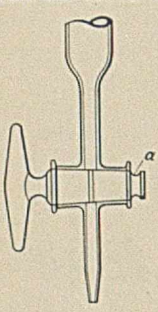

Fig 4

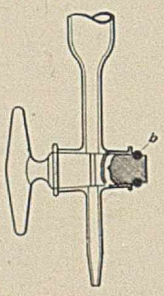

Fig 5

The form of holder devised by Dr. Munroe can be readily applied to any type of glass apparatus already constructed, and the form I here suggest can be provided on new apparatus, thus offering for either new or old apparatus a remedy for the nuisance of broken stopcocks.

Bureau of Mines,
Washington.

ALUNDUM CRUCIBLES IN GRAVIMETRIC ANALYSIS.

By Guilford L. Spencer.

Received April 29, 1912.

The writer tried unsuccessfully to use alundum crucibles in the ordinary Gooch holders, in the gravimetric determination of reducing sugars. The difficulty experienced was in washing the walls of the crucible free of the salts.

It later occurred to me to make the joint at the top of the crucible instead of near the bottom, as in the Gooch method. To do this required a special funnel and a rubber ring, which I procured through Messrs. Eimer & Amend. The arrangement of the apparatus is shown in Fig. 1. The results are satisfactory.

The air pressure causes the rubber ring to bear upon the edges of the crucible and against the wall of the funnel, making tight joints. The supporting points in the funnel leave all parts of the crucible accessible for washing.

With the glass funnel, as illustrated, there is some slight difficulty in centering the crucible. I propose to overcome this in the future by the use of a porcelain funnel with centering points, as shown in Fig. 2, or a perforated diaphragm.

I believe that with this arrangement the alundum crucible will be very useful in gravimetric work in agricultural and general laboratories. I expect soon to use it in P_2O_5 determinations. An evident advantage of this type of crucible is the absence of asbestos.

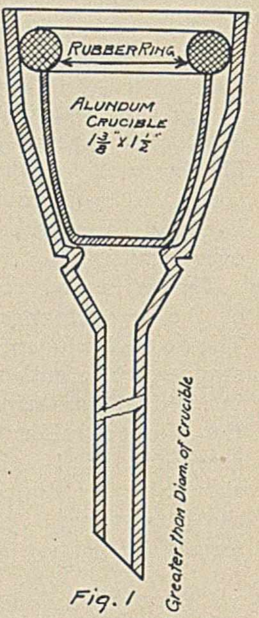

Fig. 1

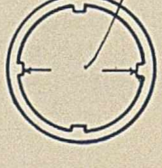

Fig 2.

The Cuban-American Sugar Company,
New York and Havana.

ADDRESSES

NATURAL GAS INVESTIGATIONS OF THE BUREAU OF MINES.[1]

By George A. Burrell.

Last year at the Pittsburgh convention of the Natural Gas Association, a resolution was passed, asking that the Bureau of Mines assist the natural gas industry in solving problems which arise in the utilization and conservation of natural gas. Although not as active in its investigations as it hopes to be in the future, some progress has been made toward a study of this important fuel.

No attempt has as yet been made toward a complete comparative study of the natural gases from different fields of the country. Some work has been accomplished in that the characteristics of the gas from a few wells in some of the more important fields have been determined, but the Bureau is gathering from many wells in all of the fields a large number of samples, and is submitting them to examination. A bulletin covering this work will be ready for distribution the latter part of the present year. Work already accomplished makes it appear that natural gas consists of paraffin hydrocarbons with nitrogen and carbon dioxide as impurities. The paraffin hydrocarbons may be methane only, or a mixture in which methane and ethane predominate with smaller percentages

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[1] Presented at the 7th annual convention of the Natural Gas Association of America, Kansas City, Mo., May 21, 22, 23, by permission from the Director of the Bureau of Mines.

of the higher paraffin hydrocarbons, or in the case of rich casing head gases, a mixture in which ethane and propane predominate. The carbon dioxide may range from a trace, as in the case of the gases of Western Pennsylvania, to as much as 30 per cent., as found in a sample of natural gas obtained from Kings County in Southern California. Nitrogen may occur in quantities ranging from a few tenths of 1 per cent. to as much as 10 or 15 per cent. As an example of an unusual and extreme case, the Bureau found that a natural gas occurring in the State of Washington contained 98 per cent. of nitrogen. In general it may be said that those gases issuing under considerable pressure in the great fields which are providing heat and light for many towns consist of paraffin hydrocarbons in which methane predominates along with smaller quantities of ethane and traces of the still higher paraffins. These gases range in heating value from 900–1100 B. t. u. per cubic foot at 0° C. and 760 mm. pressure with the average more nearly approaching the latter figure. In these days when the heating value is the important factor in determining the usefulness of a gas, such high values are very significant. Contrary to usual text-book information, the Bureau has not been able to detect, in those gases examined, the presence of olefine hydrocarbons, carbon monoxide and hydrogen, although exhaustive tests have been made for these constituents. Natural gases do not lend themselves well to the ordinary examination to which gases are usually submitted. These points will be emphasized in the forthcoming report. It is believed that an analysis of natural gas which shows carbon monoxide, hydrogen and olefine hydrocarbons should be carefully looked into regarding the method employed in examination. The composition of the gas has an important bearing, viewed from several standpoints.

First let it be emphasized that we have, in natural gas, a fuel rich in heat units, non-poisonous, diminishing in quantity and which can be replaced only as Nature sees fit, selling for less than a manufactured product which is not its equal.

From the composition can be determined the relative value of the different gases. It appears that the composition of the gas from a particular well does not vary materially over long periods of time. Sufficient data is not at hand to make this a sweeping statement covering all cases. But in the case of the natural gas supplied to Pittsburgh, the Bureau finds that its composition does not vary appreciably from its composition as determined by F. C. Phillips about 18 years ago. This gas comes from many different wells in the Appalachian fields. As a gas well diminishes in pressure however, the lighter constituents will have been removed and finally, especially where the well is subjected to reduced pressure for the obtaining of gasoline, the heavier paraffin hydrocarbons come off and these when subjected to pressure and low temperature again condense and gasoline is obtained.

Not infrequently, a warning is raised against the introduction of too much carbon monoxide into illuminating gas. Carbon monoxide gives to coal and water gas their powers of asphyxiation, and where the content is high, the intrusion of the gas into a room from a defective connection may result fatally, when we consider that as little as 0.2 or 0.3 per cent. of CO in a room, after a sufficient lapse of time, will bring about unconsciousness and death. Such being the case we are fortunate that natural gas does not contain carbon monoxide.

No one doubts the great importance of the correct determination of the genesis of natural gas and petroleum. Probably the prevailing opinion of the present day has it that natural hydrocarbons are of organic origin, although sufficient proof is not at hand to say that at least some of them may not be of inorganic origin. If of inorganic origin, say by the action of superheated water on the carbides of iron, according to Mendeléeff's hypothesis, then we may be justified in believing that natural gases should contain those constituents that are produced by the decomposition of carbides when the experiments are performed in the laboratory. We could still go farther and believe that the formation of natural gas is continuously taking place, for we are not justified in saying that the carbides have long since been exhausted. Mendeléeff's theory, however, does not stand up in the face of these chemical considerations. The theory that natural hydrocarbons are produced by the destructive distillation of either animal or vegetable matter receives the most support. If such is the case, oil and gas become stored products and are not being continuously generated at the present time. It will be seen from this brief summary that an accurate knowledge of the composition of the different gases becomes essential in order to throw all possible light on the elucidation of the genesis of natural gas. "Where can gas be found?" is the insistent demand of those who already feel the pinch of a diminishing supply. Geologists are in possession of certain facts that help to diminish the risk in drilling wells, but it is only when the drill has made the boring that doubt becomes removed.

Little need be said here about the production of gasoline from natural gas. Suffice to say that by this means a highly useful fuel is being obtained for which there is an ever-increasing demand. The industry rapidly developed from its swaddling clothes so that now it threatens to add considerably to the total quantity of gasoline produced. All natural gases, of course, are not adapted to the manufacture of gasoline. A few wells produce methane as the only hydrocarbon, and for the liquefaction of methane, a pressure of 50 atmospheres at —94° C. is required. Some gases, as Pittsburgh natural gas, some of the Oklahoma gases, and many others contain a large proportion of methane, a smaller proportion of ethane and not nearly enough of the higher paraffin hydrocarbons for the commercial production of gasoline. Other gases, casing head gases, and those drawn from the earth under reduced pressure, may be so rich in the higher paraffin hydrocarbons—butane, pentane, hexane, etc.—that five or more gallons of gasoline per 1000 cubic feet of gas may be extracted. A chemical examination will show what may be expected from a particular gas in the way of gasoline production with a given plant equipment. The Bureau is making a study of these methods of examination. Perhaps the simplest of the tests applied at the present time consists in the determination of the density of the gas or in shaking the gas with some solvent such as olive oil, cotton seed oil, clairolene oil, etc., in which the higher paraffin hydrocarbons are more soluble than the lower. It was found, for instance, that by shaking 100 cc. of a gas from which a very high yield of gasoline is obtained in 35 cc. of clairolene oil that 80 per cent. of the gas dissolved in the oil. Pittsburgh natural gas lost only 15 per cent. of its volume when treated in the same way. The latter gas cannot be used for the commercial production of gasoline. Pittsburgh natural gas has a density of 0.64 compared to air as 1 at 0° C and 760 mm. pressure while it has been found that natural gases having a density of 0.86 do produce gasoline. The author has found, however, that other gases having the same density and absorption number contain different proportions of the paraffin hydrocarbons so that it cannot be stated that all natural gases having a density of 0.86 will produce gasoline.

The Bureau has issued one publication having to do with the properties of liquefied natural gas. In the production of gasoline a very great waste has occurred, because, in order to make condensates safe for shipment, the lighter products have been allowed to evaporate. The confinement of the material in iron cylinders for use as a bottled gas is now receiving attention. A gas is produced which has a heating value of at least 2200 B. t. u. per cubic foot, and a candle power of about 45 when burned as a naked flame at the rate 5 cubic feet per hour. The use of a mantle will, of course, increase this lighting effect greatly. In order to bring this means of utilizing natural gas to your attention, Mr. I. C. Allen and the writer simply bottled in strong cylinders the condensate obtained by applying a pressure of about 500 lbs. to the square inch and a temperature of 0° C. to crude gas obtained from wells at Follansbee, W. Va. There are some here who could do the same with their casing head gas which is at present going to waste. Once bottled it is only necessary to slightly crack the valve to obtain a supply of true gas.

In experiments conducted at the Bureau, the gas was passed through a small meter, and then burned in a Junker calorimeter. Samples of the gas were also analyzed. By taking the gas from the bottom of the tank its composition remained uniform throughout the test. In the case of the exceedingly rich gas obtained at Follansbee, W. Va., about 50 cubic feet of gas per gallon of liquid were realized. For the better control of the gas as it issued from the bottle, a reducing valve was attached.

The Bureau has, of course, viewed this manner of utilizing natural gas from the standpoint of a purely technical investigation, with no axe to grind, except a step in the conservation of natural resources and believes that some of the gas at present going to waste will eventually be used this way. Millions of people are so situated that gas is not used by them, but if a bottled gas sold at a reasonable price becomes available, the outlet for the material will be large. The Bureau has recently learned that one company is already in the field for the purpose of exploiting the liquid gas. They have named their product "Gasol."

Another means of utilizing natural gas has been tried in that attempts have been made to prepare substitution products, principally chloroform, by the action of chlorine upon methane. Although seemingly difficult to do commercially, one cannot say that such will always be the case. Mention is made of these processes simply as showing that the entire utilization of natural gas may not always be along the line of combustion processes.

Probably in but few instances has surface combustion been applied in this country as yet to the use of natural gas. A 92 per cent. efficiency in the case of gas-fired boilers obtained by Prof. Bone is a noteworthy advance and opens up a wide field for the saving of gas in combustion processes. An installation is not complicated or costly.

In the every-day use of natural gas for domestic purposes, saving may be accomplished if appliances are used which are best suited to the economical combustion of natural gas. Natural gas burners require more air than coal gas burners, and if the same burner regulation is used for natural gas that works well with coal gas, the former is not being completely burned. Some natural gas appliances in use are notoriously inefficient. Progressive gas men should give this question of proper appliances serious consideration. Natural gas is cheap and the tendency may be to use more for any particular purpose than is necessary. A campaign along this line, which would result in a smaller consumption of gas per family, should help remove some of the objection to the inevitable rate rise.

In conclusion, it can be stated that the Bureau of Mines wants to do all it can to conserve the natural gas supplies. Great care must be exercised in the use of deposits which are only bubbles and which when punctured become exhausted. Reckless waste of the gas in the field should be prevented by legislation, and every effort should be made toward the education of all concerned that they may realize the necessity of conserving the supply. It is believed that the Bureau of Mines can do some efficient work along the latter line.

BUREAU OF MINES,
WASHINGTON.

A PLAN FOR THE SUPPORT OF CHEMICAL RESEARCH AND FOR THE BETTER TEACHING OF INDUSTRIAL CHEMISTRY.

By JOHN STEWART.

Received April 19, 1912.

The writer has read with some interest several papers and editorials appearing in the journals of the American Chemical Society during the past year on the subject of the teaching of industrial chemistry and the conservation of chemical research, especially that kind of chemical research which has to do with the application of chemistry to the industries. These articles are some of the effects of the increasing competition for the places held by chemists, and the unsatisfactory condition of the industrial chemist in relation to the business of which he is a part. The theme of these articles has been: What ought we to do? What can we do? What should we do to improve the condition of the industrial chemist, to increase his power for rendering useful and efficient service, and through him to benefit the business with which he is connected?

These articles have all had one important point in common, but there the uniformity ends, for each has proposed a different method of solving the problem. Some of these articles have been written by teachers of industrial chemistry who have not had actual, practical experience in the application of chemistry to the industries, if one may judge correctly from the general tone of certain statements made. But it is not intended to offer any criticism of articles heretofore published on this subject, they being in the main thoughtful and ably prepared papers. What we now need is a uniform plan of action. We have a certain unity of purpose. If we can connect with this a plan of solving the problem, which meets with general approval from our Society, or at least with the approval of a good working majority of the Division of Industrial Chemists, and will then work unitedly in accordance with this plan we should be able to accomplish some desirable results.

It is the desire of the writer to aid, if possible, in this movement toward a uniform plan of action. In order to get unity of action it is evident that we must confine ourselves to general principles, and leave details to be solved in accordance with the views of individuals and the necessities of local conditions.

The best proposition that has so far been advanced looking toward the amelioration of the condition of industrial chemistry appeared in the November, 1911, issue of THIS JOURNAL. In that number there appeared a very able editorial entitled "Facilities for Industrial Research." The author of that editorial exhibits thorough, first-hand knowledge of the conditions with which he deals. He advances as a fundamental proposition the following state ment: "But there is one field which is richer in the promise of results than all others combined; a field which will yield a more immediate, direct, and tangible return to our own industry, our own profession, and to our own members; and that is in *recognizing the necessity of systematic study of industrial problems and throwing the undivided influence of this Society into the establishment and maintenance of laboratories equipped to answer the eternal questions arising as a result of industrial progress.*"

This quotation contains at least three general principles: 1st, industrial chemical problems require systematic study; 2nd, there should be properly equipped laboratories for such study; 3rd, the American Chemical Society should work as a unit toward the establishment of such laboratories. It is not difficult to conceive that some business men who profit by the application of chemistry to industry would object strenuously to some or all of them. But it is difficult to conceive that any member of the American Chemical Society, who has a sound, thorough training in chemistry, should object to any one of them.

But there must be some other general principles to which a large body of us can agree; otherwise there can not be any further progress toward a solution of the problem. A few of them appear to be of such general acceptability that they will command the support of a large portion, at least, of the American Chemical Society.

In the first place, the establishment of chemical laboratories is generally a business proposition and they are and must be directed and controlled from a business point of view. Of course there is a large portion of the membership of the Society who dislike the term "business," and who prefer to consider their occupation a "profession" rather than a "business." Yet, if the signs of the times are read aright more and more "professional" men are going into business, and "business" is going to be the great "profession" of the not far distant future. In the second place, a business proposition must be a self-supporting proposition, otherwise it sooner or later passes from the sphere of human action. Hence, a chemical research laboratory must be a self-supporting institution.

Some business men who are reaping profits from chemical industries do not act as if they thought chemical research a paying business proposition. They appear to regard the research chemist in much the same way that many research men regard the business man. Both think the other capable of being improved upon to a very marked degree. Some business men of this type even expressly forbid the chemist in their employ to do any experimenting of any kind, and their laboratories are very poorly built, the equipment being scant and the cheapest the market affords, and chemical literature unknown, the laboratories even being without a book of tables for calculations. To this type of business man, chemistry is a two times two are four proposition; every professed chemist is expected to answer off-hand any question concerning the chemistry of any phenomena which may occur. This is not intended as a libel or a joke on the business man but is a clear, cold statement of fact.

Again, some business men recognize that chemical research, if properly directed, may be made a good paying business investment. Some of this type have established research laboratories in connection with their business.

A review of the history of the business man's treatment of the chemist is not flattering to the chemist, but, nevertheless, the business man is slowly but surely being forced (by competition) to change his methods; and the future of industrial chemistry really looks very much brighter than the past. In the judgment of the writer, the business men who manage chemical industries are not going to establish research laboratories in connection with such industries, with any great degree of rapidity. That more of such laboratories will be established is practically certain, but the process will be a slow, hard-fought one.

Now, on the other hand, how do we chemists regard research? Do we consider it a paying proposition from the business point of view? Undoubtedly most of us do, but we recognize the profits to be, in many cases, very remote; so remote, in fact, that the business man takes no chances on them. And again, we could probably all designate some pieces of work, done usually by "the other fellow" as "research work," which we would hesitate to dignify by that term. Then, too, if we regard research as a business proposition, there is no doubt that it should be directed along the lines of the most immediate and the greatest need. Glancing over *Chemical Abstracts*, we find that a large portion of the space is devoted to abstracts of research papers relating to organic chemistry: out of some 100,000 known compounds, about 75,000 of them are synthetic. Vegetable physiological and animal physiological chemistry are comparatively neglected, yet these are the fields where the natural organic compounds occur. The reason for their comparative neglect is apparently the greater difficulty of research in these lines. We need more and better research into the fundamentals of chemistry, but we also need, and need more immediately and to a greater degree, research into the problems attending the applications of chemistry to industry.

If we admit that the establishment of research laboratories is a business proposition and that the research should be self-supporting, then how is the money for the development and maintenance of the research institution going to be directed into the research treasury. Information of a certain kind is the one valuable asset of a research institution; but knowledge has a peculiar habit of leaking out, so that its benefits get more or less generally diffused among the public without any direct expense to the public. Evidently the public should pay for the development and maintenance of useful research; that is, the State Governments and the General Government should establish and maintain needed research laboratories, and it would seem that the American Chemical Society must necessarily act as a unit toward influencing the public to perform its duty.

But part of the public will object to this kind of procedure, and the strength of this objection is a very serious obstacle in the path of those who favor the move. This difficulty could be partially avoided by the adoption of a plan which appears to the writer to be a better one than that of securing annual or biennial appropriations from Congress or from State legislatures.

Let this society exert its undivided influence to prevail upon Congress and State legislatures to appropriate a sufficient fund for the establishment of research institutions in each State, these research institutions to be established in connection with State universities or agricultural and mechanical colleges, more appropriately with the latter but probably with both. Then let the Government or State aid cease but let the institution remain Government or State property, concerning the administration of which an annual report should be made by those in charge. Let the fund provided be invested in a full fledged manufacturing plant of a kind appropriate to local conditions. Let this plant be managed and operated on a business basis just as if it were the property of a private corporation, but instead of paying dividends on the original investment let the profits be used to maintain needed chemical, physical, and mechanical research laboratories and help support the teaching part of the institution with which it is connected. In this way the taxation of the people for the support of education would be diminished, and their educational facilities improved. It would also enable the people to take an effective part in the prevention of extremely high and extortionate prices for goods, which private corporations are sometimes supposed to levy. The plan would meet with opposition, but most Governmental activities which threaten to reduce *profits*, for the benefit of the people, are antagonized by the business men affected. In this way, the business which benefits by scientific research would pay the expenses of scientific research, which is not altogether true of present conditions.

To illustrate the plan, let me say that the agricultural college of a certain state is located in a rich agricultural region in which several sugar factories are flourishing. If this agricultural college were provided with a million dollar fund, it could purchase, possibly, a sugar factory already in successful operation, or if terms of sale by the owners could not be secured on a satisfactory basis, the college could build a new factory (capable of handling 600 tons of beets per day) at a cost of approximately $350,000.00 to $400,000.00. The balance of the original fund would be required as a working capital. A factory of this capacity would yield an annual profit of about $200,000.00, which could be very appropriately used to pay for the support of education and research.

On this plan, the educational institutions of the country would have the facilities as well as the expert knowledge, both practical and theoretical, to teach successfully industrial chemistry, mechanical engineering and business administration, without "aping" industrial activities on a small scale. No one institution could teach the practice of the whole field of industrial chemistry, but all could teach the general theory as now and each one would be specially prepared to teach one phase of industrial chemistry: in general it is in only one phase of industrial chemistry that the industrial chemist is going to become really expert. Degrees for industrial chemists might be put on the same basis as the Ph.D., or otherwise as the educational institutions should see fit.

Some business men would oppose this plan. But business men are already encroaching upon the field of higher education and research. They are teaching their employees the theory as well as the practice of the particular business in which they are engaged and are at the same time paying the employees wages whereby they are enabled to live while being educated. They are also establishing research laboratories in connection with their business for the study of problems which have to be met and solved. But they are doing this not for the purpose of benefitting their employees or the general public, but solely for the purpose of increasing *profits*, or saving themselves from being driven out of business by their competitors who are learning cheaper and better ways of doing things, and who are cutting prices as a consequence. It would seem, therefore, that the scientific men could very advantageously to themselves commence to encroach upon the particular field of the business man. When the scientific man gets in control of business, the scientist will fare better in the business world; but only in so far as the scientist gets control, can he hope for much consideration from the business man.

It would seem to the writer also that the American Chemical Society could, very advantageously to itself, endow itself with a fund of say $1,000,000, with which it could go into business for itself. A fund of this size would require about a $200 investment from each member. By proper management the Society could have a considerable annual income to devote to research, the cheapening of publications to the members, or otherwise as desired. There is plenty of business and technical ability in the Society to engineer such a plan to success. The Division of Industrial Chemists is composed of men who are specially fitted for the carrying out of a plan like this in certain fields at least. This kind of a proposition, proposed and carried out by a great body of scientific men, would probably be free from the suspicion that it was only "a stock jobbing proposition." The plan, once in successful operation and fairly administered, would doubtless prove very beneficial to the Society.

LOGAN, UTAH.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR.

THE MANUFACTURE OF NITRATES FROM THE ATMOSPHERE.

E. K. Scott states (*Nature*, 89, 463) that although the first experimental plant for the manufacture of calcium nitrate by the direct process of Birkeland and Eyde was started only nine years ago, already the Norwegian Hydro-Electric Nitrogen Co., which controls the Birkeland-Eyde patents, has installations aggregating 200,000 horse-power at work and probably by 1916 another 300,000 horse-power will be at work. The other electrically produced nitrogenous manure, calcium cyanamide, is manufactured by a more indirect method invented by Franck and Caro, and its manufacture is not confined to Norway. The following table gives the principal installations, and it may be noted that, although the first one on a commercial scale was erected at Piano d'Orto, in Italy, only eight years ago, there are works in operation, and being built, which by the end of next year will be making calcium cyanamide at the rate of more than a quarter of a million tons per annum.

INSTALLATIONS FOR MANUFACTURE OF CALCIUM CYANAMIDE BY THE FRANCK AND CARO PROCESS.

Name of Company.	Place of installation.	Output in tons per year.
Nitrogen Fertilizers Co. (Northwestern Cyanamide Co.)	Odda, Norway	15,000
Nitrogen Fertilizers Co. (Northwestern Cyanamide Co.)	Alby, Sweden	15,000
Societa Italiana di Prodotti Azotate	Piano d'Orto, Italy	4,000
Societa Italiana per il Carburo di Calcio	Terni, Italy	15,000
Societa Piemontese per il Carburo di Calcio	San Marcel, Italy	3,000
Société Française pour les Produits Azotes	Martigny, Switzerland	7,500
	Notre Dame de Briancon	7,500
Bayerische Stickstoff Werke	Trostberg, Bavaria	15,000
Ost-Deutscher Stickstoff. u. Chemische Werke	Bromberg, Prussia	2,500
A. G. Stickstoffdunger	Knapsack, Germany	18,000
Societa per l'Utilizzazione delle Forze Idrauliche della Dalmazia	Selenico, Dalmatia	4,000
	Dugirat, near Almissa	80,000
Japanese Nitrogen Products Co.	Kinzei, near Osaka	4,000
American Cyanide Co.	Nashville, Tenn.	4,000
	Niagara Falls, N. Y.	12,000

The Nitrogen Fertilizers Co., which owns the Odda and Alby Works, works under license from the Northwestern Cyanamide Co., which company controls England, Norway and Sweden, Belgium, and all the British colonies, protectorates and dependencies, except Egypt and Canada. The Odda plant is being enlarged, and at the beginning of next year will be producing 73,000 tons per annum. In the United States, the American Cyanamide Co. is about to erect a works in Alabama to manufacture 24,000 tons per year.

A PROCESS FOR THE FIXATION OF ATMOSPHERIC NITROGEN.

The Chemical Trade Journal (50, 622) observes that many have assumed a pessimistic attitude on the subject of the fixation of atmospheric nitrogen. This feeling is attributable, in the main, to the fact that the possibilities of the various processes so far devised have been over-popularized, and there can be no doubt as to the ultimate importance of the question. The same *Journal* notes that the price movements of nitrate of soda show evidence rather of market rigging than of any near approach to the exhaustion of the Chilean deposits. Nevertheless, the great German chemical works are keenly alive to the importance of the problem of nitrogen fixation and each is doing something toward its solution; for example, while the Badische Company have reduced their holding in the Norwegian production to nominal proportions, the German patent list bears evidence of the activity of this concern in endeavoring to devise a suitable process.

In the process for the fixation of atmospheric nitrogen described in the *Zentralblatt für de Kunstdungen-Industrie* (see *Chem. Trade J., loc. cit.*), use is made of the fact that the oxides of nitrogen result when mixtures of air with combustible gas are detonated. While this has been known for a long time, the conditions necessary to secure a relatively high yield of nitrous gases has only recently been determined and a commercial plant working on these lines has yet to be erected. The favorable conditions seem to be high pressure, high temperature, and a proportion of oxygen greater than that present in air, that is, an addition of oxygen to the gas mixture is advantageous. It has also been found that previous compression of the gas and air, preferably separately, to 5 atmospheres, notably increases the yield of nitric acid, and that preheating the air and adding 30 per cent. of oxygen have a similar effect. It is said that if these conditions are realized, as much as 12 lbs. of nitric acid per 1,000 cu. ft. of gas may be obtained.

THE CORROSION OF IRON AND STEEL.

The Chemical Engineer (15, 246) gives the following summary of the results obtained by Friend, Bentley, West and Chappell in their investigations on corrosion of iron and steel, recently presented before the Iron and Steel Institute in London:

Influence of Carbon on Corrodibility.—(*a*) In rolled, normalized, and annealed steels the corrodibility rises with carbon content to a maximum at saturation point (0.89 per cent. carbon), and falls with further increase of carbon beyond this point. (*b*) In quenched and tempered steels a continuous rise in corrodibility occurs, with increase of carbon within the range investigated (up to 0.96 per cent. carbon), no maximum corrodibility at saturation point being found in these steels.

Influence of Treatment on Corrodibility.—Quenching increases the corrodibility to a maximum; annealing tends to reduce it to a minimum; and normalizing gives intermediate values. The influence of tempering varies with the tempering temperature.

Factors Determining Corrodibility.—The electromotive forces between the pearlite and ferrite, and between the components of the pearlite itself, are the principal factors determining the corrodibility of unsaturated pearlitic steels above 0.4 per cent. carbon. In mild structural steels, the galvanic action, due to differences of potential between the constituents, is accompanied by galvanic action betweeen the ferrite crystals themselves. These differences of electro-potential between the ferrite crystals are the result of differences in their orientation. The state of division of the pearlite, and the presence of internal stresses in the steel, may also exert a considerable modifying influence on the foregoing factors. Decarbonization increases the resistance to corrosion. Three per cent. of tungsten produces practically no change in the corrodibility of carbon steels. The influence of time on the rate of corrosion varies with different steels.

USES OF ALUMINUM.

The article by Seligman on "Modern Uses of the Metal Aluminum" (*Science Progress*) calls attention to the applications of the metal in various industries. The sudden demand for aluminum in 1905 was due to the requirements of the motor-car industry; but since additional supplies were not forthcoming, the automobile industry turned to the use of thin steel sheets and frames of special steels, which were often found to be actually lighter than aluminum parts of equal strength. The increased output from 9,000 tons in 1905 to 34,000 tons in 1910 resulted in a fall in price to about one-half, and a certain increase in the earlier demand for aluminum in motor-car work. However, other uses were required to consume the enlarged supply, and in England a very important outlet has resulted from the discovery of methods whereby, with the aid of a special flux, sheets of aluminum may be fused together without the use of any extraneous solder. Vessels made in this way are of special value for chemical industries, and most of all in those involved in the manipulation of food materials. The metal resists corrosion and has the further advantage that it imparts no coloration to the materials in contact with it. In the brewing industry, fermenting tanks up to 30,000 gallons have been constructed, and vessels for fermenting under a pressure of 45 lbs. per sq. in. have been made of 1800 gallons capacity.

In this connection it may be noted that the aluminum companies of France have organized the Southern Aluminum Company, capitalized at $8,000,000.00, and a plant is to be erected at Whitney, N. C., under the direction of the electrometallurgist Héroult.

BRIQUETTING METALLIC WASTE.

A correspondent of the *Scientific American* (106, No. 21, 477) states that an Austrian, Arpad Ronay, has recently perfected and patented a process for briquetting metallic wastes without a binder. Ronay applies enormous pressure to the particles, but the application is slow, so that the individual particles may associate and come together to permit of the exclusion of air and water. No binding material whatever is employed, and the process is conducted without heat.

Metallic turnings, chips, filings, etc., are delivered into a large hopper, gravitated into the hydraulic press, and the mass is slowly subjected to increasing pressure. The briquette is then submitted to further compression, up to 2,000 atmospheres.

It is said that briquettes made by the Ronay process from cast iron borings, with a low percentage of phosphorus, can be advantageously substituted for the white iron as used in tempering furnaces; and that Bessemer plants and steel foundries, having Siemens-Martin furnaces using scrap material, find briquettes made from steel and wrought iron turnings a cheaper and more efficient fluxing medium. A number of plants have been erected in Germany for briquetting waste materials by this process, the largest being that built for the Tegel Works of Borsig, which has a capacity of six tons an hour.

THE REVIVAL OF THE KELP INDUSTRY.

Kelp, the ash produced by the incineration of various kinds of *Algae* obtainable in large quantities on the west coasts of Ireland and Scotland, and the coast of Brittany, possesses the following composition: potassium sulphate, 10 to 12 per cent.; potassium chloride, 20 to 25 per cent.; sodium carbonate, 5 per cent.; other sodium and magnesium salts, 15 to 20 per cent.; and insoluble residue, 40 to 50 per cent. One ton is procurable from 20 to 22 tons of wet sea-weed.

It is contended with much show of reason in the *Times Engineering Supplement* for May, 29, 1912, that the manufacture of kelp products would prove to be commercially successful if carried out on a comparatively large scale, with modern chemical engineering methods. The sea-weed should be heated in a retort, as proposed by Stanford, and ammonia and acetic acid recovered from the distillate. Stanford obtained 50 to 80 pounds of ammonium sulphate and 6 to 18 pounds of calcium acetate per ton of air-dried sea-weed. The residual charcoal gives up its soluble salts to hot water and can afterwards be used as fuel. The iodides become concentrated in the mother liquors and may be recovered to the extent of 12 pounds per ton of dry sea-weed in the form of free iodine.

LIGHTING BY NEON TUBES.

According to *Engineering* (92, 807), while it has been long known that a vacuum tube charged with neon gives a brilliant light with but little absorption of electric energy, yet there is a progressive absorption of the gas and the light finally extinguished. Claude has described a number of experiments made to overcome this. He found that when the tubes had small electrodes, these heated rapidly nearly to redness, and a metallic deposit formed on the glass in their vicinity. After 88 hours this deposit amounted to 1.6 g. Upon examination, neon was found occluded in the metal. Consequently, as the disappearance of the gas was due to the vaporization of the metal, Claude reasoned that the life of the tube would be lengthened by using larger electrodes, which would keep cooler. He constructed a neon tube, 45 mm. in diameter, with copper electrodes equivalent to a surface of 300 sq. cm. per ampere of current. One of these tubes worked satisfactorily for 210 hours and was then accidentally broken. Therefore, with a tube 6 m. long, with electrodes giving a surface of 500 sq. cm. per ampere, Claude found that the potential difference necessary to maintain the current only changed 4.0 per cent. in 400 hours. The efficiency was excellent, being only 0.8 watt per candle. It is of interest to note that were the energy wholly convertible into that light to which the eye is most sensitive, the output would be 55 candles per watt, according to recent measurements by Buisson and Fabry.

"GRANACIT."

"Granacit" is described by H. Fischer in *Zeitschrift für angewandte Chemie*, 25, No. 26, 1327. It is a grayish blue, finely grained, very hard and weather durable true granite, of regular crystalline structure. It has a strength of compression of 2,000 kg./sq. cm. and a density of 2.7. Only traces of water are present and the content of pyrite is small; quartz, feldspar and muscovite are the main components. "Granacit" is acted upon by acids only in a dilute and cold condition, while in a concentrated state and hot there is no action, and it is not affected by prolonged subjection to superheated steam. It is used as a special acid-resisting stone, and in the form of towers and columns for distillation, rectification, condensation, absorption, washing and reaction purposes. "Granacit" pressure and vacuum vessels are also on the market. It is especially appropriate as a material for towers for sulphite lye, vessels for acetic acid for white lead factories, phosphoric acid tubes, and in the alkali industry. "Granacit" differs from other granites in that it does not become decomposed when treated with acids. "Granacit" apparatus is being manufactured by a Dresden, Germany, firm.

THE DESTRUCTIVE ACTION OF ACIDS ON CONCRETE.

Neumann (*Tonind. Ztg.*, 36, 601) records cases in which concrete drains have become damaged, sometimes soon after construction. In every case the destructive action was traced to the presence of acid in the water which had access to the drains, either internally or externally. In one case the swampy soil surrounding the drain contained iron pyrites, and the water became charged with sulphuric acid; in other instances the atmosphere inside the drains became laden with hydrogen sulphide, which underwent slow oxidation to sulphur and sulphuric acid. Sulphuric acid was the most frequent and most powerful destroyer of underground concrete, but such acids as hydrochloric, oleic and acetic, and also carbon dioxide, were found to be almost as harmful. Neumann attributes the destructive action of acids to: (1) The formation of certain calcium and aluminum compounds, accompanied by a large increase in volume; and (2) the formation of soluble compounds (particularly calcium bicarbonate) which go into solution and cause collapse. He gives as remedies: adequate ventilation inside the drains; the use of non-porous clinker poor in lime as a basis for the concrete; and a covering for the exposed surfaces of tar, tar-felt or asphalt.

"IRONIZING," OR "FERROZINCING."

Pure iron, as is well known, is not subject to corrosion to nearly the same extent as steel, and articles made of good wrought iron also suffer less from atmospheric influences than steel. The more impure wrought iron is, the more it approaches steel in the matter of corrosion, and is therefore more in need of protection than pure iron. In view of these facts, states *Engineering* (93, 679), Sherard Cowper-Coles has brought out a new process, which he terms "ironizing" or "ferrozincing," as a means of protecting iron and steel from corrosion; this process gives a more permanent protection than zinc coating. The process consists in first coating the iron or steel with pure iron by a special electrolytic method. Pure iron is slightly electropositive to the underlying iron or steel. A zinc, nickel or brass coating is then applied to the pure iron surface, and forms, it is claimed, a more durable coating than zinc applied directly to a wrought-iron or steel surface, since the electrochemical action which is set up when once the zinc is penetrated is reduced.

A NEW PROCESS FOR ELECTRO-ZINCING.

The Engineering Review (25, 505) reports that Quentin Marino has devised a method of depositing metals on earthenware and glass by rendering the surface of the article to be coated conductive by "a chemical reaction" which does not involve the application of heat, with the result that the deposited metal is in direct and adhesive contact with the china or glass. The process, as well as the deposition of metals onto iron and steel, consists of combining a reducing agent with the depositing solution, so that all traces of oxide films, etc., are concurrently removed with the deposition of the required metal. It is said that a sound adherent metallic coating may also be produced upon wood and paper; the wood is rendered water and weather proof, while the metallized paper may be employed in making metallic joints. By the process of Marino, it is claimed that 1 to 2 grams of zinc per ampere hour at a pressure of 2 volts may be deposited upon iron or steel.

TEXTILOSE.

Paper (8, 18) states that a factory has been erected at Fleissen for the manufacture of "textilose," a substitute for jute. "Textilose" was invented by Emil Claviez, who manufactured it as a substitute for jute and cotton in his spinning and weaving establishment at Adrof, Germany. The invention consists of a material, capable of being spun, made of wood-pulp, cellulose or the like, with which is combined a fleece or nap of textile fibers, such as cotton, wool, linen, jute, or the waste obtained from a carding machine. Claviez claimed that this substance was adapted to all spinning purposes as well as for the manufacture of paper. Uniting the pulp with 10 to 20 per cent. of fleece is effected during the production of the paper on the paper-making machine, preferably at the beginning of the wire cloth, because in this manner the most intimate union is obtained. "Textilose" yarn may be used in the manufacture of bags, linen, carpets, and upholstery fabrics, and may be bleached, dyed and figured.

THE BLEACHING OF LINEN.

In a paper presented before the Manchester Literary and Philosophical Society on April 23, 1912, on the action of bleaching agents on the coloring matter of linen, R. L. Taylor showed that the coloring matter of unbleached linen is quite abnormal with regard to the action of the ordinary bleaching agents upon it, and differs from every other coloring matter. Whereas coloring matters such as indigo, Turkey-red, and the coloring matter of cotton are bleached much more rapidly by free chlorine or hypochlorous acid than by a hypochlorite, with the coloring matter of linen the exact opposite is the case, this being bleached more rapidly by a solution of a hypochlorite. Apparently the maximum bleaching effect on unbleached linen is produced by a solution of a hypochlorite which contains no free alkali, but rather some free chlorine or hypochlorous acid. Excess of alkali retards the bleaching action, just as it does in the case of other coloring matters. The addition of a chloride to the solution sometimes accelerates and sometimes retards the bleaching action (this depending upon the amount of alkali in the solution), instead of, as is the case with other coloring matters, always accelerating it (*Nature*, 89, 287).

PHOSPHORUS SLAG AS AN INSECTICIDE.

The slag or dross formed in the removal of phosphorus from iron ore has for a long time been used as a fertilizer on account of the phosphorus and lime which it contains. It is pointed out (*Scientific American*, 107, 6) that recent investigation has shown that the use of this slag is even more profitable than had at first been supposed. The cultivation of the sugar beet in Germany suffers great damage from the plant louse, and the depredations of these insects are also destructive to a large number of plants. J. P. Wagner, a sugar beet expert, recently told the National Society of Agriculture in France of a successful attempt to fight these insects by means of phosphorus slag.

He spread about 1,400 pounds of the slag to the acre on fields that were infested with the plant louse. Not only did this treatment prevent the insects from attacking the leaves, but they were driven away from leaves they had already attacked. On another field the slag was applied in larger quantities, with highly advantageous results. Wagner thinks that the slag forms a thin layer on the leaf, spreading it over the whole surface, and that it is either distasteful or injurious to the insects.

OXYGEN ADDITIONS TO IRON FURNACE BLAST.

It is stated in *The Engineering and Mining Journal* (93, 1180) that according to a report by F. W. Lührmann to the blast-furnace committee of the Verein Deutscher Eisenhüttenleute, the managers of furnaces in Mülheim-Ruhr, in Ougree, and in Kratzwieck, are using oxygen additions in the blast whenever the furnace is working cold. The oxygen is added in small amounts in the form of "Linde air," a liquid-air product containing 50 per cent. of oxygen and 50 per cent. of nitrogen. An installation to furnish 17,500 cu. ft. of oxygen per hour occupies a space of about 125 sq. ft., requires about 800 h. p. to operate it, and costs about $100,000. Lührmann finds that for each per cent. of oxygen added, there is a theoretical rise of 100° F. in blast-furnace temperature. The manufacturers interested state that 1 per cent. of oxygen on a 240-ton furnace costs about $0.50 per ton of pig. If this cost is correct, the method may be found to be of value as an emergency reserve.

NEW COMPOSITE SHEET METALS.

Three new composite sheet metals have recently appeared on the market. "*Hoyt-Silver*" is a britannia metal with an aluminum core, and is said to make silver-plated ware which is lighter, cheaper, stiffer, and stronger than that made from ordinary britannia metal. "*Alumintin*" is sheet aluminum faced upon both sides with pure block tin; it is claimed that it can be electroplated and soldered without difficulty, and that it possesses a density of 3.34. "*White-Copper Stamping Metal*" is sheet aluminum faced on both sides with an antimonial lead alloy; it is reported to be cheaper than either copper or brass, and to be stiffer and harder than antimonial lead. The specific gravity of this composite metal is 5.10. It is easily stamped without annealing and is thought to provide a satisfactory substitute for the usual antimony-lead alloys used in making badges, etc. *The Brass World* (8, 176) states that these products are made by a secret rolling process.

A NEW USE FOR BORON.

E. Weintraub has found that boron can be used for purifying and deoxidizing metallic copper, and has patented his discovery (U. S. Patent 1,023,604). The advantages claimed are that boron possesses a high affinity for oxygen, nitrogen and other gases, but no affinity for copper; and that at the same time it forms an easily fusible slag of boric acid. It is said that if 0.03–0.10 per cent. of boron is added to molten copper, copper castings free from blowholes are obtained and the copper has an electrical conductivity of from 95–98 per cent. Matthiessen standard. The copper also runs freely and fills every portion of the mold. When boron is added, the portion necessary for deoxidizing and purification is consumed, and the excess floats to the top of the fusion as a melted slag. Weintraub states that boron carbide gives equally good results and is much cheaper, while boron suboxide is still more economical.

VANADIUM BABBITT METAL.

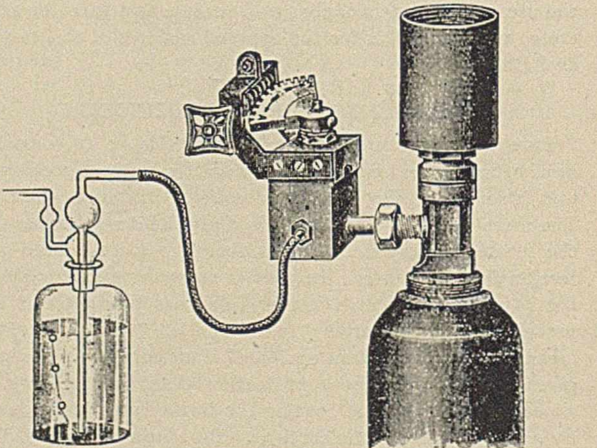
There has appeared on the market a new bearing metal, Vanadium Babbitt, which is made up approximately as follows: tin, 100 parts; antimony, 12 parts; copper and vanadium, 8 parts. The copper and vanadium are melted together, and the fusion is poured into a mixture of molten Straits tin and antimony. The vanadium permits the use of more copper than is generally found in such alloys, gives a denser grain, exceptional tensile and compression strength, and adds 100 per cent. to the life of the bearing.

A NEW VACUUM GAUGE.

According to *Engineering* (93, 539), the ordinary Bourdon type of pressure gauge is not a satisfactory instrument as applied to accurate measurement of vacua. The forces actuating it are then small and what is sometimes termed "sticktion" is accordingly very likely to cause large errors. The ordinary mercury column is also not entirely satisfactory. Water often finds its way to the top of the mercury column, and there is, moreover, some danger of the mercury being accidentally drawn over into the condenser to the ruination of the tubes. A Newcastle-upon-Tyne firm has introduced a gauge under the name of "Kenotometer" to obviate these drawbacks. This new instrument consists of a U-tube provided with a scale. The right-hand leg of this tube is closed at the top forming a barometric vacuum. The left leg of the U-tube is expanded into a vessel of comparatively large diameter. The opening into this limb at the top is through a fine nozzle, upon which, it is claimed, it is practically impossible for mercury to be drawn. This left leg of the U-tube is coupled by a rubber connection to a drying tube, which contains sufficient desiccating material to last for months and is connected up in its turn with the second mercury trap, the top of which is connected to the condenser. The scale with which the instrument is provided is fitted with a rack and pinion adjustment. On the one side it is graduated in 0.1 in. and on the other in percentages of the absolute vacuum.

A NEW FORM OF VALVE FOR GAS CYLINDERS.

A Berlin firm has placed upon the market a new form of valve for cylinders of compressed gases. Since the change in pressure of compressed gases is common, the valve retaining such gases in the ordinary steel cylinders must be constructed strong and solid for the considerable compression which exists. As a certain amount of effort is necessary to open and close, consequently the flow of gas is not constant. A fine and sure regulation of the discharged quantities of gas in a given time is necessary for various purposes. Reducing valves serve only for the regulation of pressure, whereas it is claimed that the new neck valve regulates the amount of issuing gas (German Patent 407,541).



A toothed segment of a wheel of large size, attached to a spindle and operated by a hand-wheel, controls a slight opening of the valve, and hence a very small change in the flow of the gas can be effected.

THE MEASUREMENT OF STEAM CONSUMPTION.

The steam consumed by a turbine or engine can be determined by measuring or weighing the "steam water" or condensate from the surface condenser. A method of doing this (*Industrial Engineering*, 11, 471) is presented in the indicating hot-well, which is attached to the bottom of the condenser, forming a part of the shell. The opening in the bottom of the condenser is constructed so that the condensate drains into the left-hand chamber of the hot-well, and communication from this chamber to the hot-well pump suction is established in the dividing wall. The orifice, polished and finished to insure accuracy of flow, is formed in a brass plate inserted in the partition wall. The indicating gauge is attached to the shell of the hot-well, and ball check valves are provided in each fitting, so that, should the gauge glass break, the flow of air will be prevented and the glass can be conveniently replaced. A gauge glass is also provided for the indication of the height of water in the hot-well suction compartment, in which the water must not be allowed to submerge the orifice. The scale attached to the indicating gauge reads directly in pounds of steam per hour.

A NEW JOINT FOR STEEL PIPE.

The Matheson pipe joint, which was developed for steel or wrought-iron pipe, is similar to the well known bell and spigot joint used with cast-iron pipe. When the pipe is manufactured, one end is expanded into a bell, and around the edge of the bell a reinforcing band of steel is shrunk. The spigot end of the pipe is provided with a slight depression or groove which encircles the pipe near the spigot end. According to *The Engineering and Mining Journal* (93, 1026), in laying the pipe the spigot end is placed in the bell end of the adjacent length of pipe and molten lead is poured into the bell in exactly the same way that the joint of cast-iron bell and spigot pipe is laid. The lead filling may be calked when cool, the reinforcing band adding strength to the bell to resist any tendency to expand as a result of the calking. When the pipe is to be subjected to high pressure, a bolt-flange coupling may be used in conjunction with the lead joint. The advantages claimed are that a strong tight joint is as readily obtained with steel as with cast-iron pipe and that for the same strength steel or wrought-iron pipe is lighter.

NOTES AND CORRESPONDENCE

SEA-WEED, POTASH AND IODINE. A CRITICISM.

In Senate Document No. 190, 62nd Congress, 2nd Session, "Fertilizer Resources of the United States," as well as in an address by F. K. Cameron,[1] sea-weed and especially that of the Pacific coast is mentioned as a possible source of the potash salts used in the United States.

Most of the Senate Document consists of an ordinary description of the stationary growing algae (kelps) and their ecological character. Much space has been given to the species of *fucus* growing in the litoral region. Every expert knows that this species is of no value, as these plants absorb very little valuable material.

The content of inorganic valuable materials in these kelps depends first of all on the physical conditions of their growth. Force of current, temperature, and content of salts are important factors, but other life conditions of the algae also affect their chemical composition. It is of considerable importance whether they are growing near the surface or in deeper water, in comparatively quiet straits or in the breakers of the ocean. The species which, while growing, absorb the most valuable materials are not found in any considerable amounts in the straits or sounds[2] nor in the litoral region, but are abundant out in the ocean, and about the belts of islands, girding the coast, and in these places from the limit of tidewater down to the depth of 20–25 fathoms.

The far more important "Porra" which, until lately, has been given very little consideration, deserves, technically, the greatest attention. A flourishing sea-weed industry on the Pacific coast can be imagined only on the basis of this marine plant. It grows in deeper water and in the open ocean and is consequently richer in valuable materials. It is found in great abundance, is easy to harvest along the coast during fall and winter, and can be worked at proportionately lower cost.

The Senate Document, furthermore, suggests some antiquated methods of burning sea-weed, of preparations of potassium salts, and finally of "Methods of Analyses."

I should advise the use of the "kelpash" and its contents of inorganic valuable materials as the standard scale for the valuation of sea-weed, and not the sea-weed itself. This will simplify transactions between the seller and buyer of kelp or kelpash.

Far more interesting are the colored charts, copies of the U. S. Coast Survey Chart. They ought to be combined but they should indicate the special places along the coast, where the "driftkelp" is washed ashore by the stream. As the explorations are limited to the few summer months and as this season mainly comprises all kinds of stationary growing kelp, the useful as well as the useless, we are able to find in the Senate Document little of any importance from which to form any opinion about an eventful lucrative sea-weed industry on the Pacific Coast.

The conclusion drawn from these preliminary explorations is that in the sea-weed of the west coast we have not only a source to furnish all the potash salts consumed in this country but "it means a possible production of potassium chloride about the same as, or even a little larger than, the total production in Germany," and, "taking every consideration and leaning strongly to conservatism, it might be said that it ought to be perfectly practicable to obtain an annual yield of at least a million tons of potassium chloride, worth at present prices, upwards of $30,000,000. The iodine obtainable at the same time should go far toward paying the expenses of harvesting the kelp and extracting the potash."

In the opinion of the writer, $30,000,000 a year, made by potash and perhaps a similar amount or more by iodine extracted from sea-weed on the west coast of the United States, is surely impossible in the light of the following analysis:

1. Is it possible that the Pacific sea-weed can produce sufficient raw material for the production of one million tons of potash salts?

2. Can the potash salts obtained from sea-weed containing a limited quantity of iodine (not more than $^1/_2$ per cent. in the ash of the plant) be furnished at a price similar to that of German potash salt?

To answer the first of these questions, I need only point to the simplest and primitive method of producing (burning) kelpash on the shore. The proposed technical improvements in this process have as yet never been tried practically, and do not promise any such profit as suggested in the published statements.

For the purpose of illustration, I shall use the Nereocystis Lutkeana mentioned in the Senate Document among Dr. J. W. Turrentine's "Analyses of Pacific Kelp," Sample No. 8. This marine plant (a laminaria) belongs to those containing the

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[1] THIS JOURNAL, 4, 169.

[2] For the last 10 years, I have known the kelp from the interior part of Puget Sound to be of very little, or no value.

largest quantity of both potash and iodine. It is found, as far as known, in the largest quantities at the northern part of the Pacific Coast. The dried plant contains 46.2 per cent. organic matter, 51.3 per cent. soluble salts and 2.5 per cent. ash. Of the soluble salts 23 per cent. are actual potash (K_2O) and 0.17 per cent. iodine. The total amount of ash of this plant is 53.8 per cent. The contents of the ash are then 42.7 per cent. actual potash (K_2O) corresponding to 67.7 per cent. potassium chloride (KCl) and 0.316 per cent. iodine.

If we take the above-mentioned quantity of ash as a basis, we find that it requires for the production of 1,000,000 tons of potash salts: 9,724,500 tons of wet sea-weed, containing 80 per cent. water, representing 1,948,900 tons of dried sea-weed, producing 1,048,500 tons of ash, representing 1,000,000 tons mixed potash salts.

I presume of course that the whole quantity of soluble salts is extracted as potash salts. This is indeed what is done in practice, as it is quite impossible in a huge production, as the one mentioned, to crystallize the salts singly. Of the potash present, half the quantity will come out as 80–90 per cent. potassium chloride and the other half will consist of a "mixture" of chlorides, carbonates and sulphates, mostly of potassium, sodium and a little part of magnesium containing about 16–20 per cent. actual potash (K_2O), corresponding to the German manure salts, Hartzsalt and Kainit.

For one million tons of potassium chloride, we shall have to multiply the above-mentioned amount of sea-weed and kelpash by two.

I presume that these figures will convince everybody that it is impossible to reach a production of a million tons of potassium chloride on the basis of the sea-weed of the west coast. To furnish entirely the large quantity of potash salts consumed in this country, the United States will have to find other "deposits." It might be of interest to note that the necessary quantity of kelpash containing 0.316 per cent. of iodine, used for the production of a million tons of potash salt, will furnish 7,400,000 lbs. iodine, valued at the present price at $14,000,000 or many times more than the total yearly consumption of the world at present.

Now let us see at what price this kelpash may be produced and how great an army of laborers the production of 1,048,500 tons of kelpash will require.

If the season on the Pacific Coast allows 150 working days for the harvesting and burning of the sea-weed, it will be necessary to produce 7,000 tons of ash a day. If one man produces 200 lbs. of kelpash per day,[1] at a daily wage of $2.00 (on the west coast this is rather low), the ash will cost one cent per lb. or $22.40 per long ton. This is at the present time the average price of kelpash in Scotland and Norway.

The production of 7,000 tons of ash a day for 150 days will require 7,800 men, for only the harvesting, drying and burning of the sea-weed on the shore. For the production of 1,048,500 tons of kelpash twice the number of laborers will be needed. The figures given speak for themselves. I will only add that in practice, conditions will surely be in all respects much less favorable than here anticipated.

The second question, the price of sea-weed potash in competition with German potash, will probably not be any more convincing. Yet this is a more favorable case because we are able to calculate the expense of the production, based on the contents of valuable materials as published in the Senate Document.

Continuing with the favorable marine plant, sample No. 8, Nereocystis Lutkeana, I figured as follows:

Harvesting and burning, per ton ash		$22.40
Freight and other expenses in handling the ash from the coast to the plant, estimated, per ton		2.00
Expenses of production per ton ash:		
Coal	$3.00	
Labor	4.50	
Chemicals	1.00	
Salt bags	2.00	
Commission on the sale of potash and iodine	1.50	
Administration, etc.	1.00	
Interest and depreciation	2.50	
Sundries, taxes, etc.	1.00	16.50
Total cost per ton ash		$40.90
0.316 per cent. iodine = 7.08 lbs. per ton ash at 6 pence per ounce (present price)	14.20	
95.3 per cent. soluble salts, 2134.6 lbs. per ton; of this 1067.3 lbs. are potassium chloride (80–90 per cent. KCl), according to German price $35 per 2000 lbs. net	18.67	
And 1067.3 lbs. are manure salt (20 per cent. K_2O), according to German price $13.30 per 2000 lbs. net	7.09	
Selling price per ton ash		39.96
Loss per ton ash		$ 0.94

Even if all the potash present could be extracted as potassium chloride (which is impossible) it would make only an insignificant improvement on the figures of cost given. The above-mentioned expenses are based on a personal experience of more than 20 years.

In practice the aspect will be far more unfavorable than pointed out above, because I have presumed here that the whole quantity of potash salt as well as iodine could be extracted.

A potash industry on the basis of sea-weed will first and last depend on the content of iodine in the marine plants.

One-tenth of 1 per cent. more or less of this valuable material in the kelpash can change the production from a valueless to a very remunerative business. It is certainly also very important that all of the valuable products in the plants, the organic as well as the inorganic, be utilized.

It is my opinion, nevertheless, that a great and very profitable industry could be founded if the contents of iodine in some of the species of Laminaria on the west coast prove to be satisfactory, but not an industry of any such dimensions as suggested.

Besides the content of iodine, it is of the greatest importance to use the best methods in handling the raw material as well as in the extraction of the products, and furthermore, to utilize to the utmost the valuable materials of the marine plants, both organic and inorganic.

As yet we possess very little of value and very little authentic information to solve the question "Is it possible to build up a *lucrative* industry on the abundant growth of sea-weed at the Pacific Coast?"

HENRIK KNUDSEN.

PHILADELPHIA, PA.

NIGERIAN TIN DEVELOPMENTS.

For some weeks now, great possibilities have been connected with this market, and those who have watched its developments carefully have certainly no reason to complain of the results. It must not be thought that the rise in Nigerian tin shares is devoid of justification. The history of Nigerian tin mining is very modern, although the Niger Company has been shipping tin for some years. The presence of tin in Nigeria was suspected in 1884, but it was not until 1902 that the actual existence of tin in the Bauchi district was discovered. It was in that year that the Niger Company took out a prospecting license over 1,000 square miles of territory. Transport facilities were then, of course, extremely meagre, and it was not until about 1905 that any important deposits were located.

In 1907 the Niger Company stated that it had obtained during the previous fifteen months, roughly, 240 tons of block tin. This was from the Naraguta property which produced on an

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[1] A man will have to cut, bring ashore, dry and burn about one ton of wet sea-weed.

average sixteen tons of tin a month. It was not, however, until the latter part of 1909 that the Champion Tin Fields, then known as the Champion Reefs of West Africa, took an active interest in the exploitation of the field. . . . . "The company's first subsidiary, the Tin Fields of Northern Nigeria, was registered in October, 1909; the second, the Nigerian Tin Corporation, was registered on October 14, 1909, and the Naraguta Tin Mines in January, 1910, while the Northern Nigeria (Bauchi) Tin Mines was brought out in February, 1910. The success attending these early concerns had the effect of inducing the more conservative mining houses to take an interest in the mining enterprises of the country, and to-day practically all the largest and most important mining and financial groups are represented by share interests in different companies. Although development was encouraging, operations were naturally hampered by the lack of transport facilities, the roads being mere tracks. After some pressure and a careful inspection of the district, the government consented to provide a railway, which would touch the more important discoveries, and so enable the properties to be developed on a scale adequate to the mineral resources disclosed. This railway will be ready to handle freight about the beginning of April, 1912. Up to the present time the camps on the various properties have had to depend for food, machinery and equipment entirely on loads carried on the heads of the natives, and shipments of tin have been sent down to the coast in the same way. This of course has meant an enormous cost for transportation charges. In fact, freight from the properties to England has been in the neighborhood of £50 to £60 per ton (£1 equals $4.86). The producing companies could, of course, pay even this charge and still make a very substantial profit, but it was quite impossible to get on the grounds the machinery necessary to open up on a reasonable scale the various areas. Naturally, as long as everything had to be carried on the heads of natives, the weights were strictly limited, and unfortunately hydraulic machinery consists of a good deal of dead weight, so that its transportation to the fields, until the railway was within a reasonable distance of the grounds, was out of the question.

"In spite of the difficulties which the companies have experienced, the output has been very encouraging.

"It may be mentioned that for the month of January, 1911, the output was no more than 63 tons of tin, gradually increasing until by the end of the year the total output had been brought up to 1,800 tons of tin oxide, while for the month of January of this year the yield has increased to 204 tons, the yield for the remainder of the year being expected to show the same steady increase, the general estimate being 3,000–5,000 tons. . . . .

"A very important factor in favor of the Nigerian tin district is the fact that the royalty payable to the government is only 5 per cent., whereas in the Straits Settlements it runs up to about 20 per cent.

"As we have mentioned, most of the companies are working tin alluvial either in the beds of the streams themselves or the adjacent banks. The tin deposited is probably brought down in flood time from the tin lodes in the vicinity, as well as being due to the erosion of tin lodes, which are believed to be in the beds of the streams. Until it was possible to get machinery on the grounds the prospecting for tin lodes was not very definitely pursued, but now that transport difficulties are on the verge of being overcome, several discoveries of tin lodes have been reported.

"At the meeting last week of the Anglo-Continental Mines the chairman stated that the lode had been traced about five miles, showing an average width of 30 feet, and assaying about 24 per cent. of metallic tin. If these figures are confirmed by subsequent developments, the value of the find should be nearly £40 per ton of mineralized ground."—*The African World, March 9th.*

But, as the actual values of the tin discoveries in Nigeria have to be proved, it is well to give attention to the warnings given by experts on tin mining, and not be too sanguine and indulge in too inflated anticipations on the basis of first results, although these are undoubtedly highly encouraging. The best results may yet be obtained from alluvial mining in Nigeria, and the wonderful lodes now being discovered may prove, as in other parts of the world, a failure.

W. J. YERBY.

SIERRA LEONE, AFRICA.

THE OIL OF POCHOTE.

The oil of Pochote, "Aceite de Pochote," is the oil derived from the seed of the Pochote plant (Eriodendron occidentale, Eriodendron oesculifolium), a shrub about 5–6 ft. high, that grows in the hot, humid regions of Mexico, in the Philippines and in some other climatologically similar places. For a long time this plant has been cultivated on a small scale by the native Indians who use the oil of the seeds for medicinal purposes. It is only quite recently that larger plantations have been started in an attempt to produce the oil on an industrial scale. The regions where the Pochote plant thrives in Mexico are usually those where cotton and sugar cane are cultivated. A Pochote plantation may, with proper care, last about 5–6 years, at the end of which time it has to be renewed. The renewals or new plantations are usually started with the help of the suckers that come out at the roots of the older plants. It ought to be to the interests of the American oil industry, especially the cotton seed oil industry, to follow the progress of this newly started oil industry, as it is not altogether unlikely that the Pochote oil might to some extent become a rival of the cotton seed oil.

The literature on oils and natural organic substances consulted (Lewkowitsch, Halphen, Sidersky, Abderhalden, Beilstein and others) make no mention whatever of this oil. The oil that might probably be assumed to be its nearest relative is the oil of Kapok, which also is only very scantily described by some of the above mentioned authors.

The following are the results of the examination of this oil that was sent from Oaxaca, southern Mexico.

General observations: At the temperature of 11° C. about half of the volume of the oil separated in the form of a flocculent mass.

The crude is of amber color and has a rather agreeable odor, something of the odor of coco oil. The taste is somewhat bitterish and reminds one of cold extracted cotton seed oil.

Moisture (100–105)	0.59%
Specific gravity 100/100° C.	0.9080
Specific gravity 15.5/15.5° C.	0.9253
Specific gravity 15.5/100° C.	0.8817
Saponification no., Koettstorfer value	192.0
Free fatty acids (as oleic acid)	21.91%
Acid no	43.58
Iodine no.	85.89
Reichert-Meissl no.	1.5
Hehner no.	95.1
Acetyl no.	42.68
Saponification no. of the acetylated matter	221.34
Crismer test	101.0° C.
Poutet's elaidin test	a pasty foam
Maumené test (according to Archbutt)	88.0
Thermobromic test (according to Hehner-Mitchell)	15.9
Sulfuric acid test	a reddish color
Neutralization no.	175.16
Mean molecular weight	319.70
"Titer" of fatty acids	28.7° C.
Melting point of the insoluble fatty acids	34.0° C.
Iodine no. of the insoluble fatty acids	90.31

From the above results it can be seen that the oil of Pochote might be classed among the semi-drying oils. Its characteristics resemble quite closely those of cotton seed oil. The excessive amount of free fatty acids, as well as the great difference between the saponification and the neutralization numbers and the high acetyl value, all show the partial decomposition of the sample examined. The bitter taste of the oil is probably also due to this decomposition. Should this decomposition be the result of careless handling, then there is every reason to believe, that, with proper handling and through modern methods of refining, this oil could be made to equal in quality the average cotton seed oil. S. LOMANITZ.

DIVISION OF CHEMISTRY,
CENTRAL AGRICULTURAL STATION,
SANTA JULIA, D. F., MEXICO.

LECTURES ON THE SMOKE PROBLEM.

In the fall of 1911 the Department of Industrial Research of the University of Pittsburg was provided by a Pittsburg business man with funds for a thorough investigation of the smoke nuisance. At the present time the investigation is being conducted by a staff of twenty-five specialists, of which seven are giving their entire attention to this task. Some of these men are studying the effect of smoke and soot on the atmosphere, on the weather, on plant life, on buildings, and on the public health; some are investigating the economic damage done by smoke and soot; others are making a detailed study of the mechanical devices for preventing or abating smoke; and still others are inquiring into the chemistry and physics of smoke and soot, into the laws concerning the smoke nuisance, and into the history of the subject as a whole.

Recognizing the interest in the smoke problem manifested by a large number of American cities, and in response to inquiries that have been made, the Department announces that the members of its staff are prepared to lecture on the following phases of this problem:

"The Smoke Nuisance" (a general presentation of the main phases of the subject).
"Smoke and the Public Health."
"Smoke and the Cost of Living."
"Smoke and Plant Life."
"Methods and Means of Smoke Abatement."
"The Effect of Smoke on Buildings and Building Materials."
"The Psychology of Smoke."
"The Smoke Nuisance and the Housekeeper."

These lectures will be given any place east of the Mississippi, provided the expenses of the lecturer are assumed.

For further particulars apply to Dr. R. C. Benner, Department of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

DETECTION OF FORMALDEHYDE IN FOODS.

Editor of the Journal of Industrial and Engineering Chemistry:

In view of the introduction of a mixture of nitrite and formaldehyde with the object of masking the reactions of the latter when used as a food preservative, the following experiments may be of interest.

A sample of fresh mixture was divided into four portions and treated as follows:

1. A small amount of commercial formaldehyde solution was added.
2. Small amounts of formaldehyde and sodium nitrite were added.
3. A small amount of sodium nitrite was added.
4. No addition was made.

Portions of each of these were tested with Rimini's test (phenylhydrazin hydrochlorid, sodium nitroprussid and sodium hydroxid). Prompt reactions for formaldehyde were obtained in 1 and 2; negative results in 3 and 4. Other portions of the samples were tested with the well-known test for nitrite (sulfanilic acid and alphanaphthylamin). The response of 2 and 3 was prompt and distinct. No color was produced in 1 and 4. The original mixtures were allowed to stand 24 hours at room temperature and the tests repeated with the same results as obtained at first.

It seems, therefore, easy to unmask nitrite and formaldehyde in the presence of each other. HENRY LEFFMANN.

PHILADELPHIA, June 8, 1912.

LABORATORY GENERATOR FOR HYDROCHLORIC ACID GAS.

A simpler form of apparatus than the one shown in THIS JOURNAL, 4, 452, was devised by the late Dr. Thomas M. Drown and myself about 1875 and has been used in this laboratory ever since. I am not sure whether it was published. The flask used was half filled with sulfuric acid. The funnel tube with the opening in the end reduced so that a pin will barely pass by, holding the extreme end in the flame of a Bunsen burner, is used for introducing the hydrochloric acid which is dropped in from a burette. A very steady current of gas is obtained.

EDWARD HART.

LAFAYETTE COLLEGE.
EASTON, PA.

BOOK REVIEWS

An Introduction to the Study of Fuel. By F. J. BRISLEE, D.Sc. One of a series of text-books, "Outlines of Industrial Chemistry," edited By GUY D. BENGOUGH, M.A., M.Sc. xx + 269 pp., with 62 illustrations. D. Van Nostrand Co., New York, 1912. Price, $3.00 net.

The preface states that this book is written for the purpose of bridging the gap that exists between the elementary textbooks on chemistry and the large treatises dealing with the details of combustion, design of coke ovens, producers, etc.

The general chemical principles of combustion are given, together with calculations of air required for combustion, weight and volume of products of combustion, calculation of combustion temperatures and heat losses.

One chapter is devoted to analysis of fuel and flue gases, and another chapter to calorimetry and determination of the heating value of a fuel. Both of these chapters are largely descriptive and not only lack details, but are devoid of the suggestions and precautions which are so needed by persons just taking up this line of work and for whom the book is intended. The method of coal analysis is not in conformity with good American practice, and only a passing comment is made on the method of securing a representative sample of coal, although the need of it is mentioned elsewhere in the book. Many different fuel calorimeters are described and conclusions drawn to the effect that the constant pressure, bomb, and sodium peroxide types are all equally accurate. The necessity of having calorimeter thermometers accurately calibrated is not so much as mentioned. The heating value of naphthalene is given as 9668 cal., while the U. S. Bureau of Standards give 9610. Considerable trouble has already arisen from the use of the high value of naphthalene instead of the correct one.

The chapter on high temperature measurement is covered in detail with description of many types of pyrometers, together with precautions in regard to their use and method of calibration.

The chapters on natural and artificial solid fuels give the usual characteristic composition of the various fuels, some average analyses of English coals, and a description of the methods of making charcoal and coke.

The chapter on gaseous fuels deals principally with producer and water gas, giving chemical reactions and effects of temperature and pressure. Another chapter briefly describes a few types of producers. The chapter devoted to the theory of the producer gas and water gas reaction is a review of the work of Jüptner and is quite advanced for the class of readers for whom the book is intended.

The subject of explosion and explosion engines is covered from a mathematical and theoretical viewpoint.

The remainder of the book is devoted to air supply, draft measurement, furnace efficiency, fuel economy, heat balances, furnace tests, boiler tests, and liquid fuels. These subjects are treated but briefly and not in such a manner as to enable a beginner to obtain very helpful or practical information. Less space has been devoted to these eight important questions than was given to the one subject of high temperature.

The book is written from a standpoint of English practice and consists largely of descriptive matter together with theoretical and mathematical discussion, without a great deal in the way of practical information or suggestions to guide a beginner in the study of fuel.
E. G. Bailey.

Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological. Vol. 1, year 1910. Published under the patronage of the International Association of Academies by the International Committee appointed by the Seventh Congress of Applied Chemistry which met in London, June, 1909. Quarto. xxx + 727 pp. University of Chicago Press, Chicago, 1912. Price: Bound, $5.00, or $6.54 postage prepaid; Unbound, $5.30, or $5.82 postage prepaid.

The International Committee (1909–1912) is made up of scientists from the 16 principal European countries, Canada, the United States, Argentina, Australia and New Zealand.

The list of compilers of the annual tables includes the names of thirty-one eminent European scientists. The one hundred and four abstractors represent eleven European countries, the United States and Japan. More than three hundred periodicals were examined; the printed list of almost two hundred gave useful data.

The Committee has been subsidized by the French, Dutch, Russian and Swiss Governments and by academies, scientific and industrial societies and private individuals of thirteen European nations, the United States and Japan.

This volume of the Annual Tables includes chapters on the following subjects.

1–4	Coefficient of Compressibility.
4–30	Density.
31–41	Viscosity.
42–44	Surface Tension.
44–48	Coefficients of Expansion.
48–49	Melting Points.
50–59	Specific Heats.
59–62	Thermodynamics.
62–79	Vapour Pressures.
80	Thermal Conductivity.
80–82	Radiation.
83–84	Photometry.
84–85	Reflecting Power.
86	Emissive Power.
87–93	Absorption Coefficient.
94–105	Refraction and Dispersion.
106–188	Spectroscopy.
189–217	Rotary Power.
218–243	Electricity.
243–265	Magnetism.
265–269	Radioactivity.
269–273	Electrons and Ionisation.
274–277	Atomic Weights.
278–279	Atomic Properties.
280–281	Diffusion.
281	Osmotic Pressures.
282–286	Degree of Association.
287–345	Mixtures (Change of State).
346–427	Solubility.
428–435	Thermochemistry.
436–445	Chemical Equilibrium.
445–459	Velocity of Reaction.
460–490	Conductivity of Electrolytes.
491–506	Electromotive Forces.
507–526	Colloids.
527–536	Absorption.
537–588	Crystallography and Mineralogy.
589–626	Organic Chemistry.
627–631	Essential Oils.
632–636	Oils, Fats and Waxes.
637–640	Animal Physiology.
641–642	Vegetable Physiology.
643–671	Engineering.
672–699	Metallurgy. 1. Mechanical and other Properties of Metals and Alloys.
700–721	II. Mechanical Constants.
722–726	Supplement.

Both the Index of Chapters and the Table of Contents are given in French, German, English and Italian; desired data can be easily found by referring to the Table of Contents which is to be supplemented in Vol. II (for 1911) by a General Alphabetical Index, and also by a Special Alphabetical Index of all the substances mentioned in Volumes I and II. The four above mentioned languages are paralleled throughout the volume wherever necessary to make clear the data given.

It was anticipated that this volume would appear before the end of the year 1911, but the unforeseen amount of literature to be consulted made this impossible: the Committee hopes, however, to bring out Volume II this year (1912).

The International Committee and their General Secretary, Charles Marie, are certainly to be congratulated on being able to present this substantial, well arranged and clearly printed volume in less than a year after the last 1910 issues reached Paris.
L. E. Marrs.

The Chemistry of the Radio Elements. By Frederick Soddy, F.R.S. Longmans, Green & Co., 1911. Price, $0.90.

This is one of a series of monographs on inorganic and physical chemistry, edited by Alexander Findlay, designed to give summarized accounts of the progress made in recent years along certain of the more actively pursued lines of advance. In no subject could a summarized account be more welcome than in the chemistry of the radioactive elements as the literature on the chemical side of radioactivity is even more widely scattered than that on the physical side. Neither the treatise by Rutherford—now unfortunately becoming out of date—nor the large treatise by Madame Curie, gives a connected account of the chemical properties of the radioactive elements, although a knowledge of these properties is of prime importance to the student of radioactivity. Mr. Soddy is of course one of the best qualified men to write a chemistry of the radio-elements, and into the ninety pages of this book he has condensed in orderly arrangement most that is known of the radioactive elements. One-third of the book is given to a general description of radioactivity—the three types of radiation and methods of measuring, the disintegration theory, and the classification and nomenclature of the elements.

After this introduction the radioactive elements are taken up in the order in which they stand in their respective disintegration series. Immediately under each element is given its period of active life, the type of radiation it emits, the range or absorption coefficient of the radiation, its nearest chemical analogue, and such other data as apply particularly to it. There follows a discussion of other characteristic features and of methods of separation and estimation. The description of methods for the practical estimation of the radium content of ores and solutions will be appreciated by many who would like to make such analyses.

The author brings out clearly the peculiar and very close similarity of chemical behavior of several sets of the radioactive elements, a similarity that has been the cause of no little confusion. The eighty-odd references to original articles are in themselves a very valuable guide. Though the growth of our knowledge of the radioactive elements is so rapid that slight changes could even now be made in the book, it is perfectly safe to say that no student of radioactivity, whether from the chemical or physical side, can afford to be without this little monograph.
George B. Pegram.

The Chemistry of the Rubber Industry. By Harold E. Potts. M.Sc., Member International Rubber Testing Committee. One of a series of text-books, "Outlines of Industrial Chemistry," edited by Guy D. Bengough, M.A., M.Sc. viii + 146 pp. D. Van Nostrand Co., New York, 1912. Price, $2.00 net.

This book is appropriately begun with a chapter on Colloidal Chemistry in which the salient features of colloids in general and their bearing on rubber are mentioned.

Chapter II. Raw Rubber and Coagulation. Theories for presence of latex in the tree, and effect of proteins and resins on quality of rubber are briefly noted. Methods of coagulation and their influence on the quality of the resulting rubber are pointed out. The recent work on discoloration and tackiness is mentioned. The section ends with a brief account of the washing and drying processes.

The next section deals with the rubber hydrocarbon, soluble and insoluble rubber, solutions, the researches of Harries on the constitution of rubber, and its derivatives with various reagents. The chapter is concluded with a complete account of the latest methods for crude rubber analysis.

Chapter III briefly mentions gutta percha and balata.

Chapter IV deals with mixing of rubber. Reclaimed rubber, substitutes, waxes, bitumens, inorganic compounding materials and their functions in rubber compounds are ably discussed.

Chapter V gives a short historical account of the discovery of vulcanization and a brief résumé of the work done on present theories.

Chapter VI. Vulcanized rubber and its analysis are treated in detail.

The author has succeeded in producing a very excellent book, particularly in pointing out to the general reader the significance of chemistry to the rubber industry. W. W. EVANS.

German Varnish Making. By MAX BOTTLER. Authorized Translation with notes on American Varnish and Paint Manufacture by ALVAH HORTON SABIN. Large 12mo., vii + 363 pp., with 55 figures. John Wiley & Sons, New York, 1912. Price, $3.50.

The German methods and ideas of varnish-making as set forth in Prof. Bottler's book on the subject "Die Lack und Firnisfabrikation" are here made available for non-German readers. At the same time a large amount of matter is furnished by the translator so that the original work has been very much amplified in rendering it into English; in fact about half of it appears to be added matter.

Paints are treated of particularly as to their physical constitution and properties, and much of the experimental work recently done upon this subject is described and discussed.

There are two appendices, the first of 96 pages devoted to analytical methods and containing much that is suggestive, and the second of 27 pages containing the formulas of Charles F. Crockett which have a historical interest.

The book, as was perhaps inevitable from its make-up, lacks unity and continuity but contains much valuable matter and will be found useful as a work of reference.

PARKER C. MCILHINEY.

Industrial Organic Chemistry. By SAMUEL P. SADTLER. Fourth edition, 1912, 8vo., 586 pages, 122 figures and 19 diagrams. J. B. Lippincott Co., Philadelphia. Price, $5.00 net.

The striking feature of the fourth edition of this book is the increased amount of space devoted to analytical processes, and it is gratifying to note that many official methods have been included in place of the cut-and-dried methods found in many of the books on analytical chemistry. The idea of furnishing a certain amount of descriptive matter before the analytical methods are given is a happy one, but could be carried even further by showing where the analytical determinations go hand in hand with the manufacturing operations.

The bibliography is very complete and the statistics given should be of value to those interested in any special line of industry.

The subject matter is presented in a very interesting and instructive manner, and for those desiring general information on the branches covered it will be found very helpful.

ALLEN ROGERS.

Vinegars and Catsup, Interpretation of Standards, Analyses, Etc. By R. O. BROOKS. The Spice Mill Publishing Co., 1912.

This small volume of 70 pages is a compilation of articles published by the author in "The Spice Mill" during 1909, and 1910.

Part I gives a brief classification of commercial vinegars; Parts II–V discuss the manufacture and composition of cider vinegar; Part VI describes wine vinegar; Part VII, malt vinegar; Part VIII, spirit and sugar vinegars; and Part IX, tomato catsup.

The author's purpose has been "to acquaint the manufacturing and wholesale trade with a little of the science" of the vinegar and catsup industries and his plan has upon the whole been well carried out. As an elementary treatise upon the technology of vinegar and catsup making, the book contains many facts of interest to the manufacturer as well as to the general reader. C. A. BROWNE.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York.

Alloy; Metallurgical and Technological Studies in the— Industry. By M. WEIDIG. L. 8vo., pp. 123. Price, $1.50. L. Simion Nachfolger, Berlin. (German.)

Alloys; Binary Metal— Part II. By K. BORNEMANN. 8vo. Price, $2.50. Wilhelm Knapp, Halle. (German.)

Analytical; Handbook of— Chemistry, Part II. By A. CLASSEN. 6th edition. L. 8vo., pp. 572. Price, $3.50. F. Enke, Stuttgart. (German.)

Biochemical Lexicon. By EMIL ABDERHALDEN. Vol. 7. 8vo. Price, $86.00. Julius Springer, Berlin. (German.)

Carbon; Lexicon of— Compounds. By M. M. RICHTER. Vol. 4. 3d edition. L. 8vo., pp. 4751. Price, $53.00 Leopold Voss, Leipzig. (German.)

Carbon; Percentage Tables of— Compounds. By M. M. RICHTER. L. 8vo., pp. 176. Price, $1.00. Leopold Vass, Leipzig. (German.)

Centenary Lectures. pp. 174. Price, $2.00. American Gas Institute, New York.

Chemico— Technical Calculations. By F. FISCHER. 8vo., pp. 111. Price, $1.00. Otto Spamer, Leipzig. (German.)

Chemistry; Manual of Clinical—, Microscopy and Bacteriology. (Translation.) By M. KLOPSTOCK AND A. KOWARSKY. 8vo., pp. 371. Price, $3.00. Rebman Co., New York.

Chemistry; Text-book of Inorganic and Organic—. By G. FRERICHS. L. 8vo., pp. 480. Price, $3.00. F. Enke, Stuttgart. (German.)

Coal; The Constituents of— Soluble in Phenol. By J. C. W. FRAZER AND E. J. HOFFMANN. 8vo., pp. 20. U. S. Bureau of Mines. Technical Paper No. 5.

Coal; Government— Purchases under Specifications with Analyses. By GEORGE S. POPE AND JOSEPH D. DAVIS. 8vo., pp. 97. U. S. Bureau of Mines. Bulletin 41.

Colloid Chemistry. By R. ZIGMONDY. 8vo. Price, $3.75. Otto Spamer, Leipzig. (German.)

Cotton; Mercerization of—. By P. GARDNER. 2nd edition. 8vo. Price, $2.25. Julius Springer, Berlin. (German.)

Cyanide Process; Text-book of—. By H. W. MCFARREN. 8vo. Price, $3.25. Hill Publishing Co., London.

Dyeing; Bleaching and— of Vegetable Fibrous Material. By J. HUEBNER. 8vo. Constable & Co., London.

Dyestuffs; The Industry of the Organic—. By ANDRÉ WAHL. 8vo., pp. 400. Price, $1.00. Octave Doin Et Fils, Paris. (French.)

Electrochemistry; The Fundamental Laws of—. By P. TH. MULLER. 2nd edition. 8vo. Price, $0.75. Gauthier-Villars, Paris. (French.)

Explosives; Historical Papers on Modern—. By G. W. MACDONALD. 8vo., pp. 200. Price, $2.75. D. Van Nostrand Co., New York.

Fibrous; Bleaching and Dyeing of Vegetable— Materials. By JULIUS HUEBNER. 8vo., pp. 386. Price, $3.50. Constable & Co., London.

Inorganic; Text-book of— Chemistry. By G. SENTER. 8vo., pp. 593. Price, $1.75. D. Van Nostrand Co., New York.

Materials; Laboratory Manual for Testing— of Construction,

By L. A. Waterbury. C. 8vo. Price, $1.75. Chapman & Hall. London.

Metal; Handbook of Autogenous— Working. By Th. Kautny. 2nd edition. 8vo., pp. 712. Price, $2.25. C. Marhold, Halle. (German.)

Metallurgical Manual of Iron and Steel. By H. Allen. 12mo., pp. 365. Price, $1.50. Technical Publishing Co., London.

Mine; The Factor of Safety in— Electrical Installations. By H. H. Clark. 8vo., pp. 14. U. S. Bureau of Mines. Technical Paper No. 19.

Organic Chemistry. By E. Fromm. 2nd edition. 8vo. Price, $1.75. H. Laupp, Tuebingen. (German.)

Organic; Treatise on— Chemistry Applied to the Industries. By E. Molinari. 2nd edition. 8vo., pp. 1054. Price, $3.75. U. Hoepli, Milan. (Italian.)

Petrographic Methods. (Translation.) By E. Weinschenk. Vol. 2. 8vo., pp. 396. Price, $3.50. McGraw Hill Book Co., New York.

Pulp; Wood— and its Uses. By C. F. Cross, E. J. Bevan and R. W. Sindall. 8vo., pp. 281. Price, $2.00. D. Van Nostrand Co., New York.

Rubber and Gutta Percha. By Wyndham R. Dunstan. 8vo., pp. 448. Imperial Institute, London.

Sewage Disposal. By George W. Fuller. 8vo., pp. 767. Price, $6.00. McGraw Hill Book Co., New York.

Sewage; Practical Methods of— Disposal. By Henry N. Ogden and H. Burdett Cleveland. 8vo., pp. 132. Price, $1.50. John Wiley & Sons, New York.

Spectroscopy. By E. C. C. Baly. 8vo., pp. 687. Price, $3.50. Longmans Green & Co., New York.

Sugar; Handbook of— Manufacture. By H. Schander. 5th edition. 8vo. Price, $6.25. Paul Parey, Berlin. (German.)

Sugar; Report of the Experiment Station for— Industry in Prague. By K. Preis. pp. 170. Prague, 1912. (German.)

Sugar; Theoretical and Practical Treatise of the Manufacture of Beet—. Vol. 2. 3d edition. Imp. 8vo., pp. 1292. Price, $6.50. L. Geisler, Paris. (French.)

Sugar; The United States— Beet Industry. By Roy G. Blakey. 8vo. Price, $2.00. P. S. King & Son, London.

Tar; Contributions on Peat—. By R. Loebel. 8vo., pp. 43. Thesis. Hannover. (German.)

Water Analysis for Sanitary and Technical Purposes. By H. B. Stocks. 8vo., pp. 144. Price, $1.50. D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES.

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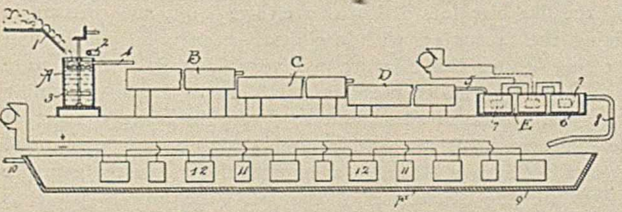
RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

METHOD OF SEPARATING AND PURIFYING FULLERS' EARTH AND ANALOGOUS MATERIAL.

U. S. Patent No. 1,024,104, to Charles C. Ruprecht, of Blakely, Alabama.

In many deposits of fullers' earth there is an excess of deleterious material, either organic or mineral. To secure the earth free from such materials, it is found necessary to wash it by mixing thoroughly with water and allowing the mixture of earth and water to pass rather slowly through long tanks or settling vats in which the excess of sand and other deleterious minerals will be quite completely deposited. It is found, however, that when this settling has been carried to a certain extent, the earth itself will settle with extreme slowness from the water and remains in suspension for weeks or months. Consequently, the mixture after the ordinary washing is very fluid, and the importance of securing the slip in the most dense condition possible to insure rapid recovery, renders it necessary to extract this excess water.

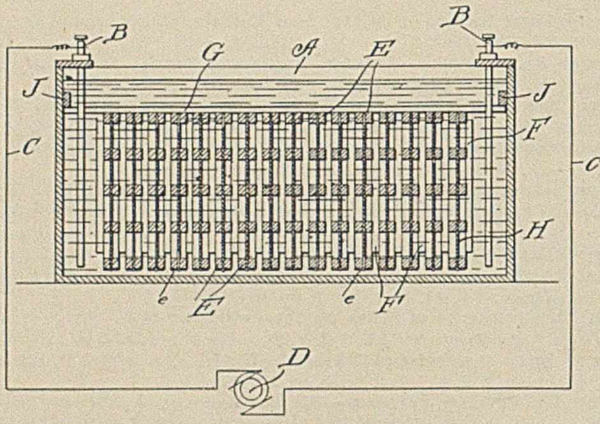


The purpose of this invention is to rapidly and economically precipitate this suspended earth, simultaneously decomposing and removing the organic contaminations. The patentee has discovered that if the water carrying the earth in suspension be electrolyzed, the earth is immediately precipitated and the deposit obtained is so hard that what little remaining water is occluded in its pores may be easily removed by some simple expedient, as by a filter press, centrifugal drier, or evaporation in a suitable kiln.

PROCESS OF CURING HIDES.

U. S. Patent No. 1,025,401, to Frank P. James, of Nashville, Tennessee, assignor to the Electric Meat Curing Company, of Cleveland, Ohio.

In the treatment of hides preparatory to tannnig, it is customary, after the hide is removed from the animal, to spread it out, cover it with salt and allow it to stand for several weeks before it is placed in the tanning vat. This curing operation is irregular in its action, some portions of the hide being cured much better than others, and a large amount of the blood is left, which, when the hide is finally converted into leather, is liable to cause it to rot in places.

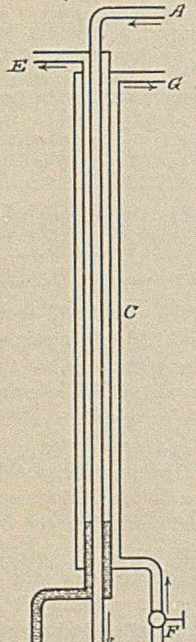


The patentee has discovered that if the fresh hide is immersed in brine, and a current of electricity passed through the brine and hide, the hide may be perfectly and evenly cured in an extremely short time. The action of the electricity is said to extract the blood from the hide while retaining the gelatin therein.

APPARATUS FOR THE SEPARATION OF HYDROGEN FROM A GASEOUS MIXTURE.

U. S. Patent No. 1,027,862, to Carl von Linde, of Munich, Germany.

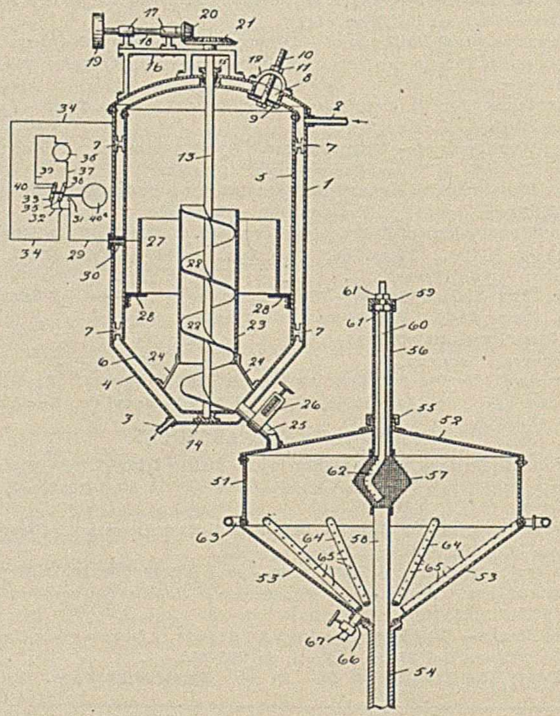
There are several processes known for the separation of gas mixtures through liquefaction and fractional distillation, but they are not generally adapted to the separation of gas mixtures containing hydrogen, because the liquefaction of hydrogen can take place only at a temperature so low that all other gases at this temperature exist only in the solid state. The object of the invention is the extraction of hydrogen from gas mixtures, such as illuminating gas or water gas, in such a manner that the less volatile constituents of the gas mixture are condensed through the influence of a reduction of temperature which may also be combined with an increase in pressure. The compression gas mixture enters the apparatus at *A* after it has been previously freed from such constituents or impurities as can bring about stoppages in the liquefying apparatus, *e. g.*, carbonic acid and sulfur compounds. In its passage to the vessel *B*, the gas mixture is reduced to such a temperature in the heat- and temperature-interchanger *C*, that the greater part of the constituents of the gas mixture are liquefied and collect in the vessel *B*. The liquefied portion flows out of this vessel through the expansion mechanism *D* into the interchanger *C*, evaporates and thereby removes heat from the compressed gas mixture flowing through the apparatus. The product of this evaporation, *e. g.*, carbon monoxide, escapes at *F*, after an interchange of temperature with that of the compressed gas mixture passing through the apparatus and can be applied in any manner desired. The portion of the gas mixture which is not liquid (hydrogen and the remaining constituents) after passing through the expansion mechanism *F* flows through the temperature-interchanger *C* in an opposite direction to that of the compressed gas mixture and escapes out of the apparatus *G* at normal temperature.



PROCESS FOR RECLAIMING VULCANIZED-RUBBER WASTE.

U. S. Patent No. 1,024,937, to Chas. S. Heller, of Akron, Ohio, assignor to Moore Architectural and Engineering Co., of Akron, Ohio.

The Heller process of reclaiming rubber, previously patented (Patent No. 978,584), consists in subjecting rubber waste to the action of a heated reclaiming solution and passing a current of electricity therethrough. Where a dilute alkaline solution was employed as the reclaiming agent, the time of the operation was cut down from about twenty-two hours to ten or eleven hours, by reason of the employment of the electric current. The patentee has now discovered that the time of the operation can be still further curtailed by periodically reversing the direction of flow of the electric current.



PROCESS FOR CONVERTING FATS, OILS, AND FISH-OILS INTO LIKE BODIES OF HIGHER MELTING POINT.

U. S. Patent No. 1,024,758, to Mose Wilbuschewitsch, of Nischninovgorod, Kanavino, Russia.

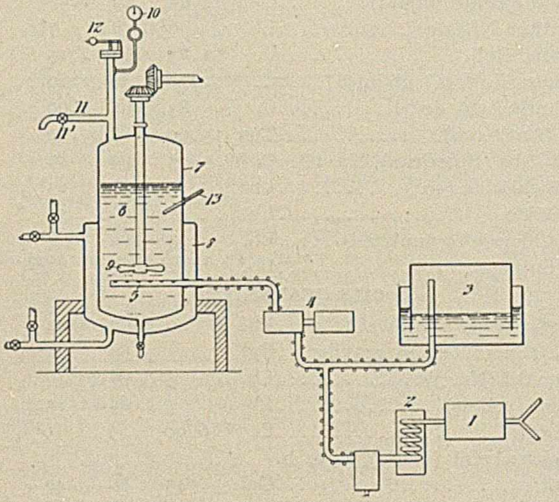
This is a contact process of converting fats, oils, fish oils, and the like into fats of higher melting point, and consists in mixing the fat or oil with the catalyst very intimately and directing against this mixture in a very finely subdivided state in an autoclave under pressure, hydrogen or a gas containing hydrogen. Since in this manner a very intimate contact of the hydrogen with the finely subdivided intimate mixture of fat and catalyst is attained, a comparatively low temperature suffices for the conversion of the fat. The process proceeds in a closed cycle of operations as the catalyst and the hydrogen not consumed are continuously returned to the process.

PROCESS OF FORMING FUSIBLE PHENOL RESINS.

U. S. Patent No. 1,027,794, to Jonas W. Alysworth, of East Orange, New Jersey, assignor of one-half to Frank L. Dyer, of Montclair, New Jersey.

This is a process of forming fusible phenol resins from phenol or cresol by condensation with formaldehyde.

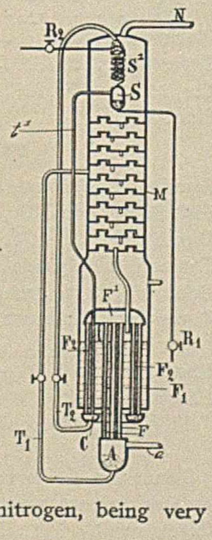
Formaldehyde is generated in the generator 1, and passes through condenser 2, which removes unchanged methylalcohol therefrom, to the gasometer 3, which is provided with an oil seal and is adapted to be steam-heated. Formaldehyde gas is taken therefrom as desired, by pump 4 and allowed to pass as bubbles from perforated pipe 5 into the liquid phenol 6 in the autoclave 7 which is provided with steam jacket 8, agitator 9, pressure gage 10, vent 11 for the escape of steam when necessary, which is regulated by a valve 11′, and safety valve 12. Provision is made for steam heating the pipes through which the formaldehyde passes, and for passing cool water through steam jacket 8, when the reaction has started, to prevent the temperature from rising above the proper reaction point. This can be regulated by thermometer 13.



METHOD OF EXTRACTING RARE GASES FROM THE AIR.

U. S. Patent No. 1,025,962, to Georges Claude, of Paris, France, assignor to Societe L'Air Liquide, Societe Anonyme Pour L'Etude Et Exploitation Des Procedes Georges Claude of Paris, France.

This invention is a process for the separation of the rarer and less condensable gases as neon and helium, from the atmosphere. It involves the application of well known processes for the liquefaction and separation of the oxygen and nitrogen contained in the air, and modifies the procedure so as to isolate the remaining difficultly condensable gases in the air under treatment.

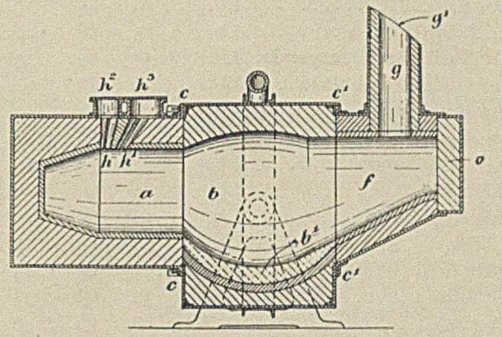


The air under pressure containing the rare gases to be separated is subjected to a process whereby the greater part of the oxygen and of the nitrogen are liquefied, and the remaining unliquefied gas or gases are then submitted to a single or repeated process of liquefaction with backward return, the principles underlying which have been disclosed in the specification of the patentee's prior U. S. Patent No. 924,428. The unliquefied gases, while still under pressure, are brought into direct contact with cold agents and finally with the liquid nitrogen or liquid rich in nitrogen obtained as above. Said nitrogen, being very cold, permits only the uncondensable rare gases, chiefly neon and helium, to preserve their gaseous state.

MANUFACTURE OF STEEL.

U. S. Patent No. 1,024,999, to Tom D. Mackie, of Bowes Park, and George Frederick Forwood, of Limpsfield, England.

According to this method of manufacture, particularly when the production of steel casting is in view, the oxidized metal and slag from the converter (which may be of any known type) are transferred to the hearth of a reverberatory furnace, and, after the removal of the slag, the metal is subjected to the action of a reducing gas, such as hydrogen, blue water-gas or the like, with the result that it becomes deoxidized. On reaching the upper portion of the furnace the reducing gas meets with air, becomes ignited and burns, with the effect that the metal is exposed to the heat generated by the combustion, but is protected from its oxidizing influences.

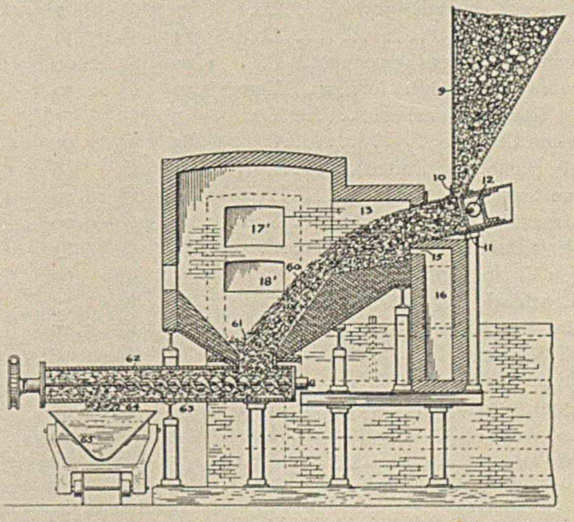


PROCESS AND APPARATUS FOR RECOVERING METALS FROM THEIR ORES.

U. S. Patent No. 1,026,999, to John A. Potter, of Los Angeles, California.

This invention is a process of smelting, roasting, calcining, and sintering all grades of ores.

It consists in heating a series of flues with waste gases from the furnace; then after stopping the waste gas supply, passing fuel gas in the reverse direction, through one of the flues, gas through another of the flues, and through a third flue reducing gas, discharging the mixture into a reducing chamber, and continuously feeding ore into this reducing chamber. The heat of combustion of the fuel gas assists the reducing gas in melting and reducing the ores. The waste gases so derived are conducted through a similar series of regenerative flues in order to develop the proper temperature and at the proper time the entire cycle is re-reversed.



MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JULY.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23	@	27
Carbon Tetrachloride (drums)	Lb.	11	@	13
Carbon Bisulphide	Lb.	9	@	10
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	15	@	16
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	2.95	@	3.16
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	18¼	@	19½
Oxalic Acid	Lb.	8⅛	@	8½
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.18	@	2.48
Starch (potato)	Lb.	5¼	@	5¾
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid, crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8¼	@	8½
Ammonium Chloride, gray	Lb.	6⅛	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	4	@	4¼
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.40	@	2.00
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5½	@	5¾
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.05	@	3.10
Lead Nitrate	Lb.	8⅜	@	8½
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¼	@	9⅞
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.45	@	2.50
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver	Flask	42.50	@	44.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	38½	@	40½
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	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.	13¼	@	13½
Tin Oxide	Lb.	47	@	50
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	40	@	44
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	6.00	@	6¼
Cottonseed Oil (crude), f. o. b. mill	Gal.	43	@	47
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	10	@	11
Lard Oil (prime winter)	Gal.	85	@	90
Linseed Oil (double-boiled)	Gal.	74	@	76
Paraffine Oil (high viscosity)	Gal.	25½	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅜
Rosin Oil (first run)	Gal.	37	@	39
Spindle Oil, No. 1	Gal.	16	@	16½
Sperm Oil (bleached winter) 38°	Gal.	72	@	74
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	62	@	65
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	22	@	23
Antimony (Hallet's)	Lb.	7¾	@	8
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	17¼	@	17½
Copper (lake)	Lb.	17⅜	@	17⅝
Lead, N. Y	Lb.	4¾	@	4⅞
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46.35	@	47.00
Silver	Oz.	60⅜	@	61⅜
Tin	Lb.	43½	@	45
Zinc	Lb.	7.40	@	7½

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.25	@	3.30
Fish Scrap, domestic, dried	Unit	2.45	&	10
Blood, dried	Unit	2.72½	@	2.75
Tankage, high grade	Unit	2.55	&	10
Bone, 4½ & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	7.00	@	7.25
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13⅛	@	0.13¼
Castor meal	Unit		nominal	
Mowrah meal	Ton	8.50	@	9.00

CHEMIST, Ph.D., age 25. Special training in industrial research, having given particular attention to fuels. First-class knowledge of analytical and general chemistry. Desires position in industrial research laboratory or other establishment where such training is desirable. Address "L. N. J.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 137-9-12

EXPERIENCED CHEMIST: University graduate, with over two years' experience in packing-house chemistry and fertilizer control. At present chief chemist for one of the largest fertilizer concerns in the business. Desires position with greater possibilities. Best of references. Address "D. A.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 132-9-12

CHEMICAL ENGINEER: Specialized in mechanical handling of materials. Experienced in investigations, reports, and superintendence. Wants position in or near Philadelphia. References exchanged. Address "Superintendent," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 130-9-12

ENERGETIC YOUNG AMERICAN, with technical education and large experience as chemist, superintendent and engineer, seeks position where results mean advancement. Unquestionable references. Address "F. M.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 136-9-12

YOUNG MAN, single, desires position as chemist with sugar mill in the Tropics, Porto Rico preferred. Experienced in both cane and beet work. Excellent references. Address "N. J. R.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 135-9-12

WANTED—Position by a 1912 graduate of Cornell University in manufacturing or business department of manufacturing concern where knowledge of chemistry and engineering is desirable. Best references. Address "A," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 131-9-12

CHEMICAL ENGINEER, B.S., age 25, 1910 graduate of reputable university, desires a position in the west. At present chemist and assistant superintendent of large eastern concern. Expecially proficient in analytical work and executive ability. Excellent references. Address "H. T. B.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 146-9-12

CHEMIST, B.S., desires responsible industrial position. Four years' experience foods and fuels in private and municipal laboratory, last two years in charge of laboratory. Address "A. D. P.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 145-9-12

CHEMIST, six years' experience in varnish, practical Asst. Superintendent, wishes position in similar line, preferably in vicinity of New York. Address "V. C.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 133-9-12

CHEMIST, graduate of eastern technical school. Six years' varied experience, both analytical and consulting. Now employed but desires position with more chance for advancement Experienced in handling men. Can furnish A 1 references. Address for full particulars, "R. T.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 142-9-12

CHEMICAL ENGINEER, graduate, 20 years' experience in various lines of chemistry, organic and inorganic (research, metallurgy, electrochemistry, physical chemistry, etc., etc.), would like to hear from some industrial or manufacturing concern who wants a man that can *do things.* Executive ability. Address for full particulars, "M. C.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 91-9-12

A Ph.D. in chemistry with twelve years' experience teaching in college desires a position to teach physical and inorganic chemistry. He can also teach other lines in connection with the above. Address "H.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 143-9-12

SITUATION wanted by analytical and pharmaceutical chemist; age 28, salary $1500. Theoretical training; M.S., B.S. and Ph.G. from a reputable institution and in addition one year's advanced work. Practical training; six years assistant state chemist and charge of the chemical laboratory of a government experiment station; one year with a large pharmaceutical concern; three months with the government on research work; three months assistant superintendent to large firm. Can handle men. A thorough training in analytical work. Address "A. E.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 144-9-12

A BRIGHT, energetic, young college graduate in the course of chemical engineering, desires a position with a large corporation where there is a good opportunity to advance. Can begin work at any time. Address J. M. Garrett, Beatrice, Nebraska. 140-9-12

CHEMIST with five years' experience desires position. Have been head chemist for large plant using chemical process. Salary to start $1500. Address "N. B. W.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 141-9-12

CHEMIST, B.S., five years' experience in paints and oils, also experienced in all kind of inorganic and organic chemistry, desires to locate with some manufacturing concern where my training and executive ability can be used to the best advantage. Have also selling ability and would consider a proposition along that line. Address "L. P. Z.," care Journal of Industrial and Engineering Chemistry, Easton, Pa 138-9-12

WANTED, position as chemist or in capacity where chemical knowledge would be advantageous, by technical graduate, five years' experience, partly in charge of public analytical and consulting laboratory, partly as chief chemist and superintendent of five departments of large metal working concern. Experienced in cost work. Now employed but desires position with more chance for advancement, preferably along executive lines. Address "M. R.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 112-8-12

WORKS CHEMIST, experienced in the manufacture of sulphuric acid (contact process), nitric acid, mixed acid, muriatic acid, electrolyte and heavy chemicals, starch and starch products, also experienced in academic work and having had two years at research work, wishes a position as chemist or assistant superintendent with industrial concern where consistent effort will be appreciated. M.A. in chemistry. Address "H. L. L.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 117-8-12

WANTED, position as chemist or assistant by young man finishing in Department of Chemistry in a university in June. No locality restrictions but wish opportunity for promotion when ability is shown. Married. References furnished as to ability and integrity. Moderate salary to start. Address "W. L. S.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 114-8-12

GRADUATE of an eastern university, A.M., with good training in analytical, organic and inorganic chemistry, with one year of research work on terpines, desires a position as teacher or industrial chemist. Good references. Address "J. V. N.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 118-8-12

CHEMIST, M.I.T. '07, desires position in Eastern States. Two years spent at research, and three years' practical experience in tanning. Thoroughly understands leather business. Address "M. I. T.," care Journal of Industrial and Engineering Chemistry, Easton, Pa. 110-8-12

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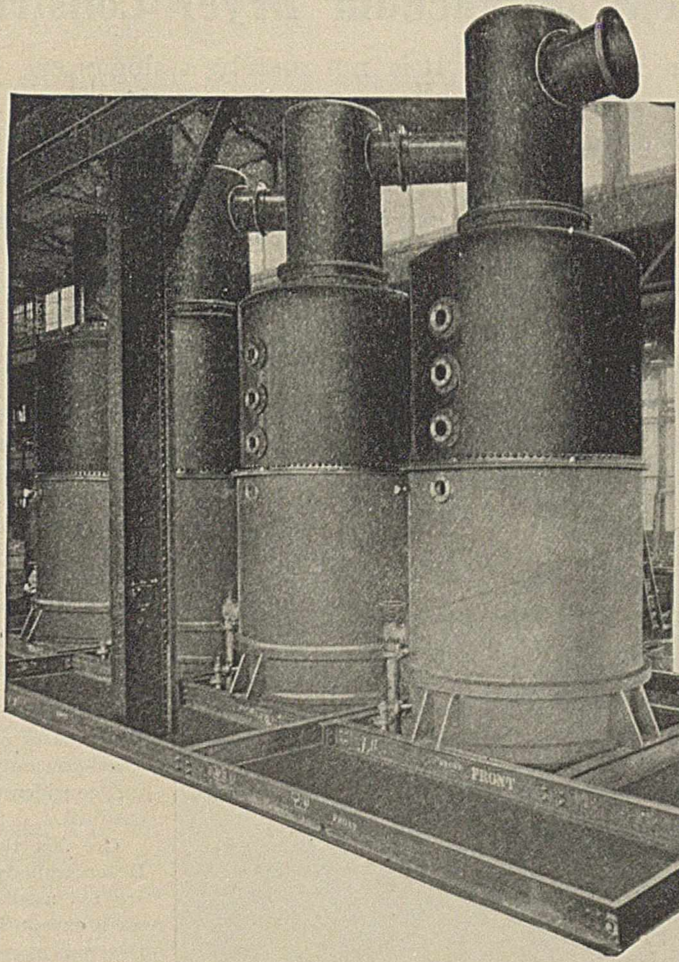

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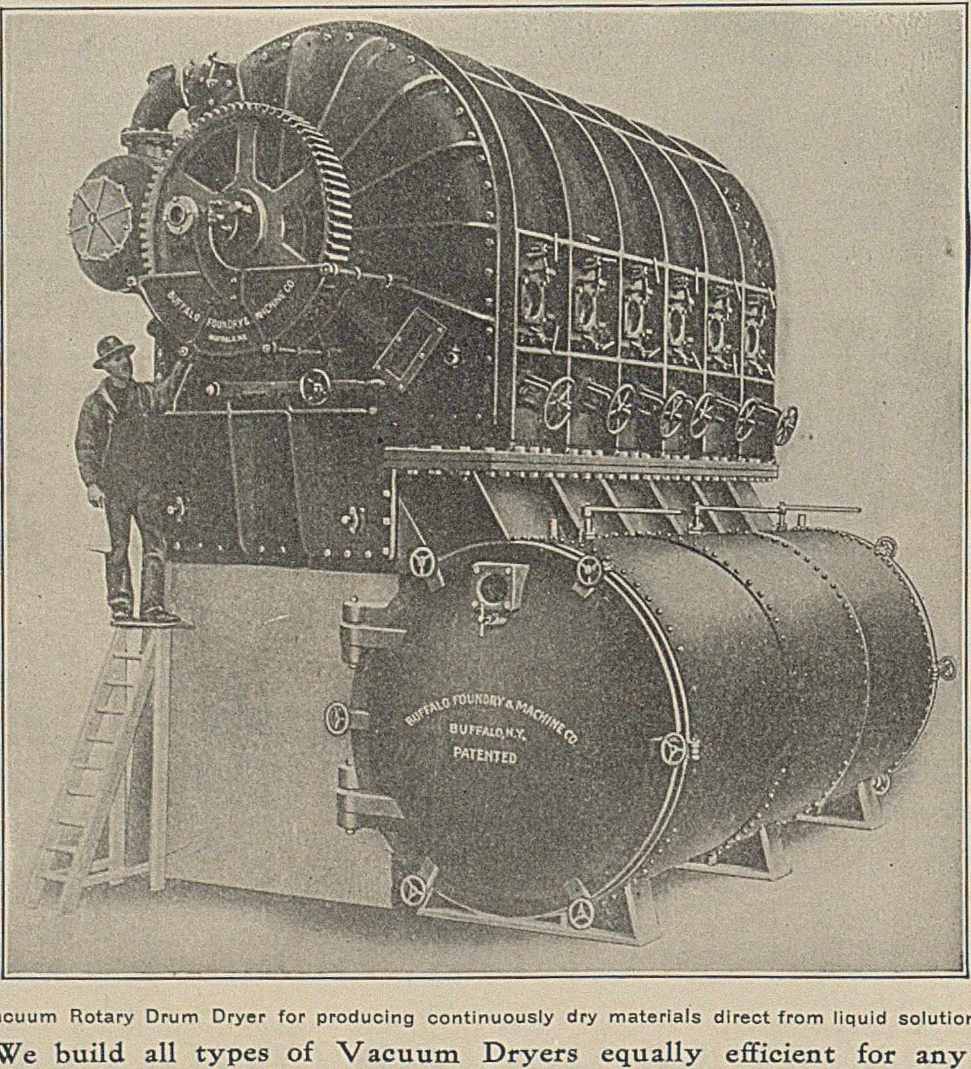

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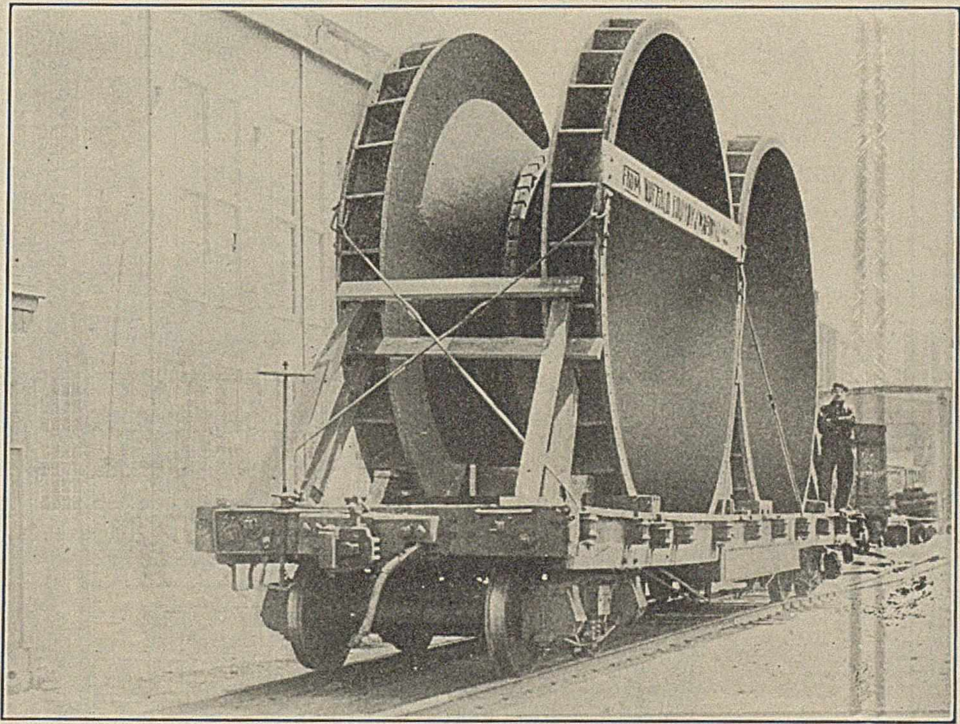

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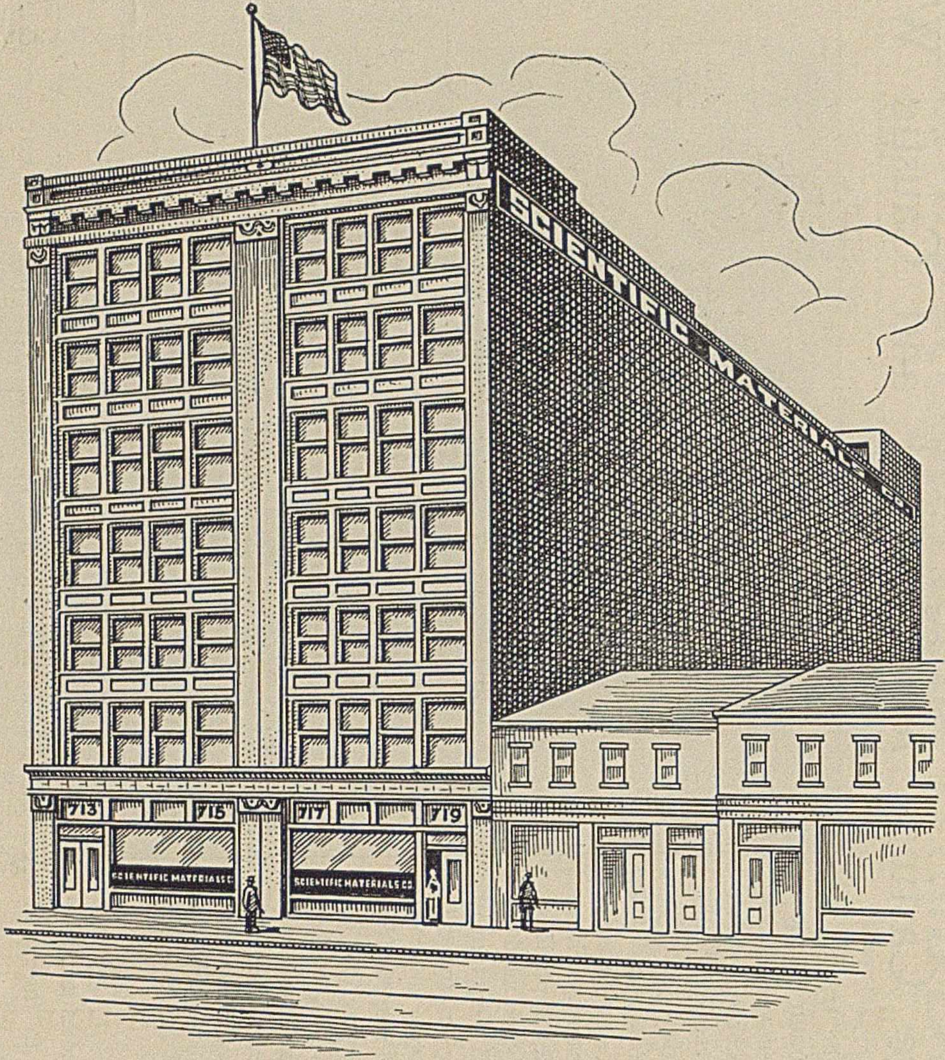
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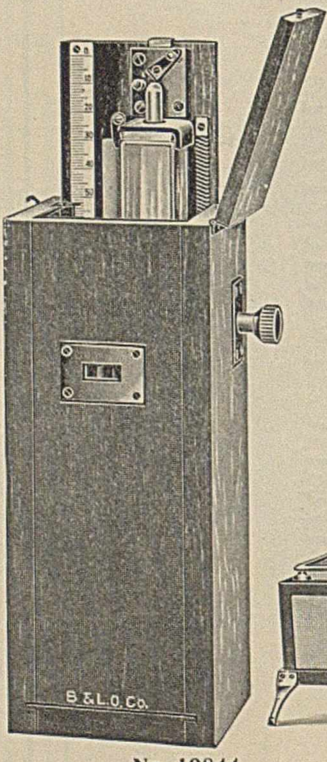
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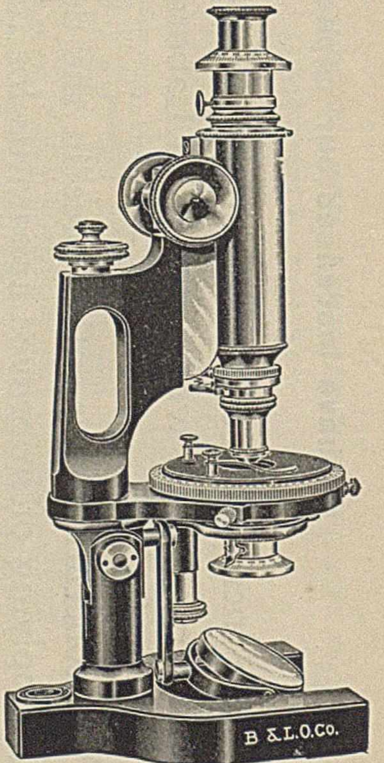
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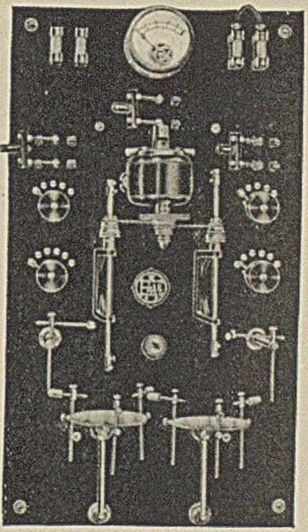

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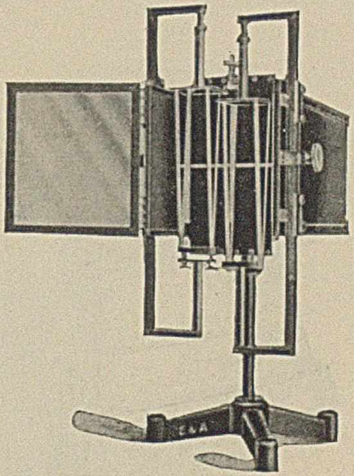

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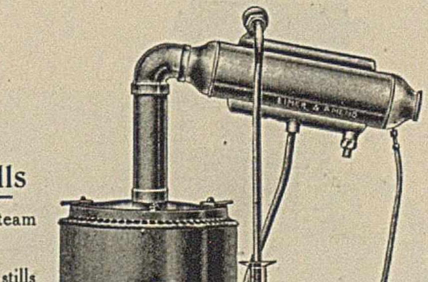

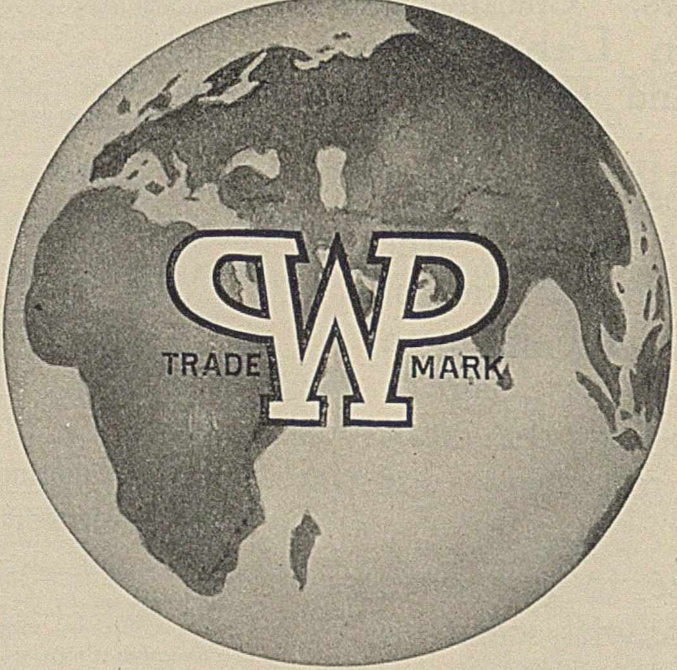
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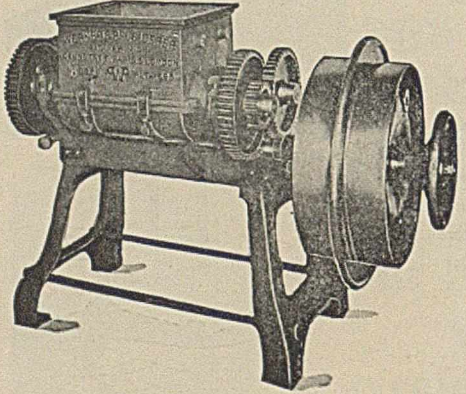

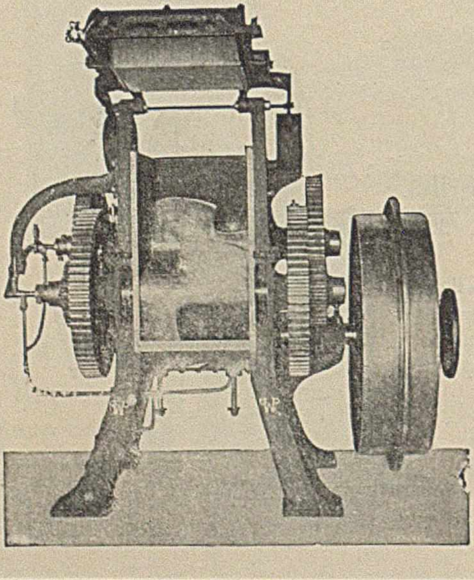

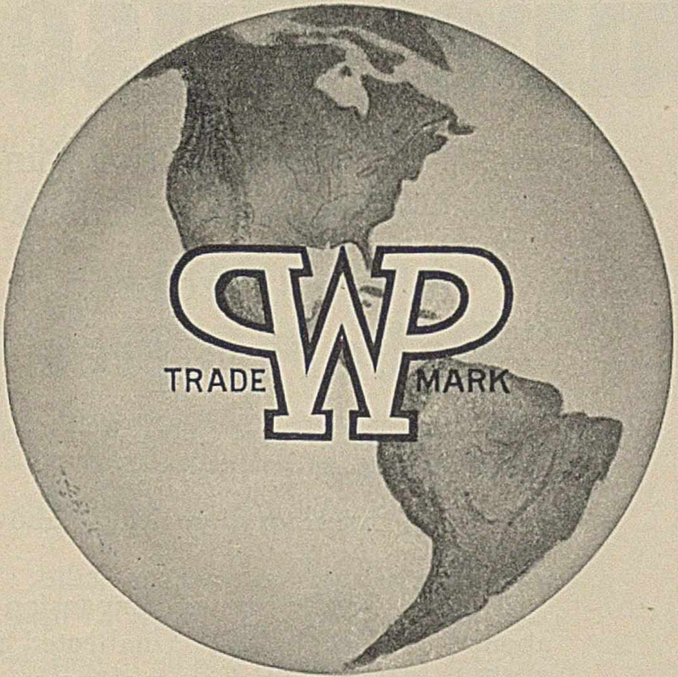
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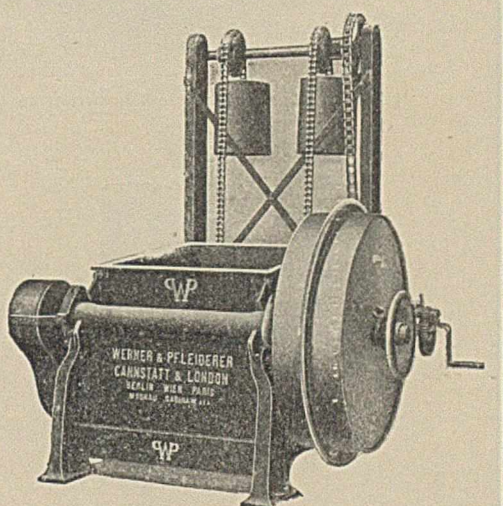
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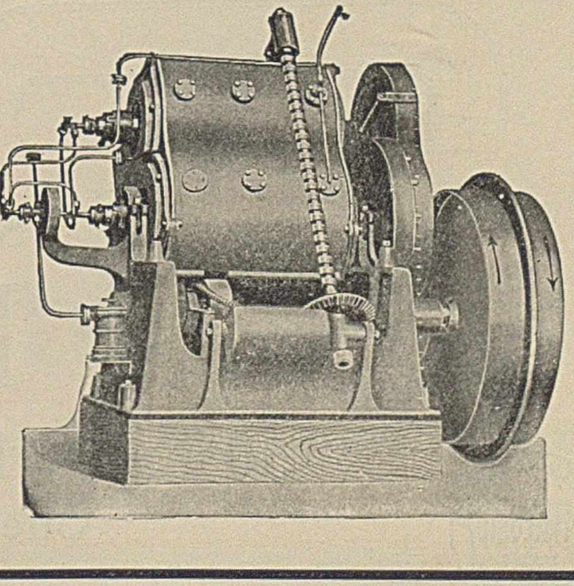

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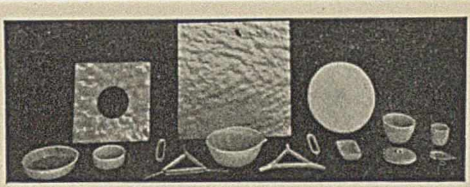

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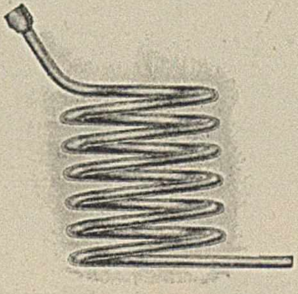

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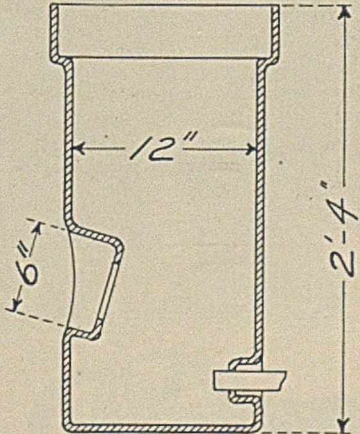

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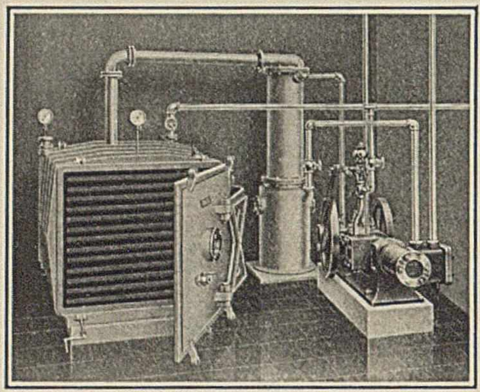

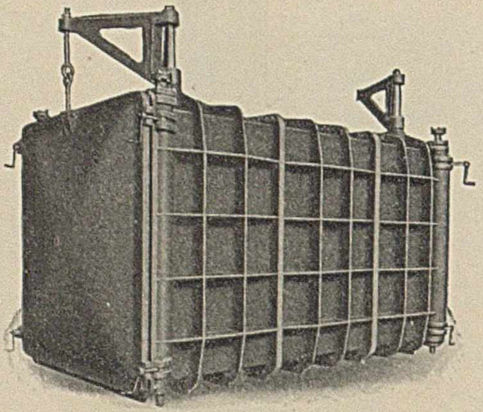

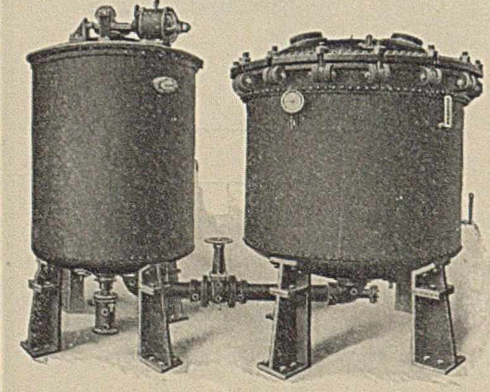

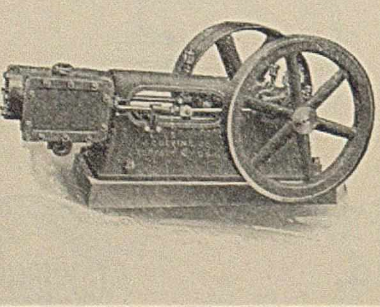

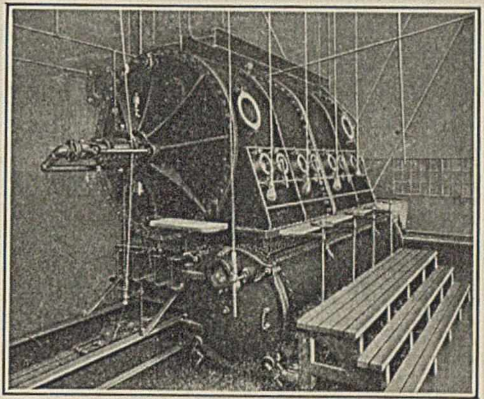

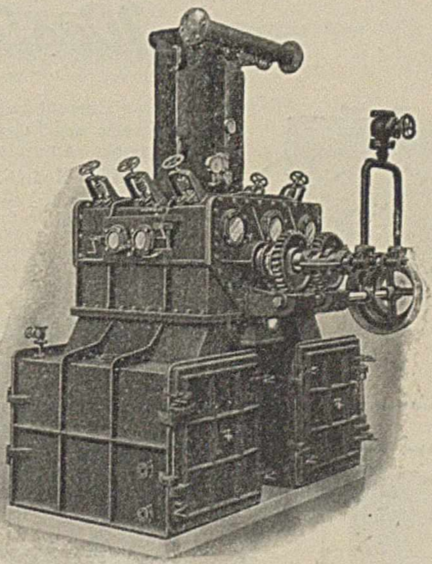

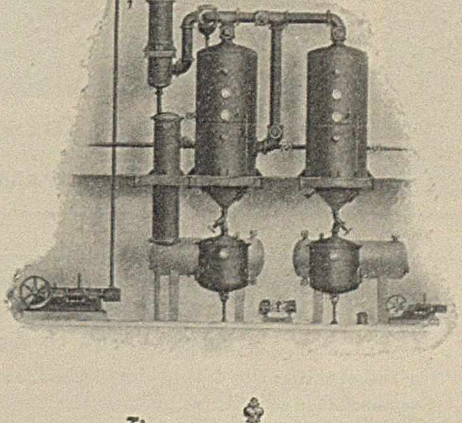

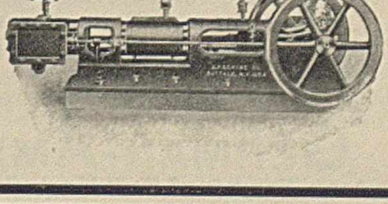

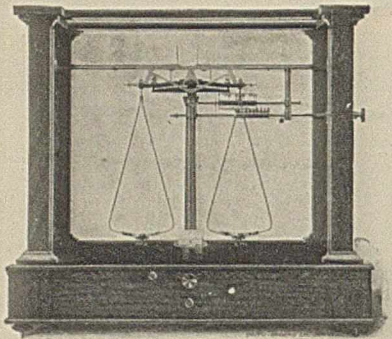

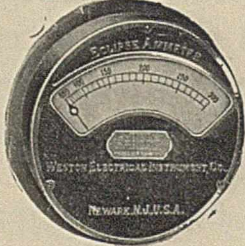


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