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EDITORIALS

THE PRODUCTION OF ETHYL ALCOHOL FROM WASTE PRODUCTS.

The first synthesis of ethyl alcohol was made about 1826, by Hennel, utilizing the reaction of ethylene and sulphuric acid to form sulphovinic acid which, upon heating with an additional quantity of sulphuric acid, yields alcohol. Berthelot improved this process by synthesizing ethylene from its elements *via* acetylene, and by making a more complete conversion of ethylene into sulphovinic acid.

The one source of the alcohol is the action of the zymase of yeast upon glucose and other fermentable sugars. The sources of the fermentable sugars may be grouped into two classes:

(1) The products of the hydrolysis of starch and allied substances by means of an amylase.

(2) Solutions of sugars obtained directly from fruits and plants and from the non-crystallizable by-products of sugar-works—such as molasses.

The most economical source of starch in our country is probably Indian corn costing about \$21.00 per ton. One ton of corn gives about ninety gallons of 94 per cent. alcohol. About two gallons of raw molasses produce one gallon of 94 per cent. alcohol, and this raw material costs about \$0.21 per gallon of 94 per cent. alcohol. The costs of the distillation of the mashes and the rectification and purification of alcohol cannot be entered into here, but the approximate cost of 95 per cent. alcohol (190 proof) to the consumer may be taken as about \$0.50 per gallon, exclusive of taxation.

Within the last two or three years, two new commercial processes for the production of alcohol have been put in operation on a comparatively large scale. The purpose of this article is to present and discuss briefly from a chemical engineering standpoint these two processes: namely, the production of alcohol from sulphite cellulose waste lyes, and the production of alcohol from sawdust.

I. ALCOHOL FROM SULPHITE LYES.

In the sulphite process for the production of pulp, for every ton of cellulose there are about ten tons of sulphite lyes (T. H. Norton, *U. S. Cons. Rep.*, Nov., 1911) which contain one-half the weight of the wood originally introduced into the boilers. Among the substances present are: dextrose and other sugars, xylose, acetic acid, tannic acid, nitrogen compounds, methyl alcohol, resins, etc., and calcium lignin-sulfonate, the chief product of the reaction. Most of the sugars in these lyes are fermentable and they constitute about 1 per cent. of the lyes, the yield of alcohol being from fifteen to seventeen and one-half gallons per ton of cellulose [C. G. Schwalbe, *Z. angew. Chem.*, **23**, 1537(1910)].

Recently in Sweden two industrial processes have been developed, that of Ekström (P. G. Ekström, Eng. Pat. 6741, March 17, 1910) at Skutskär and that of Wallin at Forss. These processes are practically identical, differing only in the neutralization of the

acid. The former uses lime, chalk, etc., and the latter waste causticization sludge. The general scheme is as follows: The lyes are first neutralized in large vats, then cooled in towers and aerated. In a mill producing ten tons of cellulose per twenty-four hours the volume of the lyes to be treated is about nine thousand gallons per day. A yeast nutrient, malt extract or dead yeast is added to the cool, neutral liquid which is transferred to the fermentation vats. After fermentation (which takes three days or more) the yeast is separated and the liquid distilled in a continuous still. The percentage of alcohol is very low and considerably more steam is used in the distillation than is required with mash from molasses which usually contains about 7 per cent. alcohol by volume. The alcohol obtained is already denatured as it contains considerable methyl alcohol (from the unfermented lyes), furfural, aldehydes, and sometimes acetone, but is practically free from terpenes.

The above process with a few minor changes is being worked on a large scale at several places in Sweden. The experimental plant at Skutskär began operations on May 24, 1909, using waste lyes from a 5,000-ton cellulose plant. In March, 1910, 560 gallons of "normal strength" alcohol were produced per 24 hours. The total for the month was about 13,000 gallons. The process yields about 6 gallons of absolute alcohol for 1000 gallons lye, and about 14 gallons for every ton of cellulose.

As the alcohol produced from waste lyes is denatured, its chief uses will necessarily be for heating and other industrial purposes. The industrial prospects of this process depend on the cost of production, conditions of taxation and capacity of the market. Estimates of the cost of production for a mill producing 340,000 gallons per annum place the cost at about \$9.50 per 100 gallons. In Sweden the tax per gallon increases with the output, so that for an annual production of 340,000 gallons, the cost of production including the tax is about \$15.50 per 100 gallons. In Germany excise regulations penalize new distilleries so that in addition to the cost of production, sulphite spirit would be subject to a tax of about \$17.00 per 100 gallons. Regarding the capacity of the market, in Sweden during the fiscal year 1908-1909 the total production of alcohol was about 5,800,000 gallons (absolute) and the imports were about 310,000 gallons. The sulphite lye mill at Larkudden is reported as having produced spirit during the year 1910 at the rate of 157,000 gallons per annum, and the annual rate of production at the present time is estimated at 250,000-400,000 gallons. The pulp mills of Sweden can produce 6,500,000 gallons of absolute alcohol per annum. It must be remembered that the present method of production from grain is always intimately connected with the agricultural industries of the country, and therefore will not be easily displaced. Also, while under special conditions (especially low taxation) the

sulphite process can be worked at a profit, yet it does not solve the problem of the disposal of the waste lyes, as only about 1 per cent. of the total weight of lyes is converted into alcohol. In fact on account of the presence of dead yeast, etc., the problem of the disposal of the lyes may be aggravated by the use of this process.

II. ALCOHOL FROM SAWDUST.

The cost of raw material is always of great importance in any industry. While Indian corn costs about \$21.00 per ton, sawdust in the vicinity of a large mill where it is a by-product can be bought at a cost of 30-50 cents a ton including handling and transportation (short distances). One ton of sawdust calculated to the dry basis can yield 20 gallons of 94 per cent. alcohol, which makes the cost of this raw material 2-2½ cents per gallon 94 per cent. alcohol, as against 24 cents for Indian corn.

For nearly one hundred years it has been known to chemists that fermentable sugars can be produced from sawdust. The reaction is usually spoken of as being very simple, all that is necessary being to add a molecule of water to the cellulose. This hydrolysis is probably as complex as it is baffling. The unknown composition of those polysaccharides which we call cellulose and the very different results obtained on hydrolysis under slightly different conditions of catalyzer, temperature and pressure indicate that somewhat intricate reactions occur, the complete chemistry of which is not known at the present time. A very large number of patents have been granted on this reaction, the main differences being in method of manipulation and the catalyzing acid used. Sulphuric acid has been used in many cases but the subsequent removal of this acid has proved a serious stumbling-block. No process that was capable of commercial application had been devised until the year 1900 when Dr. Alexander Classen was granted his first patent. The more important English patents granted him are: No. 258, Jan. 4, 1900; No. 4,199, Feb. 27, 1901; No. 12,588, June 20, 1901. "Process claimed consists in boiling cellulose in a closed vessel at a temperature of 120-145° C. with a solution containing sulphurous and sulphuric acids or sulphurous and hydrochloric acids. A solution of 2 per cent. or more of sulphurous acid and 0.2 per cent. sulphuric acid is mentioned. The sulphuric acid may be conveniently formed in the boiler by admission of air or other suitable oxidizing agent. In this way concentrations of 10 per cent. sugar may be obtained, 80-90 per cent. of which is fermentable. Conversion is complete in 15 minutes."

An experimental plant using this process was erected at Aachen and a similar plant on a larger scale was built at Highland Park near Chicago. The results were satisfactory so that it was decided to build a commercial scale plant at Hattiesburg, Miss. The capacity of the conversion cylinder was two tons. After the conversion the acid was neutralized, cleared by subsidence, pumped into large vats and fermented by yeast and then distilled. From a commercial viewpoint this plant was a complete failure. From a chemical engineering standpoint it is an excellent

example of a process which fell just short of success. The reasons given for the failure are: (1) Length of time required for conversion: 1½-2 tons requiring 4-6 hours. (2) Prolonged action produces gums and caramels and makes extraction of the sugar tedious and expensive. (3) Large quantity of acid required. (4) Lining difficulties, especially with lead linings.

Two chemical engineers, Ewen and Tomlinson, studied and undertook to improve this process. Their patent U. S. 938,308, 1909 describes their process. The converter used by Classen was about thirty feet in length and had a diameter of three feet, whereas in the Ewen and Tomlinson process the digester is much shorter, usually being about twelve feet in length and eight feet in diameter. The latter line their converter with fire-brick instead of using the troublesome lead lining. The operation seems to be fairly simple. Sulphur dioxide gas to the extent of 1 per cent. of the weight of the wood is introduced into the cylinder and live steam is turned on until a pressure of 100 lbs. is obtained. The steam is then turned off and the cylinder slowly revolved for 40-45 minutes, the temperature and pressure being kept constant. The total time of conversion is about one hour as against 4-6 hours in the old process. In operating this process it is important to raise the temperature as quickly as possible to the "critical point" which is defined as "that temperature above which the production of unfermentable substances and the destruction of the sugars become excessive and lies between 135° and 163° C." After extraction, the converted lyes have a total acidity of 0.64 per cent. (calculated to H₂SO₄) containing sulphuric, acetic acids, a small amount of sulphurous acid and aromatic compounds of the type of pyrogallol. These liquors contain about 5½ per cent. of reducible sugars calculated to dextrose. Polyphenols, tannin and furfural are usually present in small amounts. These liquors are fermented and distilled in the usual manner, some care being required in the fermentation to have present a proper food for the yeast. The distilled alcohol obtained is potable, free from the odor and taste of wood, and from methyl alcohol and fusel oils, but contains traces of furfural and aldehydes. One and one-half tons of dry wood give about 61½ gallons of 94 per cent. alcohol. From figures obtainable it appears that the efficiency of the process is from 75-80 per cent. of the theoretical yield of alcohol.

The Dupont Powder Company is operating a plant at Georgetown, South Carolina for the production of alcohol from waste woods. This plant is licensed under the Ewen and Tomlinson patents, and while no figures were obtainable, it is stated that experiments so far indicate the ultimate success of the process.

W. P. Cohoe is the inventor of a process for making fermentable glucose-like substances from cellulose and ligneous materials (U. S. Patents 985,725, 985,726, 1911). The conversion is done in two stages: first, steam is used producing acetic acid which is collected, and then steam and HCl vapors are introduced into the converter. The raw material used is generally sawdust.

The cost of production of alcohol by the sawdust process (Ruttan, *J. Soc. Chem. Ind.*, 1909, p. 1290) is said to be about equal to that of grain, although there is such an enormous difference between the cost of the raw materials. One company, however, claims to be able to manufacture alcohol by the sawdust process at a cost of \$0.07 per gallon.

Without going into the details of the chemistry involved, it is striking that, although the patents claim a conversion of cellulose into sugar, the so-called true fibrous cellulose, absorbent cotton, does not yield to this treatment. Also the material left after treatment contains cellulose which upon re-treatment yields but traces of fermentable sugar. Although authorities differ, it is claimed by some that the acid acts as a catalyzer hydrolyzing the lignone complex and a proportion of the "easily attacked cellulose." The oxy-cellulose and the "true cellulose" are said not to be seriously altered chemically.

It would seem that there is a possibility that a process might be evolved where the alcohol conversion of the wood pulp might be made first, and then the residue subsequently utilized for the production of paper pulp.

ALCAN HIRSCH.

OCCUPATIONAL DISEASES.

This subject is now receiving the attention it deserves. Hitherto the matter of diseases peculiar to industries has been in the hands of physicians. While medical men are competent to treat and cure such diseases it can readily be seen that they are unable by nature of their training to accomplish much in the elimination of the causes of occupational diseases. The physician is not the proper person to suggest to a manufacturer such changes in his processes as will eliminate the causes of the peculiar occupational ills

to which his employees are subject. This is necessarily the function of the chemical engineer and it is to him that the physician now turns for assistance.

The June number of THIS JOURNAL published an address delivered by Dr. W. Gilman Thompson, Professor of Medicine in the Cornell University Medical College, in New York City, before the New York Section of the American Chemical Society. The attention of our readers is called to the facts set forth and the points brought out in this address, and chemists will readily see the opportunity which presents itself to them, to be of assistance in this crusade of the Twentieth Century.

The New York Section of the American Chemical Society has appointed a Committee on Occupational Diseases, which is now coöperating with a similar Committee of the New York Association for Labor Legislation. The personnel of these committees is given in another column of this issue. A joint meeting of the two committees was held on May 31st, at the Chemists' Club in New York City. This meeting was addressed by Dr. Alice Hamilton, whose work of investigating lead poisoning for the U. S. Department of Labor is well known. Dr. Hamilton spoke of the difficulties she had experienced in obtaining information, and laid particular stress on the importance of the coöperation of the chemist and physician.

It will be readily seen that this is a matter for organized and systematic work by our profession, and that the campaign must be one of educating the public, the workingman, and the manufacturer. It is evident that statistics must be collected so proper lines of work can be designed. More will be accomplished by education than by inconsidered or hasty legislation, and by this method the least possible hardship will be inflicted on established industries. E. C. UHLIG.

ORIGINAL PAPERS

CORROSION OF IRON IN PURE WATER AND AIR COMBINED; THE ELECTROLYTIC THEORY AGAIN CONFIRMED.¹

By WILLIAM R. FLEMING.

In a recent article in the *Iron and Steel Institute*,² Dr. J. Newton Friend again attacks the "Electrolytic" Theory of Corrosion. In his paper, a Carnegie Scholarship Memoir, he describes an experiment which demonstrates that "Pure water and pure air combined are without visible action upon pure iron." "This shows, Friend continues, that the electrolytic theory of corrosion is untenable, and definitely confirms the older acid theory."

In this paper I shall attempt to show that iron and steel will rust in pure water and air combined, if it is given a chance. Furthermore, I shall attempt to prove that Friend's experiment is a strong confirmation of the electrolytic theory, and not destructive to it.

We have to-day only two important theories of corrosion, the "Acid" and the "Electrolytic" theories.

¹ Read before the Cincinnati Section of the A. C. S., February 14, 1912.

² *Iron and Steel Institute*, 3, 1 (1911).

The acid theory presumes that corrosion is primarily caused by acid attack. It denies the solubility of iron in pure water and denies that iron will rust in acid-free air and water combined.

The electrolytic theory presumes that iron is soluble in pure water, and that rust is subsequently formed through the influence of oxygen. The exposed surfaces of iron and steel contain segregated impurities which are supposed to give rise to differences of potential, in the presence of an electrolyte, which is generally moisture. At those points where the metal is anodic, iron passes into solution, assuming the ferrous ionic condition, while hydrogen is liberated at the cathode. Oxygen plays its part by depolarizing the hydrogen covered cathodes and by oxidizing the ferrous ions at the anodes. In its purest sense the electrolytic theory presumes that corrosion begins in a pure electrolyte, *e. g.*, water free from all traces of impurities.

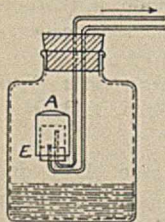
The defendants of the acid theory deny the solubility of iron in pure water and are emphatic in their claim that corrosion is "primarily the result of acid

attack." Since carbon dioxide is universally present in our atmosphere it is considered the chief cause of rusting. It attacks the iron forming ferrous carbonate and liberating hydrogen. Oxygen and moisture further react with the ferrous carbonate to form rust, freeing the carbon dioxide which in turn reacts with fresh iron. But, according to our latest notions of solutions, carbonic acid does not attack the iron directly, *e. g.*, in its atomic condition. It must first pass into solution (become ionic) before the acid can attack it. Therefore, the acid theory is but a special case under the general electrolytic theory. This has been admitted. But, while admitting the electrolytic character of corrosion, when viewed from the general standpoint of ionization as announced by Arrhenius, the defendants of the acid theory insist that iron will not assume the ionic state unless an acid is present in the electrolyte. Hence, they say, acid attack is the true beginning of corrosion.

There can be no doubt that the presence of acids (chiefly carbonic) has much to do with the *rapid* corrosion of our iron and steel. Without acids in our air and water the corrosion problem would be less formidable. This, however, is only a quantitative view-point. In attempting to get at the facts concerning the true cause of corrosion we should not allow ourselves to be blinded by mere quantitative ideas. Given pure iron in pure air and water, the factor of corrosion is very small. Likewise, with impure iron in impure air and water, the factor of corrosion is very great. But this does not interest us. We are concerned only with the true *starting point* of corrosion. It matters not how small the value of this "starting point," quantitatively, if iron is soluble in pure water even to the slightest extent, or, if iron will rust in pure water and air combined be it ever so slight, then this weakness in the metal itself is the true cause or starting point of corrosion. All influences which enter later are mere retarders or accelerators.

Below is given Friend's experiment and conclusions in his own words:

A-E is a hollow cylinder of iron or steel, closed at one end. The open end is plugged with a tightly fitting rubber stopper, bearing two glass tubes, arranged in such a manner that cold water can circulate through them. The glass bottle, containing about 100 cc. of twice normal caustic potash solution, is placed in a deep cold water bath, and heated gradually to 100° C. Its mouth is now



DR. FRIEND'S APPARATUS.

closed with a large India-rubber bung, from which hangs the metal cylinder by the glass tubes—already alluded to—and the whole is thoroughly shaken to remove every trace of carbon dioxide from the walls, air, and surface of the iron. A current of cold water is now passed through the tubes, and on immersing the bottle again in the hot water bath, pure water vapor condenses upon A-E and drips off, rapidly washing it free from alkali. That the cylinder is actually free from alkali may be

readily demonstrated by opening the apparatus, and testing with phenolphthalein, when no change in color occurs. Nevertheless, the iron remains perfectly bright for an indefinite number of days. An isolated spot of rust will often form here and there upon the surface of the metal, owing to the unavoidable traces of impurity always present in the purest metal obtainable, and if the apparatus is opened and the cylinder again polished with emery, the spots will appear again in the same places upon repetition of the experiment. Furthermore, where the iron is in contact with the India-rubber, a little corrosion takes place, owing to the presence of sulphur, etc. These points, however, do not affect the general result of the experiment. The conclusion is inevitable:

"Pure water and pure air combined are without visible action upon pure iron."

This shows that the electrolytic theory of corrosion is untenable, and definitely confirms the older acid theory.

"The experiment was now repeated in every detail, save that the caustic potash was replaced by an equal amount of a saturated solution of barium hydroxide. Although in every other respect the experiments were precisely similar, the iron always rusted in the course of an hour or two. This shows that barium hydroxide is not sufficiently powerful to remove every trace of carbon dioxide from the air in the flask. In other words, its aqueous solution is in equilibrium with a definite, although minute, partial pressure of carbon dioxide. Now Moody employed aqueous barium hydroxide solution as his source of water distilled on to the iron in his apparatus. Consequently, his metal must have rusted had it not been protected by alkali dissolving out of the glass tubing containing it. A clear explanation is thus offered for the failure of Dunstan and of Walker, each working independently of the other, to confirm Moody's results, when a different kind of glass was employed in the construction of the apparatus—a glass which was slow to yield up any soluble alkali to liquid water condensed upon its surface."

No mention is made of conditions which might influence rusting of the metal. The temperature of the metal and water on its surface, and the rapidity with which this water is changed, are conditions which influence the results. These, along with other important conditions, will be taken up fully after describing my experiments. Suffice it to say here that my experiments prove that Friend is wrong in his conclusions, and that his experiment was concluded before he had proved anything.

The apparatus used in all experiments is shown in Fig. 1.

I and S are hollow metal blocks, $1 \times 1 \times 1\frac{1}{2}$ ", with $\frac{3}{4}$ " hole $1\frac{1}{4}$ " deep. The samples in all cases received their final polishing on 0000 French emery paper.

The metal samples are connected by tubes for the circulation of cold water within them, as in Friend's experiment.

The purifying train consists of: A, dilute sulphuric acid; K₁, 50 per cent. potassium hydrate; K₂, 50 per cent. potassium hydrate; So, Soda lime; (the tube connecting bottle and train extends just to the bottom of the large rubber stopper); Sy, is a syphon; Cl, clamp on purifying train; C₂, clamp on syphon; C₃, large iron clamp for bolting down the rubber stopper.

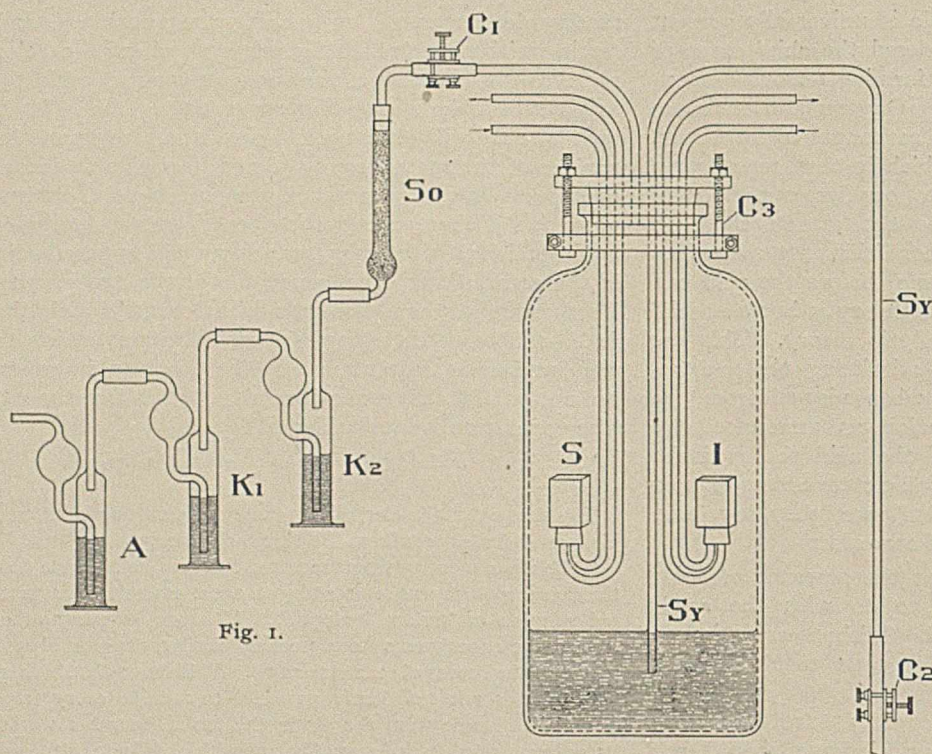


Fig. 1.

EXP. NO. 1, PART I.

Metals Used.—Genuine Open Hearth Iron and ordinary mild Open Hearth Steel.

Analyses.

	C.	Mn.	S.	P.	Si.	O.
Genuine Open Hearth Iron ¹	0.01	0.01	0.028	0.003	0.003	0.055
Open Hearth Steel.....	0.09	0.40	0.080	0.070	0.006	0.014

The bottle (2½ liters) was completely filled with saturated barium hydrate solution, recently boiled and filtered.

The large rubber stopper carrying the four condensing tubes, (with samples attached), syphon, and purifying train, was fitted tightly and bolted down securely by means of clamp C₃. No air bubbles were visible in the apparatus. The bottle was placed in a cold water bath and heat applied. C₂ was closed, and C₁ opened. The expanding solution filled the tube connecting the bottle and purifying train. Thus all air was expelled, and the necessity of removing carbon dioxide from the apparatus by mere shaking, avoided.

C₁ was then closed. C₂ was then opened to allow the expanding solution to fill the syphon. The solution was then syphoned off by opening C₁ just enough to allow the incoming air to bubble through the purifying train at the rate of four or five bubbles per second. When syphoned to the level indicated in Fig. 1, the clamp C₂, on syphon, was tightly closed. C₁ was left slightly open to avoid undue pressure or rarity of the air in the apparatus. The rubber stopper and all connections were well paraffined.

The water in the bath began to boil and cold water was made to circulate through the glass tubes and samples. Water immediately began dripping from the samples.

The experiment was continued thirty-five days. The water in the bath was boiling every minute during the whole period. Likewise, cold water was circulating rapidly through the condensing system. The temperature of the ingoing water was 4 to 5° C. The temperature of the water leaving the system varied from 10° to 15° C. At no time did it exceed 15°. From this the temperature of the metal samples was presumed to be about 8° to 12° C. The temperature of the pure con-

¹Made by Newport Rolling Mill Co.

densed water vapor on their surfaces was probably but slightly higher. These conditions were maintained every minute during the thirty-five days.

Observations:—At the end of thirty-five days not the slightest spot of rust or discoloration of any kind was visible on either the pure iron or the steel. Under the samples a ring of rust was formed by contact with the rubber stopper. This, of course, must be disregarded.

The surface area of the top and four sides of each sample was 7 sq. in. It is remarkable to think that 14 sq. in. of iron and steel can be exposed for thirty-five days to pure air and water combined without developing the slightest sign of a rust spot.

Conclusion:—This proves that iron or steel will not rust in pure air and water combined, provided the temperature of the metal does not exceed 15° C., and provided the temperature of the pure water condensing on its surface does not much exceed 15°; provided, also, that the pure water which condenses on their surfaces is being constantly renewed. Beyond this, the experiment proves nothing. It simply indicates that pure iron or steel will not rust in pure air and water combined.

EXP. NO. 1, PART 2.

At the end of thirty-five days the source of heat was removed and the apparatus taken out of the water bath. The circulation of the cold condensing water was continued until the barium hydrate solution had reached room temperature. The condensing system was then shut off. In a few hours the entire apparatus had reached room temperature, about 22° C. The metal samples were left covered with pure water, the flat tops completely, the sides with irregularly distributed patches or globules. This same water was destined to remain on the iron and steel until removed by natural evaporation at room temperature.

What was the effect of allowing the same water (at 22°) to remain on the metal (at 22°) for a protracted period? New conditions had been created in the apparatus.

Observations:—In fifteen hours the steel had developed thirty-three distinct rust spots and all of these spots were on areas covered with the pure water. The pure open hearth iron was still spotless. After twenty-four hours contact with the same water at 22° the steel contained about 50 spots; the iron was still rustless.

At the end of seventy-two hours the water had entirely evaporated from the sides of both metals. The tops were still covered with a thin layer of water. A few new spots had developed on the steel, but no rust had yet appeared on the iron.

At the end of eighty hours the water had evaporated

entirely from the tops. *Two large glaring spots of rust had developed on the top of the iron within the last eight hours.* More than seventy-two hours contact with the *same water* at 22° was necessary to produce rust on the pure open hearth iron. Less than fifteen hours contact with the *same water* produced rust on the steel.

Conclusions:—Iron or steel will rust in pure water and air combined if it is given a chance. The two most important factors which influence the development of rust are:

First, the temperature of the metal and of the pure water on its surface; second, the rate at which the pure water is renewed, changed, on the surface of the metal.

EXP. NO. 2, PART 1.

The same samples were repolished and Exp. No. 1 repeated, except that the apparatus was kept in boiling water for six days instead of thirty-five.

Again, not the slightest sign of a rust spot developed on either sample.

EXP. NO. 2, PART 2.

Apparatus cooled to room temperature as before. Rust developed in almost the same time on both the iron and steel, the iron requiring ninety hours contact with the same water, the steel about sixteen hours. The location of the rust spots does not seem to be determined entirely by impurities in the metal, but also by the distribution of the water patches on the surface.

This experiment confirmed Exp. No. 1 in every detail.

EXP. NO. 3.

Same samples used. 2-N potassium hydrate substituted for barium hydroxide. Condensation period, six days.

This experiment confirmed Nos. 1 and 2, and further showed that either potassium hydrate or barium hydrate may be used with equal effect.

EXP. NO. 4, PART 1.

Same samples used. Solution, saturated barium hydroxide. Condensation period, six days.

Both metals, as usual, were spotless at the end of six days.

EXP. NO. 4, PART 2.

The flow of cold water through the condensing tubes was almost checked. The apparatus was kept in the boiling water bath. The slowly dropping water leaving the system showed a temperature of 55° C. From this I assumed that the temperature of the metal samples and of the pure water on their surfaces was about 55–60° C.

Under these conditions the condensation of water on the samples was almost stopped. Thus new conditions were created in the experiment. The metal samples were suspended in a hot atmosphere of air and water vapor, while the temperature of the metals themselves was about 55° C. and the temperature of the almost stagnant pure water on their surfaces was about 55° C.

Observations:—In one and one-quarter hours rust began developing on the top and sides of the steel. It developed so rapidly that it could be easily observed. Small clouds of insoluble matter came up from the metal and could be seen floating through the water. It had a faint greenish color. Presumably it was ferrous hydrate.

In two hours the pure iron began to develop rust. This, too, rusted so rapidly that it could be observed.

In a few hours the tops of the samples were covered with rust, and the sides were badly spotted.

Conclusion:—This experiment clearly demonstrates that pure open hearth iron and steel will rust, and rust badly, in pure water and air combined, provided the temperature of the metal and water on its surface is sufficiently high.

This, and all preceding experiments, further prove that rust develops much faster on steel (impure iron) than on pure open hearth iron. This is in strict accordance with the electrolytic theory.

EXP. NO. 5, PART 1.

Samples, same. Solution, barium hydrate; condensation period, ten days.

No sign of rust at close of ten days.

EXP. NO. 5, PART 2.

In Part 2, Exp. No. 4, the condensing water was only partially checked. In this experiment the condensing system was shut off entirely, the apparatus being kept in the boiling water. Accordingly, the temperature of the metals and pure water on their surfaces would be higher than in Exp. No. 4. From this increase in temperature should result an increased rate of corrosion. Such was the case.

In 25 minutes the top of the steel was badly rusted and the sides considerably spotted.

In 50 minutes the iron was badly rusted.

This further demonstrated the influence of temperature and of stagnant water.

EXP. NO. 6, PART 1.

Different samples used.

	Analyses.					
	C.	M.	S.	P.	Si.	O.
Genuine Open Hearth Iron.....	0.01	0.040	0.026	0.004	0.003	0.056
Mild Open Hearth Steel..	0.12	0.38	0.040	0.076	0.007	0.009

Solution, barium hydrate. Condensation period, twelve days. At the close of twelve days not the faintest suggestion of a rust spot was visible on either sample.

EXP. NO. 6, PART 2.

After twelve days the source of heat was removed as in Exp. No. 1, Part 2.

The steel developed twenty-four rust spots in twenty hours. In ninety hours, over forty spots were visible.

The iron developed only three spots on top after ninety hours. This rust development took place at room temperature (about 22°) while the same water remained on the metal until removed by natural evaporation.

EXP. NO. 7.

Sample same as Exp. No. 6.

Solution, potassium hydrate.

Condensation period, six days.

No sign of rust, as usual.

EXP. NO. 7, PART 2.

Exp. No. 5, Part 2, repeated to confirm results on different metals.

The steel began to develop rust in 35 minutes; the iron in one hour. In one and one-half hours both were badly rusted.

EXP. NO. 8.

Other samples used.

	Analyses.					
	C.	M.	S.	P.	Si.	O.
Genuine Open Hearth Iron.....	0.01	0.03	0.027	0.003	0.003	0.061
Acid Open Hearth Steel..	0.15	1.15	0.055	0.105	0.009	0.010

Solution, potassium hydrate.

Condensation period, ten days.

At the close of ten days not the slightest suggestion of rust

appeared on either sample. In this connection it is interesting to note the high percentage of impurities (especially the manganese) in the steel.

EXP. NO. 8, PART 2.

Cooled to room temperature as in Exp. No. 1, Part 2.

In eight hours the steel was covered with rust spots. The iron, as usual, required about ninety hours to develop a few rust spots.

Aside from confirming the results of preceding experiments, this experiment further indicates the influence of impurities on the rate of rust development. As we should expect, from the electrolytic theory, increased impurities greatly increase the rate of corrosion.

EXP. NO. 9, PART 1.

Sample, same as Exp. No. 8.

Solution, barium hydrate.

Condensation period, ten days.

No rust developed, as usual.

EXP. NO. 9, PART 2.

Condensing system entirely stopped, as in Exp. No. 5, Part 2.

In fifteen minutes the top of the steel developed rust.

In 25 minutes it was covered with rust. The sides were also badly spotted.

In 45 minutes the iron began to develop rust.

In one and one-half hours the top and sides were badly rusted.

EXP. NO. 10, PART 1.

Sample, same as Exp. No. 1.

Solution, 2-N potassium hydrate.

Condensation period, six days.

No sign of rust, as usual.

EXP. NO. 10, PART 2.

Exp. No. 1, Part 1, demonstrated that iron or steel will not rust, while the temperature of the metal and water on its surface does not exceed 15° C., and while the surface water is constantly changing. In this experiment the object is to determine whether iron or steel will rust while the metal and surface water remain below 10°, with the same water lodging on the metals.

This condition was created in the bottle by removing the apparatus from the boiling water, and continuing the flow of cold condensing water through the system. In a few hours the potassium hydrate solution had reached room temperature. The temperature of the incoming condensing water was 5°, the outgoing water 7°. Therefore the temperature of the metals and of the water on their surfaces was about 6°. This condition was maintained for thirty days. At the end of this period not the slightest indication of rust was visible.

This experiment further shows the great influence of temperature on the development of rust in pure water and pure air combined. It demonstrates that pure open hearth iron or ordinary mild steel will not rust in pure water and air combined, provided the temperature of the metal and water is constantly below 7° C. This has been demonstrated in Part 1 of each experiment, but this experiment further shows that the same water remaining on the metal has little effect if the temperature remains sufficiently low.

EXP. NO. 10, PART 3.

After thirty days the cold samples were still covered with water. The condensing system was stopped and heat applied to the water bath until the water had reached 60° C.

In two hours after the water had reached 60° the steel was spotted with rust.

In four hours the steel was badly rusted.

The pure open hearth iron was still spotless.

The temperature was increased to 80°. In thirty minutes the iron began to rust. One hour later the top was covered with rust and the sides badly spotted.

Starting from a low temperature (6°), as in this experiment, and gradually raising the temperature is an excellent means of determining the temperature necessary to produce rust. It also indirectly shows the solution pressure of the metals at different temperatures. And in this way I believe we can test in a most reliable way the ability of a metal to resist corrosion in service. There can be no doubt that metals of high solution pressure will rust much faster than metals of low pressure. By this experiment we can compare these pressures, indirectly.

The carrying out of the experiment, however, is not extremely simple. It requires great care and in the hands of a careless operator it might become misleading.

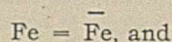
I must call attention to the way in which rust developed in these experiments at higher temperatures. At these temperatures rust developed so rapidly that observations could be made at different stages.

When rust began to develop, the metal, over a small area, assumed a light grayish color. This gradually gave way to green, which increased in intensity for a few minutes, then gradually changed to yellow or rust color.

These observations strongly indicate that rusting, in a pure electrolyte (water free from acids, bases, etc.) is due to causes which have been properly explained as follows:

Pure water is dissociated to a certain extent. It contains dissociated hydrogen and hydroxyl ions.

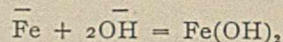
For the present purpose let \bar{H} represent the hydrogen ion, \bar{OH} the hydroxyl ion, \bar{Fe} the iron ion, etc., and H, OH and Fe represent the atomic state of the element. At the anodic points iron passes into solution,



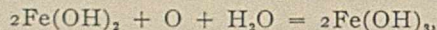
at cathodic point hydrogen is liberated;



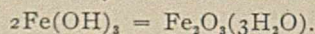
Iron and hydroxyl ions then unite chemically, to form ferrous hydroxide;



Ferrous hydroxide then reacts with water and dissolved oxygen,



which is immediately converted to the hydrated oxide,



Iron Dissolves in Pure Water and Oxygen.—If, according to the electrolytic theory, iron passes into solution in pure water, a highly polished surface should be "etched" in spots during corrosion and it should reveal the structure of the metal somewhat as by etching with dilute acids or other reagents. We know that iron passes into solution when in contact with acids. We know that structure is developed on highly polished surfaces because the metal dissolves more rapidly along the boundary lines of the grains. Therefore, if iron passes into solution in pure water the surface will be etched and structure developed. Pure water will thus act as an exceedingly dilute acid. Microscopic examination of both the pure iron and steel after each of my experiments invariably showed the true structure of the metal in many places. Most of the surface, of course, was covered with rust and

the structure obscured, but large spots of rust invariably showed the structure of the metal in many places.

Fig. 2 shows the surface of the iron before using in Exp. No. 10. Fig. 3 shows the ferrite structure which was developed in several places in the large spot of rust on top of the sample. The grains are large. A portion of the metal which was free from rust was later etched with dilute nitric acid and the same structure appeared. Fig. 4 shows the steel before Exp. No. 10; Fig. 5, the structure in places after corrosion. The ferrite grains are small and mingled with pearlite, which accounts for the structure not being as well defined as it is in the case of pure iron. The small dark areas are pearlite; some of them show lamellar structures under higher powers. It will be observed that the oooo emery scratches have been almost entirely eroded.

This proves conclusively that iron is soluble in pure water, free from all traces of acids and containing only dissolved air. It further confirms the electrolytic theory since the structure of the metal is developed only in spots—anodic points where iron passes into solution.

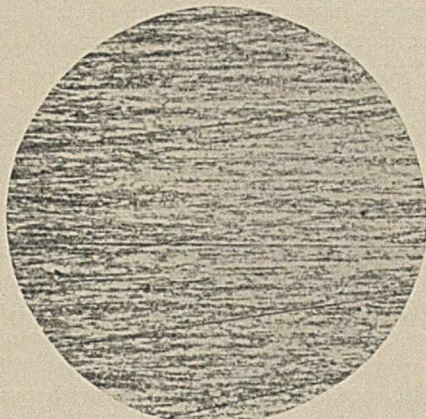


FIG. 2 X 120.

Friend observed that spots of rust formed "here and there" on the surface of his metal but disregarded it as meaningless and as having no effect on the general conclusions. These spots, however, had great significance.

In every one of my experiments, Part I, six different kinds of iron and steel were exposed from six to thirty-

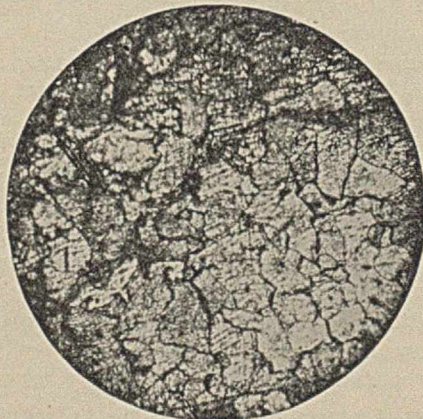


FIG. 3 X 120.

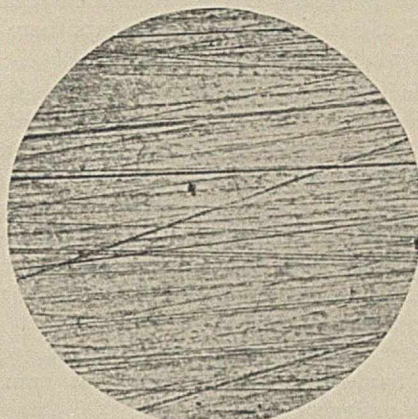


FIG. 4 X 120.

five days, and not the slightest spot of rust developed, not one minute spot on 42 sq. in. of metal. Compare this with Friend's "here and there" spots. Why did not a single spot develop in all my experiments? Simply because, in Part 1 of each, the temperature of the metals and pure water on their surfaces was kept below a certain fixed point (15° C). As the

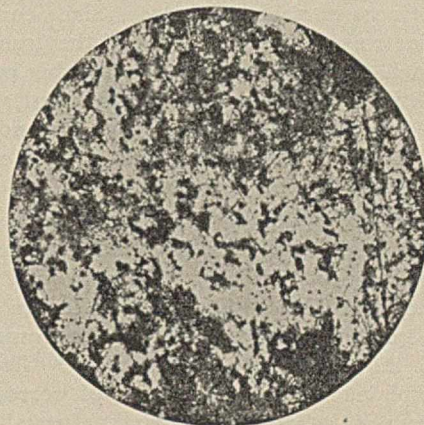


FIG. 5 X 120.

temperature of metal and water gradually increases a point is reached where "here and there" spots are developed. Was this due to impurities in the metal at these points? Yes, partially. But it was probably due mostly to the increase in solution pressure of the iron at these points, resulting from increased temperature. The surface of each metal contained points of lowest and points of highest solution pressure, and other points between these extremes. Now, with increasing temperature, the points of highest solution pressure developed rust first while the points of lowest pressure were slowest to rust. Along this line of reasoning, increasing temperature should result in an increased number of rust spots on the metal. My experiments bore this out completely. Friend gives us no information about conditions in his experiment, but, from my experiments I am convinced that his "here and there" spots were formed because the temperature was higher than in Part 1 of my experiments, or because his samples were so impure that the solution pressure at places caused rust to develop even at low temperatures.

While temperature has great influence on the development of rust in these experiments there are other influences which affect the results.

The purity of the metal determines to a great extent the rate and amount of corrosion. This is definitely indicated in my experiments. Of the impurities in steel, manganese seems to have the greatest influence on the rate of corrosion. My experiments are not exhaustive enough to warrant any sweeping conclusions regarding the influence of manganese, but as far as they go they strongly indicate that this element is an accelerator of corrosion. This is by no means new. For years, metallurgists and other scientists have held the opinion that manganese is the chief instigator of corrosion. Of this, however, there can be no doubt: *The purer the iron the more it will resist corrosion.* I believe I am justified in drawing this conclusion from my experiments. Indeed it follows directly from the electrolytic theory of corrosion, and the great majority of scientists hold this opinion.

Friend's apparatus is an ingenious device for investigating the corrosion of iron and steel in a pure electrolyte, *e. g.*, water containing only dissolved air, free from all traces of acids or bases. Since corrosion in a pure electrolyte is very probably the true starting point, much can be learned by using this apparatus. The conditions of the experiment are ideal since only the three substances concerned—iron, air and water—are brought in contact; no soluble matter coming from glass vitiates the experiment.

No theory ever advanced to explain the corrosion of iron has been so satisfactory as the "electrolytic" theory, announced by Dr. Whitney, and so ably championed by Drs. Walker and Cushman. Practically all known facts connected with corrosion are explained in the light of this theory. The "acid" theory explains many phenomena of corrosion, but it is narrow in its application and, after all, is only a special case under the general electrolytic theory. When carbonic acid enters the pure water electrolyte, it greatly increases the number of hydrogen ions, and, in addition, pollutes the electrolyte with CO_3 ions. The solution pressure of the metal is thus greatly increased and corrosion is accelerated.

Acids are only accelerators of corrosion. They are not the cause. The true starting point of corrosion is the solubility of iron in pure water, its electrolytic solution pressure. This property was given iron by nature, and with all our controversy we cannot take away that which nature gave.

GENERAL CONCLUSIONS.

1. Part 1 of each experiment confirms Friend's statement that iron or steel *will not* rust in pure water and air combined. *The failure of the metals to rust, however, was entirely due to temperature conditions and to rapidly changing pure water.*

2. Expts. No. 1, 2, 3, 6 and 8, Part 2, prove conclusively that pure iron or steel *will* rust in pure water and air combined, provided the temperature of the metal and pure water is not below 22°C ., and pro-

vided the same water remains for a sufficient time on the metals.

3. Exp. No. 4, Part 2, proves that rust is developed rapidly if the temperature of the metals and pure water is about 55°C .

4. Expts. Nos. 5, 7 and 9, Part 2, prove that still further increase in temperature results in a decided increase in the rate of corrosion.

5. Exp. No. 10, Part 2, demonstrates that the *same pure water* may remain on the metal for an indefinite period, and no rusting takes place, provided the temperature of water and metal is sufficiently low.

6. With my modification of Friend's apparatus, equally good results are obtained by using either barium hydroxide, or potassium hydroxide. Barium hydroxide is to be preferred since it is not as liable to render the metal passive.

7. In general, pure iron or steel will rust in pure water and air combined, free from all traces of acids. The amount of rust produced is a function of the temperature and of the purity of the iron.

8. The "acid" theory of corrosion is untenable.

9. All phenomena observed in these experiments are in perfect harmony with the electrolytic theory.

10. The electrolytic theory of corrosion is further confirmed by these experiments.

THE RELATIVE CORROSION OF IRON AND STEEL PIPE AS FOUND IN SERVICE.¹

By WILLIAM H. WALKER.

Received February 5, 1912.

There are few subjects relating to the corrosion of metals which have received so much attention, or around which there has centered so spirited a discussion, as the relative merits of iron (meaning thereby wrought iron) and steel. The fact that this matter is one still receiving attention, notwithstanding the great volume of accumulated and available literature, is due to a number of causes, among which may be mentioned: First, that although the words "iron" and "steel" carry with them a definite idea as to general methods of manufacture and some of the more easily discernible properties, they convey no idea as to standards of value. It is possible to make very poor iron and very good steel, and it is just as possible to make the reverse. Hence when an investigator compared the corrosion of a poor iron with a good steel, he obtained results which favored steel; when the material under study was the reverse, iron was shown to be the more resistant metal. Second, there is a woful lack of uniformity of conditions obtaining in many, if not most of the experiments which have been carried on for the purpose of comparing resistance to corrosion. Some specimens were large, some small; some cleaned of scale, others not; some immersed in deep water, others in shallow water; etc., etc. The corrosion of iron is so sensitive to changing conditions of surface, oxygen concentration, salts in solution, and the like, that only when the most careful preparation is made to maintain all conditions

¹ Abstract of a paper read before the New England Water Works Association, Dec. 13, 1911.

constant, is a comparative test of value. We will not discuss these conditions here, but take pleasure in referring the reader to that most excellent book on "The Corrosion of Iron" by Dr. J. Newton Friend,¹ where a complete treatment of the general subject will be found. Third, many times opinions are formed and expressed by the casual observer which fail to take into consideration not only the fundamental conditions necessary to accurate comparative work, but also less obvious conditions which make a comparison unreliable. For example, a person may notice the rapid rusting of a cheap grade of steel wire fencing which had originally but a wash of zinc as a substitute for galvanizing, and thus become suspicious of the durability of all steel. Or he may notice holes in a metal roof put up in place of a material known to have lasted a much longer time than the new roof. He concludes that the latter is of less value without having any knowledge of the change of conditions in the locality, class of metal and the thickness of the new roof, nature and thickness of the galvanizing or other protective coating and so forth.

Owing to the proverbial conservatism of New England the introduction of steel pipe has been slower in this territory than in other parts of the country. There is a tendency to pronounce any pipe which withstands corrosion as being wrought iron, while the fact that a pipe corrodes easily is considered by many proof in itself that it is steel.

To determine what the facts actually are in regard to the relative life of service pipes which have been in constant use for a number of years throughout New England, an investigation was undertaken in which it was proposed to seek out instances where steel and iron pipe had been used together in the same system; and further, where the two kinds of metal were separated in this system only by a coupling. Any influence which the coupling might have would be present equally with the iron and with the steel, while conditions of oxygen concentration, temperature, pressure, flow of water or steam, etc., would be as nearly identical for the two kinds of metal as it is possible to obtain. It was intended also to collect in this way material of known resistance or tendency to corrosion, in order to further test the applicability or truthfulness of the so-called "acid corrosion test." While the majority of the pipe so obtained was from hot and cold water feed systems, enough were selected from live and exhaust steam lines, hot water and steam heating systems, etc., to make the conclusions drawn of general application. The investigation was necessarily tedious in that each pipe had to be examined to determine whether it was of iron or steel, and many instances were found that would have served our purpose well, but where it was impossible to remove the pipes from the system. The pipes were sent to the laboratory where they were each split lengthwise into two halves and carefully cleaned from scale and rust by soaking in an ammonium citrate solution, with an occasional brushing. In this way the scale

¹ "The Corrosion of Iron and Steel," by J. Newton Friend. Longmans, Green & Co., New York.

and rust were removed without dissolving any of the iron. An estimation of the extent of corrosion was made by measuring with a micrometer gauge the ten deepest pits per unit distance of length. I give the measurement of those samples of pipe which were rusted to practical destruction, that is, where either the iron or the steel showed pits over one tenth of an inch in depth.

Depth of pitting.

Sample number.	Depth of pitting.		
	Mean of ten deepest pits. Inches.	Deepest pit. Inches.	Least of ten deepest pits. Inches.
W-10—Iron	0.102	0.134	0.085
W-11—Steel	0.075	0.095	0.067
W-22—Iron	0.114	0.160	0.068
W-23—Steel	0.075	0.107	0.042
W-24—Iron	0.139	0.168	0.109
W-25—Steel	0.140	0.204	0.076
X-15—Iron	0.077	0.101	0.069
X-16—Steel	0.040	0.047	0.034
X-29—Iron	0.042	0.060	0.030
X-30—Steel	0.066	0.103	0.042
X-49—Iron	0.077	0.113	0.049
X-50—Steel	0.071	0.122	0.040
X-57—Iron	0.038	0.110	0.012
X-58—Steel	0.026	0.053	0.012
X-69—Iron	0.113	0.159	0.032
X-70—Steel	0.119	0.177	0.095
X-71—Iron	0.115	0.169	0.063
X-72—Steel	0.075	0.156	0.042

The results are a splendid vindication, also, of the principle that if oxygen be excluded from water, no corrosion will take place. When the water in the lines examined was stagnant, as in fire sprinkler system for buildings, or in lines where the water was circulated over and over again without exposure to the air, as in some hot water heating systems, no corrosion was to be observed. On the other hand where fresh water was constantly added to the system, and heated within the system, corrosion was very rapid and in some cases excessive.

We were able to get sixty-four comparisons of iron and steel where the history of the installation was known. The results are as follows:

Comparison where iron was found more corroded than steel.....	20
Comparison where steel was found more corroded than iron.....	18
Comparison where steel and iron were equally corroded.....	9
Comparison where corrosion was negligible.....	17

These results again demonstrate that taken on the average there is no difference in the corrosion of iron and steel pipe. Conversations held with the engineers in charge of plants during this investigation confirm the statement already made that a pipe is frequently called steel when corrosion is found to be excessive, while it is set down as iron if it rusts but little.

In order to get some measurement of the influence of oxygen in the water of the modern hot water supply system a relatively large scale experiment was carried on at the plant of the Walworth Mfg Co. in South Boston. Two coils made up from pieces taken from the same length of pipe were each fed with water from the same source at the same temperature. In one case the water was heated to 85° C. in an open

tank, while in the other the water was heated to the same temperature in a closed tank. The feed water contained on the average 5.85 cc. of oxygen per liter, and passed through each coil at the rate of one half gallon per minute. After running 1750 hours the coil fed with water heated in an open tank had lost 22 grams, while the coil fed with water heated in a closed tank had lost 155 grams. In neither case was the oxygen completely removed; if the water in the open tank had been gently *boiled*, corrosion in the coil fed with this water would have been entirely prevented.

In order to show what relation may exist between the so-called acid corrosion test and the real corrosion as found in service, eleven pairs of iron and steel were selected and subjected to 20 per cent. sulfuric acid for four hours at room temperature. Four pairs were selected in which the steel was decidedly better than the iron in service, four in which the iron had shown decidedly better than the steel, and three in which there was no difference between the two metals.

In six instances the relative corrosion as shown by the sulfuric acid test corresponded with the corrosion as found in service. In five instances corrosion as shown by the acid test was exactly contrary to that found in service. Although the greatest care was taken to have the specimens of the same size, cleaned in the same way, and in the same physical condition, the results show that no reliance can be placed in this accelerated acid test, but that it may be entirely erroneous and very misleading. Not only did the acid test not agree with service test when steel was compared with iron, but the steels failed to agree among themselves, and the irons showed no agreement when considered by themselves.

I wish to express my appreciation of the work of Messrs. James J. Wilson and Francis Worcester, assistants in the laboratory, without whose aid this investigation could not have been made.

RESEARCH LABORATORY OF APPLIED CHEMISTRY,
MASS. INST. OF TECHNOLOGY,
BOSTON, 1912.

DESCRIPTION OF THE EXPLOSION TEST AT THE EXPERIMENTAL MINE OF THE UNITED STATES BUREAU OF MINES, FEBRUARY 24, 1912.¹

By GEORGE S. RICE.

Received March 11, 1912.

On the morning of the 24th of February, 1912, there was conducted at the Experimental Mine, near Bruceton, Pa., the 14th and last of the first series of such explosion tests.

The mine consists of a pair of entries in the Pittsburgh seam, about 750 feet long from the outcrop opening to the face. These entries are connected by three cross-cuts; in the first of these from the mine mouth, was a reinforced concrete stopping, the behavior of which in the explosion was one of the points of interest, since the stopping was built of a known strength, 100 to 150 pounds to the square inch. The second cross-cut had a 15-foot sand bag stopping supported by a timber frame. The third cross-cut

was allowed to remain open so that the ventilating currents could pass through it. The fan was located at the end of an external 120-foot steel galley leading into a passageway lined with reinforced concrete which in turn entered the air course of the pair of entries above described. The fan at the time of the explosion acted as a blowing-fan: the air entering the air course passed to the last cross-cut, then into the main entry, thence returning on the main entry to the outside. The outer 200 feet of this entry is lined with reinforced concrete. For recording pressures, the velocity of the pressure wave, and the velocity of the flame wave, instruments were placed at stations 100 feet apart. The wiring connecting the stations is intricate, there being 34 separate wires in the cable which led from the face of the mine through the different stations to the outside, and thence to the bomb-proof observatory which contains some of the recording instruments. This is also the control or firing station. The entries or passageways are about 7 feet high and 8 to 9 feet wide, the usual dimensions in mines in the Pittsburgh bed.

The principal object was to determine how and why coal dust explodes, in order that means for prevention and limitation might be suggested from the experiments and tried out subsequently. For the purpose of understanding the nature of coal dust explosions and for the comparison of different remedies, instruments were provided, as without instruments it would not be known whether the checking or prevention of the dust explosion was a matter of accident or otherwise. In order to obtain consistent results, the coal dust employed in the tests had to be of known kind and size and distributed evenly. To accomplish such distribution, shelving three inches wide was placed along the walls with the coal dust on these. In the test of February 24th, one pound per linear foot of entry was used on the shelving with one pound per linear foot on the floor of the entry. In the previous public demonstration and explosion on October 31, 1911, one pound per linear foot had been used on shelves, but none on the floor. In other words, in the explosion of February 24th, double the quantity was used.

The real consideration in loading was the amount per cubic foot of space, since a limiting influence in any explosion is the quantity of oxygen available for the combustion. If the coal dust is completely burned, only 12/100ths of an ounce is required to use up all the oxygen in a cubic foot of air. As a matter of fact, there is rarely complete combustion; usually there is a considerable amount of fixed carbon not consumed. The gases distilled from the coal are thus chiefly brought into play. When the loading is two pounds per linear foot there is about 64/100ths of an ounce of dust per cubic foot of air or five times that which is theoretically necessary to use up all of the oxygen.

The coal dust loading in the main entry extended from the mouth to the face. The loading was also continued through the last cross-cut into the air course and out same for 200 feet. At this point there was

¹ Printed by permission of the Director, United States Bureau of Mines.

a Taffanel stone dust barrier, consisting of a group of 13 shelves about five feet apart center to center, placed across the passageway about five feet above the track. Each shelf consisted of two one-inch boards, 10 inches wide, making the total width of a shelf 20 inches, on which finely ground stone dust was placed: there were about $2\frac{1}{2}$ cubic feet, or about 200 pounds, of stone dust on each shelf. This style of barrier has been particularly developed by M. Taffanel at the Liévin, France, testing station, where, in an external gallery, it has proved very effectual in arresting coal dust explosions. The system has been generally adopted in French coal mines.

Beyond the barrier of stone dust there were 50 feet more of coal dust loading. Small tufts of loose guncotton (loose guncotton is inflammable but not explosive) were placed at intervals throughout the mine, in addition to the flame circuit breakers in the main entry, to determine the extent of the flame.

The initiation of the explosion was at the face of the main entry, by a single blown-out shot of three pounds of black powder stemmed with 5 inches of fire-clay. In order to insure that the shot would blow out, the hole was cased with $1\frac{1}{2}$ inch pipe. A similar hole was prepared in case of failure of the first, but was not fired. The shot was ignited by an electric detonator connected through the cable with the observatory. The wires of the flame circuit breaker were placed immediately in front of the hole so as to obtain a record of the moment the flame started from the cannon.

EXPLOSION AND THE RESULTS.

After the party of mine inspectors and others interested in mining had inspected the mine, Mining Engineer L. M. Jones and Mine Foreman Howarth connected up the fire lines, no one else being in the mine. Then having spread some coal dust in front of the holes, they came out of the mine. A locked switch at the outside and a similar locked switch in the observatory were thrown in to complete the firing line. All was then ready for pressing the button. The visitors having assembled at vantage points where they would be safe, the boiler plant whistle was blown and three minutes afterward the button was pressed. Two and a half seconds later, as shown by the records, a black cloud of dust shot out of the main entrance accompanied by a tongue of flame and a violent detonation occurred. The smoke from the entrance increased in volume for a few seconds and then a reverse current, caused by a vacuum in the mine, set in and the smoke did not again come out for a number of minutes after the ventilation had been reestablished by hanging brattices across the air course and over the conduit openings. The flame did not issue from the air course and a later investigation of the tufts of guncotton showed that it had not come closer than 60 to 75 feet from the mouth. It seems probable that the non-appearance of the flame at the mouth of the air course or any extreme violence, was due in part at least to the Taffanel stone dust barrier. This was smashed to pieces, as would be expected in opposing so violent an explosion, but

this effect is what was desired as it threw into the explosive wave a large mass of finely divided dust which was intended to cool the flame. From the point where the explosion originated in the face of the main entry through the last cross-cut and through the barrier, a distance of 340 feet, the explosive force was sufficient to throw down the upper two feet of the sand-bag stopping in the second cross-cut. The flame penetrated through the barrier. In spite of the considerable violence shown at the barrier, there was practically no violence shown beyond it. It may be well to state here that some previous tests were made in which the barrier was closer to the origin of the explosion and in these cases the flame was always extinguished while passing through the barrier.

THE EFFECTS OF THE EXPLOSION IN THE MAIN ENTRY.

The shot which caused the ignition had blown out a small crater in the coal in spite of the pipe linings which had been broken open; except within a few feet of the shot there was little violence for a considerable distance, but there was much evidence of flame in the last cross-cut. At the second cross-cut in which there was the second sand-bag stopping, the upper two feet were thrown down, the first part of the bags towards the air course, and the upper part toward the main entry. Probably the first effect was from the explosion in the main entry and the second was due to the explosive wave in the air course, which, with the added length of the last cross-cut, had a longer distance to travel. Beyond the middle cross-cut, the shelving, made of 3×4 inch hardwood timber, in many places was displaced and in some places broken. The track ballast in some places was lifted, evidently by the depressive wave, or vacuum, following the explosive wave. The violence increased in going out, in the neighborhood of station 150, the concrete arches having been lifted in several places, breaking the face of the concrete and exposing the arched iron reinforcement ($\frac{3}{4}$ -inch square rods). At this station the manometer indicated a pressure of over 110 pounds per square inch—this pressure being measured at right angles to the explosive waves would therefore be considered static pressure. The pressure at the station fifty feet from the mouth was less than that at station 150. Outside the mine the gates were recessed behind concrete buttresses and these were carried bodily away. Fifty feet outside the entrance there had been an empty car. This was thrown to the opposite side of the ravine, a distance of 200 feet.

The pressure circuit breakers and the flame circuit breakers indicated that the explosion traveled quite slowly at first but rapidly increased in velocity going outward, showing a speed of over 2083 feet per second obtained between stations 450 and 350 and also between stations 350 and 250. Beyond this the circuit breakers failed to work. An interesting fact in connection with the recording of the velocities of the advance wave and the flame was that the flame, while much behind the advance wave at the start, caught up rapidly with it as the entrance was reached.

CONCLUSIONS.

As a demonstration the experiment was less spectacular than that of October 31, 1911, as on that occasion the flame burst from all the openings, whereas in the experiment of February 24th the flame appeared only at the main entrance. Also, it did not spread so widely as in the previous demonstration. There was a quick flash projected through the center of the cloud of dust. In the explosion of October 31, 1911, the manometers did not have springs strong enough to indicate the pressures, which difficulty had been removed on February 24th, so that a pressure of over 110 pounds was shown by the manometer at station 150. The detailed information obtained from the various readings will appear in a publication of the bureau on the work of the Experimental Mine.

As regards the efficiency of the Taffanel barrier the evidence is not conclusive. The flame was not immediately extinguished by the barrier, but traveled 200 feet farther; nevertheless, without the barrier, it is probable that, with the large amount of dust being carried from the loading farther in, the flame would have gone to the entrance. This is the more probable since the violence shown by the smashing of the barrier indicates that the explosion had attained considerable violence at this stage. It is intended to make systematic tests of such barriers in the next series of tests.

THE EXPANSION COEFFICIENT OF GRAPHITE.

By ARTHUR L. DAY AND ROBERT B. SOSMAN.

Received March 9, 1912.

As a basis for the measurement of the specific volumes of silicates at high temperatures we found it necessary to know approximately the expansion coefficient of Acheson artificial graphite up to 1600°.

1500°; the results obtained form the material of the present paper.

The expansion was measured directly on a bar 3 mm. by 5 mm., by 700 mm. long, with a comparator which has been used in this laboratory for measuring the expansion coefficients of alloys of platinum with rhodium and iridium.¹ The comparator consists of two micrometer microscopes held at a fixed distance of 500 mm. apart by invar bars; upon this system is mounted another invar bar by which any changes in this fixed distance amounting to 0.001 mm. or more can be detected.

Two points on the graphite bar, 500 mm. apart, were marked by flattened pieces of platinum wire bound around it, each having a fine line cut at the middle of the wire. The bar was heated by sending a heavy current through it, and a uniform temperature along its length was obtained by slightly adjusting its thickness. It was surrounded by a tube of Marquardt porcelain, and this again by a wide glass tube, each free to expand independently of the bar. The space within the tube was kept filled with carbon monoxide. The apparatus is shown in plan and section in Fig. 1.

In the reducing atmosphere a thermoelement could not be used. The temperature was, therefore, found by noting the melting point of small fragments of aluminum (658°), silver (960°), copper (1083°) and the mineral diopside (1391°), lying upon the bar. Intermediate temperatures were read by means of a Holborn-Kurlbaum optical pyrometer, which thus served simply as a device for interpolating between the melting points. It was not necessary to obtain great accuracy in the temperature measurement, as the expansion is small.

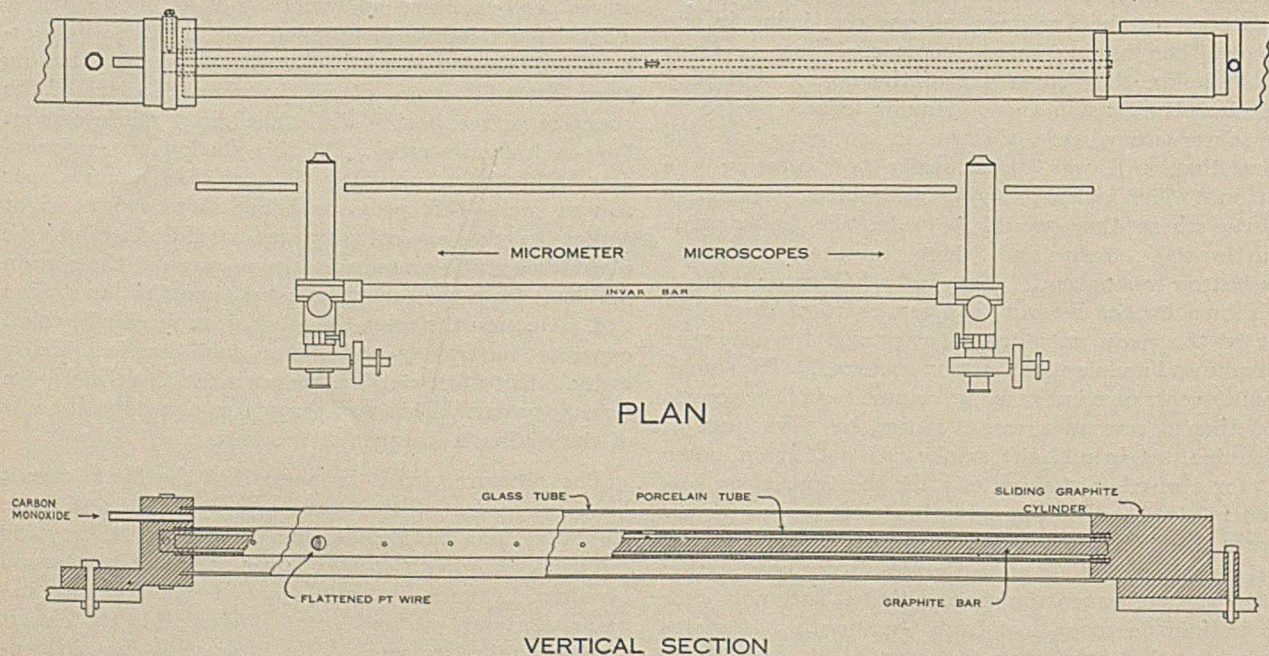


FIG. 1. APPARATUS FOR DETERMINING THE EXPANSION COEFFICIENT OF GRAPHITE.

The published data on graphite are so inconsistent and cover so small a temperature range that we redetermined this constant over the range from 0° to

Below 700° the expansion is so small that we found

¹ Day and Sosman, *Am. J. Sci.*, **26**, 425-436 (1908); **29**, 111-114 (1910); *Carnegie Pub.*, **157**, 27-36, 61-63 (1911).

it necessary, in order to obtain accurate measurements of the coefficient, to use the method which we had previously employed for the platinum alloys: namely, to heat the bar in a narrow tubular resistance furnace, and read the expansion on a series of very fine lines 0.2 mm. apart, drawn with a dividing engine. These lines were drawn upon the polished ends of small plugs of silver or platinum set into the graphite at points 500 mm. apart. Up to red heat (700°) the bar could be protected fairly well against oxidation, and contamination of the thermoelement could be prevented by enclosing it in Jena glass capillaries.

Table I contains the data. In the first two columns are given the date and the temperature at the time of the measurement. In the third column is the initial

mm.; and the fifth, the mean linear expansion coefficient ($\Delta l/l_0 t$) from 0° to t° . The coefficient is plotted against temperature centigrade in the curve of Fig. 2.

The coefficient is seen to be very small, though increasing rapidly with rising temperature. The total expansion up to 1000° is only about one-fifth of that of platinum. Two samples of graphite were used, but no systematic difference exceeding the error of measurement was observed.

The greatest uncertainty arises from permanent changes in length of the bar during heating. In every case where the change was measurable, the bar was longer than before heating, as if this somewhat porous material had failed, after expanding, to entirely pull itself together again. The largest change noted was 0.046

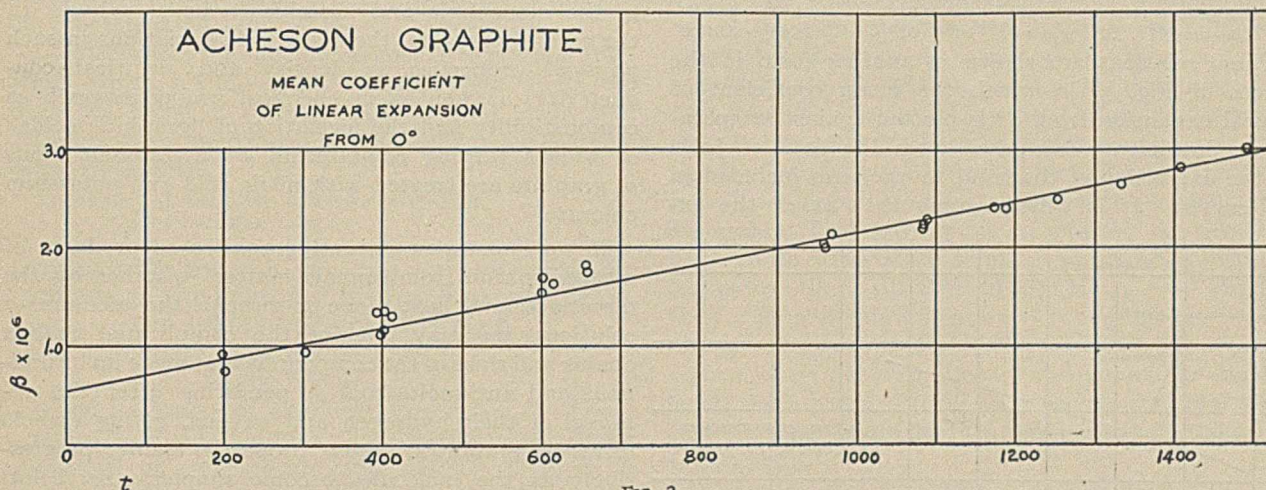


FIG. 2.

distance at 0°, between two reference lines on the silver or platinum markers on the graphite bar, in mm.; this distance was frequently changed slightly by resetting the silver or platinum markers. The fourth column contains the expansion from 0°, in

mm., which is 0.009 per cent. on the total length, and therefore quite negligible when the total length or volume is being considered.

Within the limits of error, the results may be expressed by the formula

$$10^6 \beta = 0.55 + 0.0016t$$

in which β is the mean linear coefficient ($\frac{\Delta l}{l_0 t}$) from 0°. The "true coefficient" α , or rate of expansion ($\frac{1}{l_0} \cdot \frac{dl}{dt}$) at any temperature t would be therefore:

$$10^6 \alpha = 0.55 + 0.0032t.$$

If this equation continues to hold below 0°, the true coefficient would become zero at about -170° ; in other words this would be the temperature of maximum density. According to Fizeau's measurements, diamond has a similar point of maximum density or zero expansion at -42° .

The published figures on the expansion coefficient of graphite vary widely. We do not know of any previous determinations on Acheson graphite, nor have the manufacturers a record of any. The following data have been obtained on natural graphites:

Date.	t .	l_0 .	Expansion from 0° to t° .	Mean linear expansion coefficient $\times 10^6$.
I. Self-heating Bar.				
2 Dec., 1910.	658°	499.94	0.60	1.82
"	658		0.58	1.77
5 Dec.	970	500.16	1.04	2.14
"	1085		1.21	2.23
6 Dec.	960	500.11	0.98	2.05
"	1085		1.19	2.20
"	1175		1.42	2.41
"	1255		1.56	2.49
7 Dec.	960	500.13	0.97	2.02
"	1090		1.25	2.29
"	1190		1.42	2.40
"	1335		1.77	2.65
"	1410		1.98	2.82
"	1495		2.25	3.02
II. Platinum Resistance Furnace.				
6 Jan., 1912.	198	500.974	0.090	0.91
"	396		0.265	1.34
8 Jan.	202	501.020	0.075	0.74
"	401		0.228	1.13
10 Jan.	304	501.016	0.145	0.95
23 Jan.	401	501.433	0.229	1.14
"	602		0.467	1.55
31 Jan.	403	501.279	0.274	1.35
"	604		0.514	1.69
12 Feb.	413	501.291	0.272	1.31
"	616		0.506	1.64

Source.	Observer.	Range.	$\beta \times 10^6$.
"Batougol" (Siberian) graphite.....	Fizeau ¹	10° to 85°	7.45 + 0.0051t
"Siberian" graphite....	Muraoka ²		3.8
"Cumberland" graphite Dewar ³		At -190° (from 17°)	24.4

¹ *Compt. rend.*, 68, 1125-1131 (1869). *Pogg. Ann.*, 138, 26-31 (1869). Fizeau's values are for α , the true coefficient; we have calculated the mean coefficient from 0° from the original values.

² *Ann. Physik*, 13, 307-318 (1881).

³ *Proc. Roy. Soc. London*, 70, 237-246 (1901).

For pencil-graphite, Muraoka found the value 0.95×10^{-6} . But as this is a mixture containing only 52 per cent. of graphite, this value is hardly comparable with data on pure materials.

The wide range of these data is striking, especially when taken in comparison with the expansion coefficients of other forms of carbon, and of carbon compounds. It will be seen from the following table that from the expansion coefficient of diamond to that of anthracite we have an increase of forty-fold.

Form.	Observer.	Range.	$\beta \times 10^6$.
Diamond.....	Fizeau ¹	10° to 85°	0.60 + 0.0072 <i>t</i>
Arc carbons (of coke)....	Muraoka		0.32
Arc carbons.....	Muraoka		1.5
Arc carbons.....	Muraoka		2.05
Arc carbons.....	Muraoka		3.0
Gas carbon (retorts).....	Fizeau ²	10° to 85°	4.96 + 0.0055 <i>t</i>
Anthracite (Pennsylvania)	Fizeau ²	10° to 85°	24.02 — 0.0408 <i>t</i>
Coal (Charleroy).....	Fizeau ²	10° to 85°	26.63 + 0.0148 <i>t</i>

These relations are shown in another form in the curves of Fig. 3, in which the mean coefficient of cubical expansion from 0° is plotted against temperature. Coefficients calculated from the data of Joly³ on the expansion of diamond to 750° are included in the curves. It is worth noting that at 0° the ex-

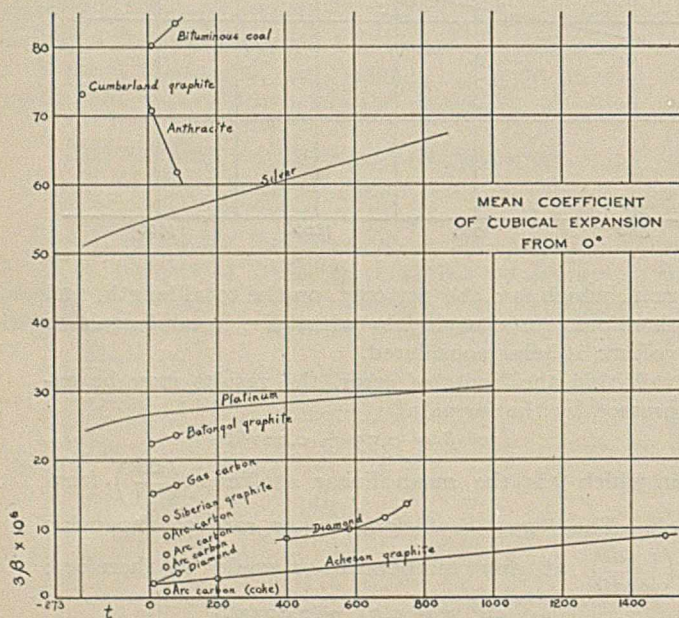


FIG. 3.

pansion coefficient of Acheson graphite and of Fizeau's diamond are practically the same.

A rough parallelism is immediately evident between the temperatures of formation and the expansion coefficients of the different varieties of carbon in the two tables above. The highest coefficient is possessed by bituminous coal, which is followed closely by anthracite. The Cumberland (Borrowdale, England) graphite investigated by Dewar stands next in order, and very near anthracite. This graphite has been formed in company with intrusions of igneous rock into clay-slates containing organic matter. The purer and better crystallized Batougol graphite, with a lower coefficient, occurs in veins in granite and syenite.⁴

Various samples of arc light and retort carbon, all of which probably have been heated in the process of manufacture to a higher temperature than any of the natural graphites, stand next in the order of decreasing expansion. Lowest of all (excepting one sample of arc carbon made of coke) come diamond and Acheson artificial graphite. The formation temperature of diamond is unknown. The artificial graphite is made by heating anthracite, petroleum coke, etc., to a temperature above 2200°.¹

The view has been repeatedly expressed, by Moissan,² Luzi,³ and others, that none of the three forms of carbon as at present distinguished, not even diamond, can be looked upon as a substance of fixed and reproducible properties, comparable for instance to the monoclinic and rhombic forms of sulfur. In the case of graphite, there are wide variations in such physical properties as density and electrical conductivity, as well as in chemical properties such as combustibility and the formation of "graphitic acids" of widely varying composition when different kinds of graphite are treated with nitric acid and potassium chlorate.

If we look upon natural graphites as products of metamorphism from organic matter, whether by the direct action of heat alone or through the medium of solutions, we may imagine the complicated carbon chains and rings of the compounds that make up bituminous and anthracite coal as persisting after the removal of their hydrogen and oxygen, giving a whole series of "graphites" whose properties change progressively as the molecules become simpler. Berthelot⁴ held this view as regards amorphous carbon.

Arsem,⁵ as a result of his studies on the graphitization of different forms of "amorphous" carbon, and the densities of the resulting products, reaches this tentative conclusion: "Graphite in the most restricted sense of the term is an allotropic form of carbon having a definite and perhaps not very complex molecular configuration... When an organic compound is decomposed, there results a mixture of substances constantly increasing in complexity until finally carbon is obtained. This carbon need not be regarded as a simple substance, but may be considered to be a mixture of many varieties of carbon each with a different number and arrangement of atoms in the molecule... In a given sample of amorphous carbon, some of the molecules will be capable of easily undergoing rearrangement under the influence of heat to form graphite molecules, while others will not, and the proportion of molecules capable of such change will determine the character of the final product."

Arsem's definition is as follows: "Graphite is that allotropic form of carbon having a specific gravity of 2.25-2.26." This is the specific gravity of Acheson graphite, and all the graphites made by Arsem were equal to or less than this. "Those varieties of carbon which have some of the physical properties of graphite,

¹ Gillet, *Jour. Phys. Chem.*, **15**, 302 (1911).

² *Chimie Minérale*, **1905**, II, 222.

³ Donath, "Der Graphit," **1904**, 11.

⁴ *Ann. chim. phys.*, [4] **9**, 475 (1866).

⁵ *THIS JOURNAL*, **3**, 799-804 (1911).

¹ *Pogg. Ann.*, **128**, 583 (1866).

² *Compt. rend.*, **68**, 1125-1131 (1869).

³ *Trans. Dublin Soc.*, [2] **6**, 283-304 (1897).

⁴ Donath, "Der Graphit," **1904**.

such as color, softness, and streak, but a lower specific gravity, may perhaps be regarded as impure graphites; that is to say, mixtures of graphite with other forms of carbon."

Against the view set down in preceding paragraphs, that so-called graphite is not a simple and reproducible substance, we have the recent work of LeChatelier and Wologdine.¹ They found that the density of Acheson graphite and of five natural graphites, after purification to remove ash and compression to drive out air, was 2.255, and conclude that this property defines graphite as a simple and reproducible substance. But it should be noted that their process of purification involved fusion at a red heat with potash, a treatment which might produce profound changes in the graphite itself.

In conclusion, the wide divergence in expansion coefficient which we have noted above seems quite beyond the range of possible experimental error, and indicates some fundamental difference between these various graphites.

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION,
WASHINGTON, MAR., 1912.

A VOLUMETRIC METHOD FOR THE DETERMINATION OF THORIUM IN THE PRESENCE OF OTHER RARE EARTHS. THE ANALYSIS OF MONAZITE SAND.

By F. J. METZGER AND F. W. ZONS.

Received February 13, 1912.

When an excess of ammonium molybdate solution is added to a solution of a thorium salt under proper conditions of temperature and acidity, thorium is quantitatively precipitated as molybdate. Other rare earths, such as cerium, lanthanum, neodymium, praseodymium, erbium, yttrium, gadolinium, etc., give no precipitation whatever under similar conditions.

The above facts, observed by one of us some years ago, forms the basis for the method described in this paper.

The thorium molybdate precipitate is somewhat gelatinous in character, pale yellow in color, and settles very slowly. In our earlier experiments an attempt was made to filter off the precipitated thorium and make the determination gravimetrically, but owing to the slimy nature of the precipitate, filtration and washing were impossible.

The usual indicators for molybdenum were tried with the hope that a direct titration of the thorium could be made, but without success.

Cazeneuve² found diphenyl carbazide to be a sensitive reagent for certain metallic salts, as those of copper, mercury, iron and also for chromates. Lecoq³ used an alcoholic solution of diphenyl carbazide as a test for molybdenum. A pink coloration is produced, and the author states that the test is more sensitive after the solution of diphenyl carbazide has been allowed to stand for some time. In order to test the applicability of this indicator, a number of titrations of pure thorium nitrate solution were made, and the results obtained were concordant. The indicator is used "outside" on a white indented tile, the end of

the titration being marked by the appearance of a pink coloration which lasts about fifteen seconds. Some experience is required to identify the end point. This is gained in standardizing the ammonium molybdate against a standard thorium nitrate solution. *It is necessary to use a solution of the indicator at least two weeks old*, as the freshly prepared solution requires a considerable excess of molybdenum to produce a pink coloration. The titration is made at room temperature, in the presence of acetic acid.

The solutions used in the experimental part of the work were as follows: *Thorium nitrate*—A solution of pure thorium nitrate accurately standardized by precipitating as oxalate, igniting and weighing as oxide. *Potassium permanganate*—An approximately 0.1 N solution standardized against specially prepared Mohr's salt; 1 cc. = 0.005835 Fe. *Ammonium molybdate*—Approximately 20 grams ammonium molybdate per liter. In order that the thorium-molybdenum ratio in the precipitate might be determined, this solution was carefully standardized by acidifying, reducing in a Jones reductor and titrating with permanganate as usual. The average of a number of titrations gave 10 cc. molybdate solution = 28.2 cc. KMnO₄. Assuming the reduction to be MoO₃ → Mo₂₄O₃₇, then 1 cc. molybdate solution = 0.0098136 Mo. *Indicator*—0.5 gram of diphenyl carbazide¹ dissolved in 200 cc. of 95 per cent. alcohol and allowed to stand at least two weeks before using. The solution when ready for use should be yellowish in color, but show no pink tinge.

In order to obtain uniformity in acidity of the solutions for titration and to have the conditions analogous to those obtaining in the analysis of a monazite sand, a number of determinations were made as follows:

A known amount of thorium solution, or thorium solution with the addition of other rare earths, was placed in a casserole and evaporated to dryness on a water bath. To the dry residue 4 cc. of glacial acetic acid were added, then 300 cc. of water. When the salts were dissolved, the cold solution was titrated with ammonium molybdate. The molybdate solution should be added a few tenths of a cc. at a time, with vigorous stirring after each addition, finally finishing drop by drop. The end point is reached when a drop of the solution produces the previously described pink coloration when brought in contact with a few drops of indicator on a white tile. After a little experience the end point can be determined with great accuracy. The following table shows the results obtained:

¹ A convenient and satisfactory method for the preparation of this compound is as follows: Add 23 grams of phenyl hydrazine to 7 grams of urea in a flask, and heat in an oil bath at 160–170° for six hours, using a reflux air condenser. Allow to cool, add 50 cc. ethyl ether, heat on a hot plate for one hour, decant and add 50 cc. ethyl ether, heating for two hours longer; a white precipitate is obtained, the residue of reagents going into solution in the ether. Decant the ether, dissolve the precipitate of impure diphenyl carbazide in alcohol and reprecipitate by pouring into excess of water; decant the water, redissolve the precipitate in alcohol and pour again into excess of water. Filter on a Büchner funnel, wash and dry at 105°. Yield, 14.3 grams diphenyl carbazide. M. p. 150°–151°. *The diphenyl carbazide is white when first precipitated but in time turns brownish yellow. A trace of impurity causes it to turn pink; hence all vessels, dropping tubes, etc., must be scrupulously clean. The indicator, when on the white tile, should be yellowish or brownish yellow.*

¹ *Compt. rend.*, 146, 49–53 (1908).

² *Ibid.*, 131, 346 (1900).

³ *Jour. Chem. Soc.*, 86², 369 (1904).

No.	ThO ₂ Gram.	Other earths present.	Molybdate solution. Cc.
1.....	0.0500	0	3.65
2.....	0.0500	0	3.65
3.....	0.0852	0	6.4
4.....	0.0852	0	6.4
5.....	0.0852	0	6.5
6.....	0.1000	0	7.35
7.....	0.1000	0	7.4
8.....	0.0500	0.1 Nd ₂ O ₃	3.9
9.....	0.0500	0.1 Pr ₂ O ₃	3.9
10.....	0.0500	0.1 La ₂ O ₃	3.9
11.....	0.0852	0.1 La ₂ O ₃	7.1
12.....	0.0852	0.1 La ₂ O ₃	7.1
13.....	0.0852	0.1 Pr ₂ O ₃	7.2
14.....	0.0852	0.1 CeO ₂	7.1
15.....	0.0852	0.1 gram each of Ce, La, Pr, Nd	7.1
16.....	0.0852	0.1 gram each of Ce, La, Pr, Nd	7.2
17.....	0.0852	0.1 gram each of Y, Gd, Er	7.2
18.....	0.0852	0.1 CeO ₂	7.1
19.....	0.0852	0.1 "	7.1
20.....	0.0852	0.1 "	7.1
21.....	0.0852	0.1 "	7.1
22.....	0.0852	0.2 "	7.1
23.....	0.0852	0.3 "	7.2
24.....	0.0852	0.3 "	7.1
25.....	0.0852	0.3 "	7.1
26.....	0.0852	0.6 "	7.1
27.....	0.0852	0.6 "	7.1
28.....	0.0852	0.6 "	7.2
29.....	0.0852	0.6 "	7.2
30.....	0.0852	4.26 "	7.1
31.....	0.0852	4.26 "	7.1

In titrations Nos. 11 to 31, the total dilution varied between 150 cc. and 300 cc., and one gram of sodium acetate was added to each to counteract any possible mineral acid present. These results show that although the consumption of molybdate solution was greater when other rare earths were present, the volume of molybdate was the same whether the added rare earth was small or large in amount. From this it was assumed that the concentration of acetic acid was insufficient to entirely prevent the precipitation of rare earths other than thorium.

Another set of titrations with increased acidity resulted as follows:

No.	Dilu- tion.		Acetic acid (glacial).		Other earths.	Molyb- date.
	Cc.	Sodium acetate. Gram.	Cc.	ThO ₂ . Gram.		
32.....	300	1	10	0.0852	0	6.4
33.....	300	1	10	0.0852	0	6.5
34.....	300	1	20	0.0852	0	6.4
35.....	300	1	20	0.0852	0	6.4
36.....	300	1	20	0.0852	0.1 gram each	6.45
37.....	300	1	20	0.0852	of Pr, La, Nd, Gd	6.4

The values here obtained are in satisfactory agreement with those obtained with thorium alone, the increased acidity preventing interference by the other rare earths.

Composition of Precipitate.—Taking the value of the KMnO₄ already given (1 cc. = 0.005835 Fe) and its equivalent in terms of molybdate solution (28.2 cc. KMnO₄ = 10 cc. molybdate) then 1 cc. molybdate = 0.0098136 Mo. The average of the eleven titrations of thorium alone (Nos. 1-7 and 32-35) gives 0.0815 ThO₂ = 6.095 cc. molybdate, or a ratio Th : Mo = 1 : 2.017. Similarly, the average of titrations 36

and 37 with impurity present gives Th : Mo = 1 : 2.03. It is therefore probable that the precipitate is a normal thorium molybdate.

Analysis of Monazite Sand.—In order to test the accuracy of the method for the determination of thorium in monazite sand, samples of North Carolina and Brazil sands which had been analyzed by the fumaric acid method, the thiosulphate-ammonium oxalate method and the metanitrobenzoic acid method² were analyzed.

The volumetric method is carried out as follows: To one gram of the powdered sand in a porcelain crucible is added 10-15 cc. of concentrated sulphuric acid. After several hours heating, the crucible is cooled and the contents transferred, a little at a time and with constant stirring, to about 700 cc. water which has been cooled to near 0°. After standing several hours (over night if convenient) to insure complete solution of the sulphates, the solution is filtered and the residue washed thoroughly with cold water. The filtrate is nearly neutralized with dilute ammonia, 50 cc. of a cold saturated solution of oxalic acid added, and allowed to stand over night. The oxalates are filtered and washed with a dilute oxalic acid solution. When thoroughly washed, transfer precipitate and paper to a beaker, add 20-25 cc. of strong potassium hydroxide solution and heat to boiling. Dilute, filter and wash with hot water. Dissolve the precipitate of rare earth hydroxides off the filter by means of hot, dilute nitric acid. Evaporate to dryness on a water bath. Add a few cubic centimeters of water and again evaporate to dryness to remove free acid. To the dry residue add 20 cc. glacial acetic acid, dilute with 300 cc. water, add one gram sodium acetate and stir until dissolved. Titrate at room temperature with standard ammonium molybdate solution as already described.

The following results were obtained:

	Percentage ThO ₂ .				
	Volumetric method.	Metanitrobenzoic acid method. ²	Fumaric acid method.	Thiosulphate ammonium oxalate method.	
No. 3 Brazil.....	4.80	4.76	4.85	4.90	
	4.80	4.85			
	4.98	4.99			
	4.99				
	4.99				
	4.99				
	5.05				
	5.05				
	5.05				
	Average.....	4.97	4.87	4.85	4.90
	No. 363 Brazil concentrate.....	5.58	5.60	5.70	5.63
5.65		5.65			
5.65		5.67			
5.65		5.70			
5.65		5.73			
5.72					
5.72					
Average.....	5.66	5.67	5.70	5.63	

¹ For a description of these methods, the reader is referred to the original articles: F. J. Meazger, *Jour. Amer. Chem. Soc.*, 24, 901. A. C. Neish, *Ibid.*, 26, 780.

² Analyses by this method were made by Dr. A. C. Neish.

	Percentage ThO ₂			
	Volumetric method.	Metanitrobenzoic acid method.	Fumaric acid method.	Thiosulphate ammonium oxalate method.
No. 625 Brazil.....	4.85 4.92 4.92 4.98 5.1 5.3 ¹		4.88 4.89	
Average (omitting last).....	4.95			

The following were analyzed by the volumetric method but not checked by other methods:

No. 626 North Carolina.	No. 631 North Carolina.
4.84	5.11
4.84	5.11

CONCLUSIONS.

1. At room temperature thorium is precipitated quantitatively from a cold acetic acid solution (20 cc. glacial acetic acid and 300 cc. water) by means of ammonium molybdate.

2. Other rare earths found in monazite sand are not precipitated under the conditions defined in "I."

3. The ratio of thorium to molybdenum (1 : 2.017 and 1 : 2.03) indicates that the precipitate is a normal thorium molybdate.

4. By observing proper conditions of acidity, thorium may be accurately titrated by means of ammonium molybdate. Other rare earths have no effect on this titration.

CONTRIBUTION No. 207, HAVEMEYER LABORATORIES,
COLUMBIA UNIVERSITY.

THE RESENES OF RESINS AND OLEORESINS.

By CHAS. H. HERTY AND W. S. DICKSON.

Received February 1, 1912.

The oleoresinous exudate of pine trees, commonly called "crude turpentine," consists of a mixture of a volatile oil, acids and unsaponifiable matter. On distillation with steam the volatile oil, "spirits of turpentine," passes off; the residual resin, freed from excess of water by heating, solidifies on cooling and constitutes commercial "rosin." The name "resene" has been applied by Tschirch² to the non-volatile, unsaponifiable constituent of such resins and oleoresins.

Though the composition of crude turpentine varies considerably in different specimens, an average analysis of specimens collected by the usual commercial methods would show approximately:

	Per cent.
Spirits of turpentine.....	20
Acids.....	74
Resene.....	6

Resenes, according to their origin, show varying physical states, some being colorless solids while many are very viscous liquids, extremely sticky and non-crystallizable. They are composed of carbon, hydrogen and oxygen, but the per cent. of oxygen is usually smaller than in the accompanying acids. Toward reagents they are very resistant, especially

toward alkalies. Although containing oxygen, they show, according to Tschirch,² none of the usual reactions indicating the presence of hydroxyl, carboxyl, aldehyde or ketone oxygen, nor are they ethereal salts or lactones. Tschirch inclines to the view that they belong to the class of oxyterpenes or oxypolyterpenes.

While much work has been done upon the volatile oils and the acids of oleoresins, little attention has been paid to the resenes, except ultimate analyses and approximate statements of the proportion present in isolated specimens studied. In connection with an investigation carried out in this laboratory in collaboration with the United States Forest Service, there remained a large number of specimens of resin from well identified individual trees growing in Florida. It seemed desirable, therefore, to study more closely the question of the proportions of resene in these specimens. The investigation was extended to the resins of conifers growing near this laboratory, and to specimens collected in other countries. Finally the amount of resene was determined in several oleoresins obtained in perfectly fresh condition from individual trees in Florida. These specimens were collected from the two species of pines from which crude turpentine is commercially obtained in this country, *Pinus Palustris*, (Longleaf Pine) and *Pinus Heterophylla* (Cuban or Slash Pine).

The resins were prepared by distilling the oleoresins in a current of steam slightly superheated, the temperature being raised to 140° C. toward the end of the distillation. After complete removal of the volatile oil, the residue was kept at 140° C. in the oil bath surrounding the distillation flask until all water was driven off. The molten resin was then filtered through absorbent cotton and cooled to solidification in glass or iron molds.

The determination of resene in the resins was carried out in the usual manner. The weighed specimen, about two grams, was dissolved in a considerable excess of *N/2* alcoholic potassium hydroxide, allowed to stand at room temperature eighteen hours, diluted with water until separation of the resene began and the solution cleared by the addition of a small quantity of ninety-five per cent. alcohol. This solution was then extracted three times with petroleum ether, boiling below 40°. The combined extracts were shaken out with fifty per cent. alcohol to remove slight amounts of dissolved potassium salts of resin acids. After drawing off the petroleum ether extract into a weighed glass evaporating dish, it was allowed to evaporate spontaneously to constant weight.

In the case of the oleoresins, after spontaneous evaporation of most of the petroleum ether the residue was heated for five hours on a steam bath in order to remove completely the petroleum ether and the volatile oil. Considerable difficulty was experienced at the outset in these evaporations due to the tendency of the material to "crawl" over the rim of the vessel.

¹ The authors are unable to account for this high result.

² Tschirch, "Die Harze und die Harzbehälter," Second edition, p. 1079.

¹ *Loc. cit.*

This was entirely overcome by using a thin coating of vaseline on the rim of the vessel.

The following results were obtained:

TABLE I.—PER CENT. OF RESENE IN RESINS FROM DIFFERENT SPECIES.

Species.	Local name.	Origin.	Per cent. resene.
<i>Pinus Taeda</i>	Loblolly Pine	North Carolina	4.10
Palustris	Longleaf Pine	Florida	5.67
Maritima	Maritime Pine	France	7.37
Heterophylla	Cuban or Slash Pine	Florida	7.38
Serotina	Pond Pine	Florida	7.65
Echinata	Old Field Pine	North Carolina	8.71
Species unknown		Central America	8.94
Sabiniana	Digger Pine	California	9.66
Laricio	Schwarzkiefer	Austria	14.05

In order to test the variation of the amount of resene in trees of the same species two sets of determinations were carried out on trees of different diameters. The results follow:

TABLE II.—PINUS PALUSTRIS (LONGLEAF PINE).

Tree no.	Diameter Per cent. resene	
	(inches).	in resin.
1	7.3	5.26
2	15.0	5.95
3	21.0	9.68
4	13.0	7.45
5	8.7	5.67
6	9.0	5.45
7	13.5	6.22

TABLE III.—PINUS HETEROPHYLLA (CUBAN OR SLASH PINE).

Tree no.	Diameter Per cent. resene	
	(inches).	in resin.
1	7.0	7.87
2	14.5	7.36
3	24.5	7.20
4	12.3	7.25
5	8.2	6.58
6	13.0	7.84
7	9.0	7.00

To determine possible variations in the per cent. of the resene in different seasons of the same year two trees were selected, one each, *Pinus Palustris*, tree No. 2, Table II, and *Pinus Heterophylla*, tree No. 2, Table III. Beginning in the early Spring the oleoresins were collected from these at regular periods of four weeks until the close of the season in the Fall. From the resins prepared from these specimens the following results were obtained:

TABLE IV.

Collection no.	Per cent. resene in resin from	
	<i>Pinus Palustris</i> .	<i>Pinus Heterophylla</i> .
1	5.31	7.36
2	5.44	7.67
3	5.95	7.23
4	6.02	8.17
5	6.09	7.38
6	6.53	7.43
7	5.24	7.77

It is scarcely probable that in the case of *Pinus Palustris* any significance is to be attached to the gradual increase in the per cent. of resene as the season advanced until the last collection.

Further determinations were made of the per cent. of resene in specimens of oleoresin collected with great care in Florida and promptly analyzed. The following results were obtained:

TABLE V.
Per cent. resene in oleoresin of

Tree no.	Per cent. resene in oleoresin of	
	<i>Pinus Palustris</i> .	<i>Pinus Heterophylla</i> .
1	7.10	6.83
2	3.84	6.76
3	7.33	6.96

Finally, a specimen of "scrape" (Gum Thus) was obtained from a Longleaf pine (*Pinus Palustris*). This scrape is the hardened mass which gradually collects on the scarified surface of the tree as a result of the crystallization of the resin acids of the oleo-resin. It receives its name from the fact that at the end of the season it is scraped from the surface of the trees by means of a sharp tool. It contains approximately one-half as much spirits of turpentine as the ordinary oleoresin collected from the receptacles. The resin was prepared from this scrape by distillation with steam as above. On analysis it showed 3.14 per cent. of resene.

In continuation of this work, there is now being carried out in this laboratory an investigation of the composition of the resene of *Pinus Heterophylla*.

UNIVERSITY OF NORTH CAROLINA.

A METHOD OF EXAMINING CHINA WOOD OIL.

By PARKER C. McILHINEY.

Received April 2, 1912.

The examination of china wood oil to determine its quality and to detect the presence of foreign oil presents several difficulties. The iodine figure is not far removed from that of several other oils, the saponification figure is identical with that of many others and although the specific gravity and the refractive index are higher than those of almost any other fatty oil, the difference in these respects from some other oils is not sufficiently great to furnish satisfactory data in all cases.

The most marked characteristic of china wood oil is its property of solidifying readily under the influence of heat or when acted upon by iodine. Heating the oil to a temperature of from 240–280° C. and noting the readiness with which the oil jellies and the consistency of the jelly produced have been extensively used as commercial tests for grading the oil. It is difficult, however, to conduct such a test under conditions which will give numerical values to the results, these being usually stated in terms of the apparent hardness or softness of the jelly, or else in terms of the number of minutes required to jelly at some given temperature. The latter method is open to several serious objections and it is difficult to reproduce in a second experiment the conditions of the first.

The behavior of the oil when iodine dissolved in a suitable solvent is added to it, furnishes a well known qualitative method of identifying china wood oil and particularly of distinguishing it from linseed oil, but since the test as usually carried out gives merely a jelly, no quantitative results are obtainable from them.

It was thought that if this test could be made quantitative so that a separation could be effected between the solidified and the liquid resulting from the action of iodine upon the oil, a valuable and quantitative method of testing the oil might be obtained, particularly as such a test would be directly related to the most important and characteristic property of the oil. A series of experiments conducted with this end in view showed that acetic acid of 99 $\frac{1}{2}$ per cent. strength or thereabouts was a solvent in which

both the iodine and the oil could be dissolved and out of which the solidified product separated readily so that it might be removed from the liquid portion; furthermore, that this liquid portion could be dissolved in a petroleum solvent boiling under 80°C . while the solid product from the china wood oil was practically insoluble in this solvent. Based upon these facts the following method of analysis was devised:

Weigh into an Erlenmeyer flask about 5 grams of the oil to be examined, add to it 10 cc. of 99 $\frac{1}{2}$ per cent. acetic acid and after warming it so that there is a perfect mixture of oil and acid, add to it 50 cc. of a solution of iodine in 99 $\frac{1}{2}$ per cent. acetic acid containing 15 grams of iodine per liter. The acetic acid solution of iodine should be warmed so that when added to the oil solution to be tested it will not chill it. Upon adding the iodine solution there results an almost instantaneous separation of some solid product from the solution in large amount. The solution is allowed to rest for half an hour to insure complete reaction and then 50 cc. of petroleum solvent (b. p. below 80°C .) added and allowed to mix thoroughly with the contents of the flask. The liquid is then drained off from the flask into a separatory funnel and another portion of 50 cc. of petroleum solvent added to the solid residue which has been allowed to remain in the flask so as to wash out of it the residue of liquid products; after pouring off this solvent the solid residue is extracted a third time with 50 cc. of petroleum solvent, the solutions being united in the separatory funnel. Water is now added to the contents of the separatory funnel and this causes a separation of the liquid into two layers, one of petroleum solvent carrying the liquid portions of the reaction in solution and the other of water united with acetic acid. This latter is drawn off and the petroleum solvent repeatedly washed with water till it is free from acetic acid and then shaken out with a solution of potassium iodide to remove free iodine which may be present; after a final washing with water it is transferred to a flask, the solvent evaporated off and the residue weighed. The weight of this residue is a measure of the proportion of those constituents of the oil under examination which are not solidified by the action of iodine.

Broadly stated, the process gives results showing that only a small fraction of china wood oil remains liquid at the conclusion of this process while other oils remain entirely liquid and soluble in the petroleum solvent and if the process be applied to known mixtures of a given sample of china wood oil with soya bean oil the proportion of soya bean oil may be determined with reasonable accuracy. In order to make such a determination, however, upon oils of unknown origin, it is necessary that the per cent. of liquid products which may conveniently be described as "per cent. of soluble iodides" of true china wood oil and also the variation in this per cent. given by different varieties and samples of true china wood oil should be known. In order to investigate this matter it is necessary to obtain a considerable number of authentic samples of such oils and these samples are to be ob-

tained only in China and in the other countries where this oil is produced. The method is, however, submitted as one suitable for the investigation of the oil and particularly as a method for determining the grade of the oil in respect to its most characteristic property.

As the writer has been unable to obtain any considerable number of original small samples of the oil, he refrains from giving the exact figures obtained upon the commercial samples which have been examined but hopes that others may apply the process to authentic samples as they are obtained.

7 EAST 42ND STREET, NEW YORK.

ON THE INDICES OF REFRACTION OF CHINA WOOD OIL.

By LOUIS ELSBERG WISE.

Received May 11, 1912.

The increasing use of china wood oil in the paint and varnish industries has created the necessity for a proper examination and standardization of this important article of commerce. Much of this drying oil is sent to European and American ports through Hankow, and a rumor is now current that there have been varied attempts to adulterate these shipments with cheaper products, such as soya bean oil. Whether or not these reports are based on fact, the author of this paper is in no position to decide, but he has found it a proper time to review the recent literature, relating to the characteristic properties of the raw material, and to find, if possible, some method by which the purity of the oil could be gauged.

The important characteristics of the oil¹ are its odor, its peculiar drying properties (in which it differs markedly from linseed), its high specific gravity and its coagulation on heating. The saponification, iodine and acid numbers appear to be of little value in judging the oil.

The jelly which is formed on application of heat is elastic and insoluble in the common solvents. It is ordinarily believed that the gelatinization is due to a polymerization; it is undoubtedly *not* caused by oxygen absorption, and it immediately distinguishes wood oil from the other common drying oils.

Several chemists² have recently made a study of the physical characteristics of the "go-back" (the varnish maker's name for this coagulation product), and a number of chemical examinations³, have been made, which up to the present have led to widely divergent results. A further investigation of the "go-back," as well as the relation between its properties and its technical use, is being made by Mr. Eugene G. Bloch, of our laboratory, and the results of this research may be published at some future date.

Another striking peculiarity of the oil is its high index of refraction. Lewkowitsch states that the refractive index is much higher than that of any other drying oil, and this statement suggested the study of the refractive indices of a number of commercial

¹ Lewkowitsch, *Chemical Technology of Oils, Fats and Waxes*, 2, 62.

² *Private communication.*

³ Lewkowitsch, 3, 99. Nash, *Private communication to Lewkowitsch. Norman, Chem. Ztg.*, 99 (1907).

samples. The data obtained is recorded in the tables given below.*

All attempts to get samples of wood oil of known source and purity were without avail. The difficulty was due to the primitive condition in the collection of the oil and its shipment to the coast from the country districts of China.¹ We received a sample from Mr. Bacon (also purchased on the open market) which is supposed to be a standard, but its source has not been indicated.

The results tabulated below, therefore, represent the refractive indices of *commercial* wood oils shipped to us for use in the manufacture of varnish. The shipments cover a period of approximately eight months, during 1911-1912. Some of them have proved unsatisfactory in the processes of manufacture, and there is some indication that a relation exists between the refractive index and the "working quality" of the oil. That question can be settled only by a far more extended research. Gross adulteration is certainly indicated very clearly and rapidly by the use of the refractometer, and whether foreign oils, present in small quantities may be detected, will depend very largely on the results of future coöperative investigation.

TABLE I.

Mark.	Index of refraction at 25° C.
A.3.20.12.....	1.5148
A No. 1 A.....	1.5118
A No. 2 A.....	1.5130
A No. 3 A.....	1.5164
A No. 4 A.....	1.5153
A No. 9A (R. M. S. 3534).....	1.5154
A No. 10 A (R. M. S. 3528).....	1.5174
S. L. J.....	1.5168
Sample from Mr. Bacon.....	1.5186
C \triangle 55 C.....	1.5121
C \triangle 75 C.....	1.5116
C \triangle 83 C.....	1.5167
A No. 19.....	1.5163
R. M. S. 3505.....	1.5099
W. K. C. W. O.....	1.5110

The results in Tables II and III require little comment; they show clearly that the admixture of small amounts of other drying oils lowers the refractive index.

TABLE II.

Sample.	Index of refraction at 25° C.
100 per cent. wood oil (mark A.3.20.12.....)	1.5147
95 per cent. wood oil, 5 per cent. soya bean oil	1.5122
95 per cent. wood oil, 5 per cent. linseed oil...	1.5128
90 per cent. wood oil, 10 per cent. linseed oil...	1.5114
100 per cent. soya bean oil.....	1.4751
100 per cent. linseed oil.....	1.4810

TABLE III.

Sample.	Index of refraction at 25° C.
100 per cent. wood oil (Bacon's sample).....	1.5186
95 per cent. wood oil, 5 per cent. soya bean oil	1.5163
95 per cent. wood oil, 5 per cent. tallow oil....	1.5161
100 per cent. tallow oil.....	1.4833

All indices of refraction were taken *without* the use of water circulation. All refractometric readings were made in the Advanced Physics Laboratory of Columbia University.

* The explanation of these high refractive indices will probably be found in the examination of the chief constituent of the oil, namely, the remarkable glyceride of oleomargaric acid, which is present in *none* of the other common drying oils.

¹ Private communication.

In conclusion, I beg to thank Mr. Bloch, chemist for the Standard Varnish Works, for his material aid, Dr. C. C. Trowbridge, of the Department of Physics of Columbia University, for his kind advice and Dr. Parker C. McIlhiney for his just criticism and his help.

LABORATORIES OF THE STANDARD VARNISH WORKS,
ELM PARK, N. Y.

THE REFRACTIVE INDEX OF BEESWAX.¹

By L. FELDSTEIN.

Received Jan. 5, 1912.

Lewkowitsch, in "Chemical Technology and Analysis of Oils, Fats, and Waxes," recommends refractometric examination as a preliminary test in the examination of beeswax, giving as the limits between which pure beeswax should fall, 42.9°-45.6°; butyro-refractometer scale, calculated to 40° C. These figures were obtained from the work of Werder² and Berg,³ who made the determinations at temperatures ranging between 70° and 84° C. and then calculated them to 40° C. Neither Werder nor Berg in their original articles give the figures actually observed nor explain how their calculations were made, but it is assumed that they added to the observed figures the correction 0.55° butyro for each degree centigrade between the observed figures and 40° C., the correction value 0.55° being generally used for all fats and oils when calculated to 40° C. In this laboratory an Abbe-Zeiss direct-reading refractometer is used, and for beeswax a correction of 0.00037 per degree centigrade was found necessary. This figure was obtained by taking the refractive index at 65°, 75°, and 85° C. and dividing the difference in the reading by the difference in degrees centigrade. This correction of 0.00037 per degree centigrade was found to be practically constant between these temperature limits not only for all pure beeswax examined, but also for those which, upon further examination, showed adulteration.

As beeswax is a solid at 40° C. and the refractive index is always read on the melted wax at some temperature above 63° C., it seems desirable to eliminate the use of the calculation to 40° C. and to set limits for the refractive index of pure beeswax at some temperature above the melting point. For this purpose a number of samples of known purity and origin, obtained from the Bureau of Entomology, United States Department of Agriculture, and some others purchased on the open market were examined. All of these have been analyzed by the drug laboratory of the Bureau of Chemistry. The readings were made at 65°, 75°, and 85° C., and the results are given in the following tables. Table I consists of the figures obtained on the samples of pure beeswax secured from the Bureau of Entomology. Table II shows the results on those samples obtained in the open market, many of them adulterated samples. In the column headed "Remarks" are placed conclusions as to the nature of the sample based on the chemical analysis:

¹ Contribution from the Contracts Laboratory, Bureau of Chemistry Washington, D. C.

² Chem. Ztg., 22, 59 (1898).

³ Ibid., 27, 752 (1903).

TABLE I.—REFRACTIVE INDEX READINGS AT DIFFERENT TEMPERATURES ON BEESWAX SAMPLES OF KNOWN PURITY.

Contract laboratory No.	Refractive index.			Locality.
	At 65° C.	At 75° C.	At 85° C.	
12616.....	1.4458	1.4424	1.4390	Not given
12617.....	1.4458	1.4425	1.4391	"
12618.....	1.4456	1.4420	1.4380	"
12619.....	1.4454	1.4418	1.4378	"
12620.....	1.4449	1.4414	1.4380	Mexico
12621.....	1.4453	1.4416	1.4377	North Carolina
12622.....	1.4460	1.4426	1.4388	Wisconsin
12623.....	1.4441	1.4403	1.4365	Cuba
12624.....	1.4449	1.4412	1.4375	Habana
12625.....	1.4448	1.4410	1.4374	Haiti
12626.....	1.4448	1.4414	1.4374	Southern States
12627.....	1.4458	1.4424	1.4387	Africa
12628.....	1.4456	1.4420	1.4384	New York
12629.....	1.4488	1.4451	1.4415	San Domingo
12656.....	1.4440	1.4402	1.4363	Not given
12657.....	1.4443	1.4406	1.4367	Wisconsin
12658.....	1.4460	1.4424	1.4388	Illinois
12659.....	1.4449	1.4413	1.4377	Texas
12660.....	1.4444	1.4405	1.4368	Iowa
12661.....	1.4450	1.4413	1.4378	Utah
12662.....	1.4458	1.4422	1.4384	Iowa
12663.....	1.4444	1.4405	1.4368	California
12664.....	1.4436	1.4398	1.4361	Hilo
12665.....	1.4434	1.4398	1.4361	"
12666.....	1.4435	1.4400	1.4362	"
12667.....	1.4447	1.4410	1.4375	Not given
12801.....	1.4470	1.4433	1.4395	Minnesota

TABLE II.—REFRACTIVE INDEX READINGS AT DIFFERENT TEMPERATURES ON COMMERCIAL SAMPLES.

Contract laboratory No.	Refractive index.			Remarks.
	At 65° C.	At 75° C.	At 85° C.	
12630.....	1.4463	1.4425	1.4389	Pure wax
12631.....	1.4459	1.4425	1.4387	"
12632 ¹	1.4379	1.4340	1.4302	Paraffin present
12633.....	1.4456	1.4421	1.4387	Pure wax
12634 ¹	1.4380	1.4344	1.4307	Paraffin present
12635 ¹	1.4379	1.4342	1.4302	Stearic acid and paraffin present
12636.....	1.4540	1.4505	Resin present
12637 ¹	1.4375	1.4338	1.4301	Paraffin present
12638 ¹	1.4350	1.4313	1.4275	"
12639.....	1.4448	1.4410	1.4372	Pure wax
12640.....	1.4454	1.4416	1.4380	"
12641 ¹	1.4421	1.4384	1.4346	Paraffin present
12642 ¹	1.4363	1.4323	1.4284	"
12643.....	1.4447	1.4410	1.4372	Pure wax
12644.....	1.4437	1.4400	1.4364	"
12645.....	1.4440	1.4402	1.4368	"
12646.....	1.4445	1.4410	1.4372	"
12647.....	1.4438	1.4401	1.4362	"
12648 ¹	1.4421	1.4384	1.4348	Paraffin present
12649 ¹	1.4335	1.4300	1.4260	Stearic acid and paraffin present
12650 ¹	1.4342	1.4304	1.4268	Paraffin present
12651.....	1.4439	1.4402	1.4365	"
12652 ¹	1.4345	1.4307	1.4269	"
12653.....	1.4445	1.4408	1.4372	Pure wax
12654 ¹	1.4355	1.4318	1.4280	Paraffin present
12655.....	1.4441	1.4406	1.4369	Pure wax

Upon examining the tables it will be found that the refractive index at 75° C. for pure beeswax falls between 1.4398-1.4451. Table II shows that the refractive indices of all those samples bought in the open market, which on chemical analysis appeared to be pure, fell within the limits for pure beeswax (1.4398-1.4451), while of the adulterated samples only one fell within these limits. This sample was No. 12651, which has a refractive index of 1.4402, a figure very close to the lowest value obtained for pure beeswax. In this instance it is quite possible that the beeswax had a high refractive index and was adulterated with a small amount of paraffin

¹ Grossly adulterated samples.

One sample (No. 12636), showing a high refractive index of 1.4540, proved on chemical examination to have resin in it. It was not possible to obtain a clear reading of this wax at 65° C. Those samples which have a very low refractive index proved to be grossly adulterated with either paraffin or stearic acid or both. A temperature of 75° C. was selected because at this point all beeswaxes are liquid, a clear, sharp line can be obtained in the refractometer, and it is comparatively easy to make the reading.

It is seen that the determination of the refractive index of beeswaxes is of great help in detecting gross adulteration and will generally reveal small adulterations, samples containing only a small amount of foreign material generally giving figures outside the limits mentioned, namely, 1.4398-1.4451 at 75° C. The results obtained show also that it is both unnecessary and unwise to calculate the refractive index to the butyro scale at 40° C., for the following reasons: (1) It is unreasonable to report the refractive index of a wax at a temperature at which it is an opaque solid, when the actual reading is made on the melted wax. (2) The calculation consumes time. (3) A clear reading can be obtained at 75° C. and the figures obtained can be reported unchanged.

THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

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(Continued from June No.)

VIII. The Examination of Anaesthetic Chloroform.

4. THE DETECTION OF WATER IN CHLOROFORM.

Since pure chloroform is not hygroscopic in the ordinary sense, and 100 cc. dissolve but 0.152 cc. of water at 22°,¹ such chloroform is not likely to contain appreciable amounts of water. In the case of anaesthetic chloroform, 0.025-0.05 per cent. by volume of water is introduced by the alcohol; it may be said, therefore, that the maximum amount of water likely to be present in anaesthetic chloroform is approximately 0.2 per cent. by volume, although the usual amount is about 0.05 per cent., according to our experience. Tests for the presence of water in anaesthetic chloroform are generally not specified. Since, however, the presence of water facilitates oxidation, it is at least desirable that the amount present is not excessive; and occasions may arise which require anhydrous chloroform. The authors are able to present tests, by the application of which both of these conditions may be met.

A. Tests Based upon the Evolution of Gas.

(a) *The Test with Calcium Carbide.*—Vitali² found that calcium carbide serves for the detection of water in chloroform; and we have learned that it is both a convenient and generally suitable reagent for the presence of water, even in minute amounts, in chloroform of all grades. It is the test which we recommend for establishing the anhydrous nature of a chloroform desired in a water-free condition.

¹ Herz, *Ber.*, 31, 2670.² *Boll. chim. farm.*, 37, 257; cf. Baskerville and Hamor, *This Journal*, 3, 311.

When pure chloroform containing an addition of 0.025 per cent. by volume of water is agitated with anhydrous cupric sulphate, no reaction indicative of the presence of water is had; whereas if 20 cc. of the same chloroform is gently boiled over 1 gram of calcium carbide, and the gas evolved is passed into an ammoniacal silver nitrate solution, a pronounced acetylene reaction is obtained. In fact, since 1 gram of water yields, at 0° and 760 mm., 580 cc. of acetylene, the merest traces of water may be detected in chloroform of all grades by boiling the sample under examination over clean crystals of calcium carbide, and passing the vapors evolved into ammoniacal silver nitrate solution.

(b) *The Action of Copper-Zinc Couple on Chloroform.*—Gladstone and Tribe¹ found that copper-zinc couple did not act on pure chloroform, but that in the presence of alcohol at +60° C., methane was evolved, together with a small amount of acetylene, and in the presence of water, methane was evolved even at +12° C. This reaction is not adaptable as a test for the presence of water.

(c) *The Action of Sodium on Chloroform.*—Sodium acts on chloroform containing water,² but in such a manner that it cannot be employed as a reagent for the presence of water in this case.

(d) *The Test with Anthraquinone and Sodium Amalgam.*—The authors have reported³ that "hydro-anthraquinone" serves for the detection of both water and alcohol in ethyl ether. When several mg. of anthraquinone and a small piece of 2 per cent. sodium amalgam are added to 20 cc. of anaesthetic chloroform containing 0.8 per cent. of absolute alcohol and 0.025–0.065 per cent. of water, an alcohol reaction alone is obtained; with anaesthetic chloroform containing 0.115 per cent. of water, a faint, but decided, water reaction is had, although this is somewhat masked by the alcohol reaction, the amalgam becoming colored green and red in places. The test is not recommended for the detection of water in chloroform containing alcohol.

B. Tests Dependent upon the Production of a Turbidity.

(a) *Tests wherein the Chloroform is Cooled to Low Temperatures.*—Behal and Francois⁴ considered that the simplest test for the presence of water in chloroform was to bring some of the crystals of ice obtained by submitting chloroform to a temperature of –20° to –40° in contact with mercuric ammonium iodide, when red mercuric iodide resulted. Chloroform freed from water does not afford any crystals of ice when exposed to the low temperature, and therefore pure chloroform should comply with this qualitative test; but since the addition of 5 parts of 98 per cent. alcohol in 1,000

¹ *J. Chem. Soc.*, 28, 508.

² Kern, *Chem. News*, 31, 121. The reaction is in apparent accordance with this equation: $\text{CHCl}_3 + 3\text{Na} + \text{H}_2\text{O} = 2\text{NaCl} + \text{NaOH} + \text{HCl} + \text{C} + \text{H}$. With pure chloroform, however, sodium formate is obtained, and the variables of anaesthetic chloroform would render the use of sodium as a test of no value. The action of sodium on anaesthetic chloroform will be discussed more fully in Section 5.

³ *THIS JOURNAL*, 3, 310.

⁴ *J. Pharm. Chim.*, 5, 417 (1897). It is almost needless to state that none of the samples of chloroform examined by Behal and François complied with this test.

causes them to appear, the test cannot be used for determining whether or not anaesthetic chloroform contains a permissible amount of water. The French *Codex* requires that anaesthetic chloroform shall not become turbid on cooling to –10°. Chloroform of the grade official in France should readily comply with this requirement for the following reasons: Chloroform saturated with water at +20° becomes turbid white or grayish on sudden cooling to –20°, owing to the formation of dispersed ice; but in a water concentration below 0.05 per cent. by weight of water in chloroform, there is no turbidity, although, according to Ostwald,¹ the Tyndall effect is pronounced down to 0.02 per cent. water.

(b) *The Test with Paraffin Oil.*—According to Crismer,² the "liquid paraffin" of the German pharmacopoeia³ mixes in all proportions with anhydrous chloroform, but if water is present the liquid becomes turbid.

In order to determine the delicacy of this test, a sample of anaesthetic chloroform containing 0.8 per cent. by volume of alcohol and 0.04 per cent. by volume of water was taken. When 10 cc. of this sample were agitated with an equal volume of paraffin oil (sp. gr. = 0.880), the oil dissolved to a clear solution, without any evidence of a turbidity. When the water content was increased to 0.065 per cent. by volume, the solution still remained clear and transparent; but when 0.09 per cent. of water was present, a faint yet decided turbidity resulted. When chloroform contains 0.118 per cent. of water, the reaction is very pronounced.

C. Tests Based on the Color Assumed by the Hydration of a Dehydrated Compound.

(a) *The Test with Anhydrous Cupric Sulphate.*—Since anhydrous cupric sulphate is a very satisfactory reagent for the presence of water in ethyl ether, the salt was tried in this connection. None of the commercial or anaesthetic chloroforms examined by us gave a response, when 20 cc. were shaken with 1 gram of anhydrous cupric sulphate during one hour; in fact, only a faint reaction was had with anaesthetic chloroform containing 0.115 per cent. of water, and a marked response was obtained only when the saturation point of the chloroform was reached.

D. Recommendations.

Pure chloroform and anhydrous anaesthetic chloroform should comply with test A (a); and anaesthetic chloroform should readily conform to test B (b), although it is highly expedient that the amount of water present be reduced to a trace, if not totally excluded, which could be accomplished by preserving anhydrous chloroform with anhydrous alcohol.

5. THE DETECTION AND ESTIMATION OF ALCOHOL IN CHLOROFORM.

The presence of ethyl alcohol in chloroform, in amounts varying from 0.25–1.00 per cent., has been almost universally recognized as necessary; in fact, all grades of chloroform on the market contain alcohol.

¹ *Z. Chem. Ind. Kolloide*, 6, 183.

² *Ber.*, 17, 649.

³ B. p. = 215–240° under 6 mm. pressure.

Therefore, whenever it is desirable that chloroform intended for certain chemical work should be alcohol-free, it is necessary to resort to methods of purification which serve to eliminate alcohol; but in such cases it is always important that the purified chloroform be tested to prove the absence of alcohol, for which purpose sensitive qualitative tests are necessary. In the case of anaesthetic chloroform, the amount of alcohol present need not exceed the specified pharmacopoeial limits, and then, in general, qualitative tests are valueless in practice¹ and it is necessary to determine the amount present by a determination of the specific gravity or, preferably, by a quantitative estimation of the amount of alcohol. It should be mentioned here, however, that at the present time alcohol is seldom present in anaesthetic chloroform in excessive amounts.² Anaesthetic chloroforms on the American market generally contain 0.50–0.84 cc. of alcohol, calculated as absolute, per 100 cc., and only one sample examined by us contained as much as 0.97 cc. of absolute alcohol.³

With the object of finding just what tests and methods of estimation are suitable and reliable, all of the schemes for the detection and determination of alcohol in chloroform were studied, and where the method appeared worthy it was tried out. For convenience sake, these methods will be considered in classes.

A. Physical Methods.

(a) *The Determination of the Amount of Alcohol from the Density.*—It has been quite a general practice to infer the amount of alcohol present in any sample of chloroform from the specific gravity of the sample in question, and it is generally considered that this inference may be accomplished accurately; but as alcohol does not reduce the density in exact ratio to its amount, several investigators have found it necessary to determine the specific gravity of known mixtures of absolute alcohol and chloroform.⁴

Provided the past history of the sample is known, the density of anaesthetic chloroform is an indication of the amount of alcohol present, and therefore the percentage of alcohol may be approximately estimated therefrom; but we consider that after a determination of the specific gravity has been made, no conclusions

¹ Cf. Dott, *Pharm. J.*, [3] 12, 769.

² Much of the chloroform in America in 1875 was, however, contaminated with alcohol; for, according to the report of Meigs, it possessed a density of 1.45 (see Normandy-Noad's *Commercial Hand-book of Chemical Analysis*, 1875, p. 122).

³ The official chloroform of the *Pharmacopoeia of the United States* is specified as a liquid consisting of 99–99.4 per cent. by weight of absolute chloroform and 0.6–1 per cent. of alcohol.

⁴ Remys (*Arch. Pharm.*, [3] 5, 31), assuming that "pure" chloroform possesses a density of 1.500 at 15° C., stated that the presence of 1/8 per cent. of alcohol reduced the density by 0.002 and 0.5 per cent. by 0.008. Rump (*Am. Chemist*, 6, 359) gave the same results. Besnou (see *U. S. Dispensatory*, 18th edition, p. 378; and Vremont in Stohmann and Kerl's *Technischen Chemie*, 2, 646) determined the specific gravities at 4.5° C. of mixtures of the "purest commercial" chloroform with small quantities of alcohol. Schacht and Biltz (*Pharm. J.*, 1893, 1005) obtained the following data:

	At 15° C.
"Pure" chloroform.....	1.5020
"Pure" chloroform with 0.25 per cent. alcohol.....	1.4977
"Pure" chloroform with 0.50 per cent. alcohol.....	1.4939
"Pure" chloroform with 1.00 per cent. alcohol.....	1.4854
"Pure" chloroform with 2.00 per cent. alcohol.....	1.4705

as to the percentage of alcohol should be arrived at until a quantitative estimation is carried out.

(b) *The Influence of Alcohol on the Boiling Point.*—While alcohol may be readily identified in anaesthetic chloroform by fractionation,⁵ and may be partially eliminated by this means, the variables of such chloroform render the determination of its boiling point valueless as a criterion of purity.

B. Chemical Methods.

1. Tests Based on the Oxidation of Alcohol:—

(a) *The Chromic Acid Test.*—Several⁶ have proposed that sulphuric acid and potassium dichromate be used as a reagent for the detection of alcohol in chloroform. The test serves to prove the absence of alcohol,³ and is given in the pharmacopoeias of Italy and Spain.

Based on the oxidation of alcohol by chromic acid, Nicloux⁴ devised a method for the estimation of alcohol in chloroform, according to which the small proportion of alcohol added is separated by shaking 5 cc. of the sample with 20 cc. of water; 5 cc. of the alcoholic solution (containing not more than 1 part in 500) are mixed in a test tube with 0.1–0.2 cc. of a solution of potassium dichromate (19 g. per l.), and then with pure sulphuric acid (sp. gr. 1.84), added cautiously. When sulphuric acid is added in sufficient quantity (4.5–6 cc.), the solution is decolorized; and the liquid is now gradually titrated with the dichromate solution, being shaken and gently heated after every addition, until the color changes from greenish blue to a permanent greenish color. This change, we may note, is most readily recognized in solutions containing less than 0.2 per cent. of alcohol. It is advisable to make a second determination in which the amount of dichromate used in the first experiment, less 0.1 cc., is run in at once, the sulphuric acid added, and the liquid is heated to boiling. The contents of the tube should remain greenish blue, while in another determination in which 0.1 cc. more than the first reading is added, the color should change to greenish yellow. The number of cc. consumed, divided by 1,000, gives the amount of absolute alcohol in cc. per cc. of solution. When the proportion of alcohol is less than 0.1 per cent., the strength of the dichromate solution should be doubled. Although Pozzi-Escot⁵ found that in order to obtain comparable results with the method

¹ On this point, see also Rump, *Am. Chemist*, 6, 359; Behal and François, *J. Pharm. Chim.*, 5, 417 (1897); Ryland, *Am. Chem. J.*, 22, 384. On the boiling points of alcohol and chloroform mixtures, see Thayer, *J. Phys. Chem.*, 3, 37; Wade and Finnemore, *J. Chem. Soc.*, 85, 940.

² Cottell, *J. Pharm. Chim.*, [3] 13, 359; Procter, *Am. J. Pharm.*, 1856, 213; Fleischmann, *Polyt. Notizblatt*, 34, 47; Gay, *J. Pharm. Chim.*, 4, 259. Rusconi, *Arch. farmacol. sper.*, 8, 196. Cf., however, Lepage, *J. Pharm. Chim.*, 1860, 93. Thresh (*Chem. News*, 38, 251; see also, *Pharm. J.*, [3] 11, 319) proposed a method according to which the sample of chloroform is agitated with an equal volume of water, the aqueous solution is distilled with potassium dichromate and sulphuric acid, and the distillate is tested for the presence of aldehyde by means of potassium or sodium hydroxide. The presence of 0.5 per cent. of alcohol is thus made evident. The amount of aldehyde produced may also be approximately determined colorimetrically by means of the reagent of François (*Chem. News*, 76, 7).

³ See *Pharm. J.*, [3] 22, 1041. It is, of course, very fallible, since many substances give the same reaction as alcohol.

⁴ *Bull. soc. chim.*, [3] 35, 330 (1906). The potassium dichromate method of estimation is detailed in the French Codex.

⁵ *Ann. chim. anal.*, 1902, 11, 12.

of Nicloux for the estimation of alcohol in dilute solutions,¹ it was essential to maintain absolutely identical conditions, and that even then discordant results might be obtained in duplicate experiments; yet when the procedure above described is followed exactly, the method is very useful. There is but one important source of error, and that is that agitation of 5 cc. of chloroform containing alcohol with 20 cc. of water does not serve to deprive the chloroform of all the alcohol present; this can be accomplished, however, by repeatedly shaking the sample under examination with double its volume of water, which operation should be repeated at least ten times. The water-extracts may then be combined, and a suitable amount taken for analysis.

Behal and Francois² modified the method of Nicloux³ by extracting the alcohol by agitation with sulphuric acid, diluting the acid solution with water, and then gently distilling; a portion of the distillate is boiled with sulphuric acid, and dichromate solution (16.97 g. per l.) is added until a green, but not greenish yellow, tint is reached. Each 2 cc. of the solution corresponds to 0.01 gram of absolute alcohol. This method gives concordant and quite accurate results under the conditions observed. If, however, the result obtained indicates a higher amount of alcohol than 2 cc. per 1,000, it is necessary to dilute the distillate with water, and then repeat the determination.

(b) *The Test with Alkaline Potassium Permanganate.*—Since pure chloroform will not reduce an alkaline solution of potassium permanganate, Yvon⁴ recommended a reagent (potassium permanganate, 1 part; "alcoholic potash," 10 parts; water, 250 parts) which changed from a violet to a green color when mixed with "impure" chloroform.⁵ Since, however, the change is caused by alcohol equally with more objectionable impurities, the test is of no value, except in examining pure chloroform,⁶ and in this case barium hydroxide should be used in place of potassium hydroxide.⁷

An analogous test is that proposed by Jolles⁸ for the detection of aldehyde, ethylene, etc., in chloroform. Jolles found that pure chloroform did not act on potassium manganate, whereas an addition of about

2 per cent. of alcohol or similar oxidizable matter quickly caused a reduction.¹

(c) *The Molybdic Acid Test.*—Davy² found that a solution of molybdic acid in concentrated sulphuric acid served as a reagent for the detection of alcohol in chloroform; but since this test is only capable of detecting the presence of 1 part of alcohol in 1,000 parts of chloroform³ and reducing substances in general give the reaction, it cannot be said to be of value.⁴

(d) *The Nitric Acid Test.*—Kossa⁵ has found that nitric acid (50 per cent.) and ethyl alcohol (90 per cent.) give a decided color reaction,⁶ but this behavior is not applicable as a test for the presence of alcohol in chloroform, since it is lacking in sensitiveness.

2. The Iodoform Test:—

Undoubtedly the most delicate test for the presence of alcohol in chloroform is that of Lieben, as modified by Hager. Usually it is directed that the sample under examination be agitated with 5 volumes of water, the liquid passed through a wet filter, and that the filtrate be then examined. We recommend the following procedure for the separation of alcohol from chloroform: 10 cc. of the chloroform under examination are shaken in a separatory funnel with 4 cc. of concentrated sulphuric acid, which combines with any alcohol; the extraction is again repeated with 4 cc. of sulphuric acid, and finally with 2 cc. The sulphuric acid solution (10 cc.) is now mixed with 40 cc. of water, and the diluted solution is gently distilled until the distillate amounts to about 20 cc. In this way the ethyl-sulphuric acid is decomposed into sulphuric acid and alcohol, and the iodoform test may now be applied to 10 cc. of the distillate. Add 6 drops of a 10 per cent. solution of potassium hydroxide, and warm the liquid to about 50° C. A solution of potassium iodide, 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. If alcohol is present, iodoform is gradually deposited at the bottom of the tube in yellow crystals.⁷

This test is not peculiar to alcohol, being produced also by acetone, aldehyde, isopropyl alcohol, propyl and butyl alcohols and aldehydes, various ethers, etc.; but pure chloroform should give absolutely no response when the test is applied in the manner indicated, 3.

3. Tests based on Solubility:—

(a) *Tests wherein Various Dyes are Employed.*—Regnault⁸ stated that if chloroform contained a trace

¹ See Loevy and Jolles, *Chem. Ztg.*, 11, 1394.

² *Chem. News*, 34, 137; see also Boettger, *Z. Allg. Oest. Ap. Ver.*, 1879, 431.

³ See Dott, *Ibid.*, 191. Dott pointed out that a determination of the density is a more delicate test for the presence of alcohol.

⁴ Cf. Gladstone and Tribe, *J. Chem. Soc.*, 43, 346.

⁵ *Pharm. Centralh.*, 46, 893.

⁶ A white cloudy layer appears at the surface of contact after the alcohol is carefully poured on to an equal amount of the acid, and soon afterwards a green or bluish green ring is observed on the lower side of this; the green layer sinks gradually, effervescence occurs, and aldehyde "is formed."

⁷ For details concerning the iodoform test, see Hager, *Z. anal. Chem.*, 9, 492; *Pharm. J.*, [3] 1, 683; *Pharm. Centralh.*, 1870, 155. This test is capable of detecting 1 part of alcohol in 2000 of water.

⁸ *J. Pharm. Chim.*, [4] 29, 402.

¹ *Bull. soc. chim.*, [3] 17, 424; *J. Pharm. Chim.*, [6] 5, 424.

² *J. Pharm. Chim.*, [6] 5, 417.

³ *Bull. de la Soc. Therap.*, 3, 860.

⁴ *Mon. Sci.*, [3] 12, 262 (1882); *J. Pharm. Chim.*, [5] 5, 225.

⁵ Yvon found that the rapidity of the change depends on the purity of the chloroform, and suggested that all chloroform which reduces the reagent within ten minutes should be considered incompletely purified or altered. Gay (*J. Pharm. Chim.*, 4, 259) devised a method for estimating approximately the amount of alcohol in chloroform by means of Mohr's solution; this method is rapid, but the results obtainable are too indefinite.

⁶ Dott, Clark and also Gilmour (*Pharm. J.*, [3] 12, 769) discredited Yvon's proposed test as an indication of the purity of anaesthetic chloroform. Martindale (*Ibid.*, [3] 12, 734) found that the British chloroform of 1882 would not stand Yvon's test, but considered that this failure was not due to the alcohol present; this was denied by Clark (*Ibid.*, 760), who, considering it necessary to add alcohol, stated that Yvon's test is worthless when such a procedure is followed. Preston (*Ibid.*, 981) believed that Yvon's test is a failure, since chloroform containing dangerous impurities cannot be differentiated from anaesthetic chloroform by its use alone. On this test, see also Portes, *Ibid.*, [3] 12, 268; and Lotze, *Rep. anal. Chem.*, 1883, 29.

⁷ Cf. De Koninck, *Z. angew. Chem.*, 1889, 4.

⁸ *Chem. Ztg.*, 11, 786.

of alcohol, it was colored purple on agitation with "Hofmann's violet," which is quite insoluble in pure chloroform; and also reported that chloroform should not dissolve or be colored by "aniline blue"¹ or fuchsine.² Stuedeler recommended fuchsine for the detection of alcohol in chloroform;³ and Allen⁴ attempted to apply rosaniline acetate in the estimation of alcohol. The *Nueva Farmacopea Mexicana*⁵ gives the "aniline violet"⁶ test. Behal and Francois⁷ rejected the magenta test as too delicate, they having been unable to prepare chloroform which was not rapidly colored in contact with air by this reagent; it is indeed difficult to prepare chloroform which affords no coloration with rosaniline acetate, for example, and it is sufficient to require that pure chloroform shall give but a very slight coloration, if any, after continued agitation.

(b) *The Test with Potassium Hydroxide.*—Potassium hydroxide is quite insoluble in anhydrous chloroform, but dissolves sensibly in the presence of water or alcohol. Blachez⁸ therefore proposed the following test for the presence of alcohol: Add to the sample a small piece of potassium hydroxide, and leave the mixture at rest for several minutes; decant the chloroform, shake with water, and add a solution of a copper salt to the aqueous extract; if a precipitate forms, it may be generally assumed that the chloroform contains alcohol.

A more reliable method, however, is to add to the chloroform under examination a small piece of fused potassium hydroxide and red litmus paper; if the latter assumes a blue color on being shaken with the chloroform, the presence of either water or alcohol is indicated.

To distinguish between water and alcohol, the sample may be agitated with ignited potassium carbonate, which treatment removes any water present; if the chloroform still possesses the power of dissolving potassium hydroxide, the presence of alcohol may be assumed. Pure chloroform should comply with this test.

(c) *The Test with Iodine.*—It was pointed out in 1869⁹ that when chloroform is free from alcohol or ether, the color produced when iodine is dissolved in it is bright red; but when either alcohol or ether is present, the color of the solution is brown.¹⁰ Siebold¹¹ proposed

¹ Regnault probably referred to rosaniline blue.

² *Mon. sci.*, [3] 12, 262.

³ The sample becomes colored red if alcohol is present, and the depth of the coloration varies with the proportion of alcohol.

⁴ *Analyst*, 2, 97. Chloroform containing alcohol still dissolves rosaniline acetate after treatment with calcium chloride; agitation with concentrated sulphuric acid eliminates alcohol and water, but the product retains so much acid it cannot be directly tested with fuchsine; the acid may be got rid of by means of potassium carbonate, but the chloroform retains sufficient alkali to prevent the coloration, and barium carbonate is more satisfactory; but when the dealcoholized chloroform is fractionated, these difficulties are not encountered.

⁵ 1904, p. 477.

⁶ Methyl-aniline violet is undoubtedly referred to.

⁷ *J. Pharm. Chim.*, 5, 417 (1897).

⁸ *Neues Jahrb. Pharm.*, August, 1869; *J. Pharm. Chim.*, [4] 9, 289; *Z. anal. Chem.*, 8, 472; *Russ. Z. Pharm.*, 8, 582. See also Vogel, *N. Rep. Pharm.*, 18, 306.

⁹ *Pharm. Z. Russland*, March, 1869.

¹⁰ In order to distinguish between alcohol and ether, a crystal of fuchsine was added to the chloroform; when a red solution ensued, the presence of alcohol was assumed.

¹¹ *Pharm. J.*, [3] 10, 213.

a method¹ for the detection and approximate estimation of alcohol in chloroform by the use of iodine, but it is not delicate.²

(d) Oudemans³ found that the proportion of alcohol contained in chloroform may be determined by means of cinchonine,⁴ but the method is neither delicate nor practical.

4. Miscellaneous Tests.

The other tests which have been proposed for the detection of alcohol in chloroform are the iron dinitrosulphide test of Roussin,⁵ the sulphuric acid test of Guthrie,⁶ the test with sodium proposed by Hardy,⁷ the potassium test of Mialhe,⁸ the test depending upon the solution of the alcohol in water which originated with Soubeiran,⁹ the albumen test of Kappeler,¹⁰ and the almond oil test.¹¹ These tests are either not

¹ A small quantity of iodine is introduced into 10–15 cc. of the sample, which is then shaken until the solution has acquired a purple or purplish red color, but not opaque; the solution is decanted from the undissolved iodine, and is divided into two parts, which are placed in two separate test tubes of equal diameter. One is shaken with about four times its volume of water, and the other is kept for comparison. The water absorbs alcohol, and what settles down is a solution of iodine in chloroform, the color of which will be exactly the same as that of the other portion if the chloroform is "pure," but will be distinctly different if the sample contains alcohol.

² With 2 per cent. of alcohol or more, the difference is striking; with 1 per cent., it is distinct; and with 0.5 per cent., it is discernible; but 0.25 per cent. may only be definitely detected by resorting to distillation and then using the first portion of the distillate.

³ *Ann.*, 166, 1; *Z. anal. Chem.*, 11, 409.

⁴ 10 cc. of the sample are shaken with an excess of pure, dry cinchonine in a flask; the latter is kept for an hour at 17° C., with frequent agitation, and the liquid is then passed through a dry filter and 5 cc. of the filtrate are evaporated to dryness in a small beaker. The amount of residual alkaloid is then determined. Pure chloroform yields 21 mg., while chloroform containing 1 per cent. of alcohol yields 67 mg.

⁵ *J. Pharm. Chim.*, [3] 34, 206; see also *Am. Apoth. Ztg.*, 20, 32. Pure chloroform shaken up with iron dinitrosulphide remains colorless; but if it contains alcohol, ether or wood spirit, it acquires a dark color. Kappeler, referring to this test in his *Anaesthetica*, states that the reaction is also caused by aldehyde and amyl alcohol. According to Lepage (*J. Pharm. Chim.*, 1860, 93), the test of Roussin will detect one-thousandth part of alcohol. On this test, see also *Pharm. Centr.*, 1899, 199.

⁶ *Am. J. Sci.*, [1] 22, 105. In 1832, Guthrie stated that sulphuric acid affords "a fine test of the presence of alcohol; if alcohol be present, so soon as the chloric ether is all over, the acid acts upon the alcohol which it has detained, and generates sulphuric ether, which is instantly indicated by its peculiar flavor; if no alcohol be present, no sulphuric ether will be produced."

⁷ *Pharm. J.*, [2] 4, 62; *Chem. News*, 5, 286. Hardy considered that when a small piece of sodium remains unattacked in chloroform, the latter is pure. When, however, the sample contains alcohol or other substances susceptible of alteration, a disengagement of gas occurs. Traub (*Pharm. Centralh.*, 33, 245) stated that there should be no deposit of colored sodium chloride; he confused alcohol with aldehyde.

⁸ *J. Chim. Méd.*, [3] 4, 279.

⁹ See Kessler, *J. Pharm. Chim.*, [3] 13, 161. Mialhe (*Pharm. J.*, 7, 345) proposed that a small quantity of the chloroform be dropped on some distilled water, when, if the sample is pure, it remains transparent; if, however, it contains alcohol, the globules acquire a milky opacity. With 1/300th part of absolute alcohol, the opalescence is marked (Mialhe).

Letheby (Normandy-Noad's *Commercial Hand-book of Chemical Analysis*, 1875, p. 121) adopted a similar test, but recommended that the amount of alcohol dissolved be determined by the diminution in bulk of the chloroform after shaking with water. The proportion of alcohol in anaesthetic chloroform can be determined only with tolerable accuracy by means of this method when the quantity present exceeds 1 per cent. "On the Estimation of Alcohol by Glycerine," see Hager, *Z. anal. Chem.*, 1889, 375; and "On the Solubility of Chloroform in Water," cf. Chancel and Parmentier, *Compt. rend.*, 106, 577.

¹⁰ *Anaesthetica, Loc. cit.* Kappeler stated that alcohol may be recognized in chloroform by the coagulation which occurs in the white of egg when a few drops of the sample are added.

¹¹ This test was also devised by Soubeiran. Lepage found that it will not serve to detect a smaller quantity of alcohol than 5–6 per cent. (*Pharm. J.*, 11, 213). Hager (*Kommentar*, 1865, p. 439) gave the limit of delicacy as 4–5 per cent. of alcohol.

characteristic of the presence of alcohol alone or are wanting in necessary delicacy, and all are unsatisfactory.

C. Recommendations.

(a) Pure chloroform should possess a correct specific gravity and boiling point, and should give no response when tests 1 (a), 1 (b), 2 and 3 (b) are applied.

(b) In the case of anaesthetic and commercial chloroform, a determination of the density should first be made, and then a quantitative estimation of the amount of alcohol present by the method of Nicloux as elaborated by the authors [1 (a), *supra*]. Anaesthetic chloroform should not contain over 1 cc. of alcohol, calculated as absolute, in 100.

6. THE DETECTION OF ACETONE IN CHLOROFORM.

Since chloroform is now largely manufactured from acetone, this is a probable contaminant of anaesthetic and commercial chloroform, and it is sometimes necessary to test for it—a difficult procedure if present in likely amounts.

Pure chloroform complying with the iodoform test as described is assuredly free from acetone; but the detection of acetone in anaesthetic and commercial chloroform presents greater difficulties. The tests wherein advantage is taken of the solubility of mercuric oxide in acetone (Reynolds) and of the solubility of mercuric sulphate in acetone (Denigès) are not applicable in this case. This is principally due to the fact that chloroform containing any likely amounts of acetone will not part with sufficient of the compound to afford a response; in fact, we obtained negative results with chloroform containing 1 part of acetone in 500 of anaesthetic chloroform. The tests with silver nitrate solution,¹ potassium hydroxide and hydrated oxide of silver² are not decisive, being generally indicative of the presence of acetaldehyde, and for this reason alone cannot be considered in this connection.

We have found the following test satisfactory in the absence of all but comparative traces of acetaldehyde: 10 cc. of the sample of anaesthetic or commercial chloroform 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 then allowed to stand 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 there results an amethystine color. On adding solid ammonium sulphate to the mixture, then shaking and allowing to stand several minutes, in the case of acetone-free anaesthetic chloroform a yellow color results, while in the presence of acetone the amethyst color disappears, but reappears on standing 5 minutes. This test must be conducted in the cold.³ It is also subject

¹ Scholvien (*Pharm. Ztg.*, **32**, 686) pointed out that owing to the fact that chloroform was then (1888) prepared to a considerable extent from acetone, this substance is likely to occur as an impurity, the boiling points of the two bodies only differing by 5° C. Gerrard (*Pharm. J.*, [3] **23**, 231) found that on distilling 200 cc. of chloroform the last 2 or 3 cc. of residue contained traces of acetone bodies.

² See Gay, *J. Pharm. Chim.*, **4**, 259.

³ See *The Detection of Aldehyde in Chloroform, Section 9.*

⁴ The presence of 2 parts of acetaldehyde in 1,000 gives an intense reaction; when, however, the proportion becomes greater than 1 : 3300, acetaldehyde no longer interferes.

to the limitations of solubility referred to above, but is the only convenient test to our knowledge and anaesthetic chloroform should give a negative reaction when it is applied. In the presence of 1 part of acetone in 500 of anaesthetic chloroform, the amethyst color is marked; when the proportion is 1 : 1,000, 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 stand five minutes, when a decided amethystine color is observed. The coloration is, in all cases, rendered apparent by comparing with a blank.

We recommend that the above test be applied to the suspected chloroform direct, and then to the first 10 per cent. distillate and to the 10 per cent. residuum, obtained by the fractionation of 100 cc. of the sample; and anaesthetic chloroform should give a negative result in all cases.

7. THE DETECTION OF METHYL ALCOHOL AND OTHER METHYL COMPOUNDS IN CHLOROFORM.

Reference has been made to the manufacture of chloroform from "methylated spirit."² When such chloroform is properly purified, it is identical with that prepared from alcohol or acetone; but it is only in anaesthetic or commercial chloroform prepared from "methylated spirit" that one may reasonably suspect the presence of methyl alcohol. Various tests have been proposed in the past for the detection of this then probable contaminant;³ but chloroforms now on the market are, so far as we have been able to ascertain, free from methyl alcohol, formaldehyde and formic acid, and, at all events, it is unnecessary to test for the presence of these substances in anaesthetic and commercial chloroforms at present on the American market.

8. THE DETECTION OF ETHYL ETHER IN CHLOROFORM.

From 1865-1875, ethyl ether was regarded as one of the general contaminants of anaesthetic chloroform and various tests were devised for its detection.⁴ It

¹ Cf. Rothera's test for the presence of acetone in urine (*J. Physiol.*, **37**, 491).

² See III, 2, in this paper.

³ Ulex (*Arch. Pharm.*, [3] **5**, 523) stated that methyl alcohol may be detected in chloroform by means of sulphuric acid; but this is correct only when furfural is also present. Kappeler (*Loc. cit.*) reported that chloroform containing methyl compounds forms a black oily layer when treated with zinc chloride; and Langbeck stated that silver nitrate may be used for distinguishing between the so-called methylated chloroform and that from alcohol, a precipitate of silver oxide being formed when "methyl" is present. Dott (*Pharm. J.*, [3] **9**, 524) showed that the test of Langbeck is worthless for the purpose claimed.

According to Normandy and Noad (*Commercial Hand-book of Chemical Analysis*, 1875, p. 123), one of the best indications of the presence of methyl compounds is the effect which they produce upon the animal system!

The presence of methyl alcohol in chloroform may be determined by fractionation. 0.42 gram of methyl alcohol to 99.58 gram of chloroform forms a mixture which is said to begin to boil at 54.43° C.

⁴ It was stated, for example, that any considerable admixture of ethyl ether with chloroform would be indicated by the inflammability and diminished density of the liquid. On the specific gravities of chloroform-ether mixtures, see Katz, *Apoth. Ztg.*, **17**, 514. Rosenthaler (*Arch. Pharm.*, **244**, 24) found that when chloroform and ethyl ether are mixed, under varying conditions, a notable rise of temperature invariably ensues.

Rabourdin (*Compt. rend.*, **31**, 786) reported that ether may be detected in chloroform by the addition of a trace of iodine—a test of absolutely no value.

Ether may be detected in anaesthetic chloroform by fractionation of the sample; this is the only suitable method (cf. *Farmacopea Italiana*, fourth edition, p. 1357).

is unnecessary to look for the presence of such an improbable impurity at the present time.

9. THE DETECTION OF ACETALDEHYDE IN CHLOROFORM.

Chloroform, whether made from alcohol or acetone, should be, and is, so far as we have been able to ascertain, free from appreciable amounts of acetaldehyde,¹ although in the past such contamination was quite general, owing to the use of impure alcohol, to imperfections in purification, and to careless storage. The alcohol present in anaesthetic chloroform is generally 95 per cent. rectified spirit, which should not contain over 1 part of acetaldehyde by volume in 10,000. Assuming the presence of this amount of aldehyde, and an addition of 1 per cent. of such alcohol to properly purified chloroform, it will be apparent that the anaesthetic chloroform manufactured in this way will contain a negligible amount of acetaldehyde. Since acetaldehyde is, however, the primary product of the oxidation of anaesthetic chloroform, delicate characteristic tests for its presence are necessary; and by the application of these it may be determined whether chloroform has been purified by means of a method serving to eliminate any acetaldehyde occurring in the crude product and whether the sample under examination has been stored in such a way as to prevent, at least for ordinary periods of time, oxidation of the alcohol present.

A. There have been a few tests proposed for the detection of acetaldehyde in chloroform. Of these, the silver nitrate² and "hydrate of silver oxide"³ tests are not decisive; the test of Rusconi⁴ is, among other things, lacking in necessary delicacy, while the test with potassium hydroxide,⁵ the most satisfactory of

the recommended tests, is not altogether characteristic of the presence of acetaldehyde, and there are, in addition, certain sources of error.¹

Pure chloroform complying with the iodoform and chromic acid tests is certainly free from acetaldehyde; but the definite recognition of small amounts of this substance in anaesthetic chloroform presents greater difficulties.

We have found that when acetaldehyde is present in anaesthetic or commercial chloroform in appreciable amounts, it may be readily detected by agitating 5 cc. of the sample with an equal volume of the reagent of Francois (22 cc. sulphurous acid, 30 cc. 1 : 1,000 rosaniline acetate solution, and 3 cc. sulphuric acid), which also shows the presence of those very unusual contaminants, furfural and chloral.² The presence of 3 parts of acetaldehyde by volume in 10,000 of chloroform may thus be readily made evident, and even smaller amounts may be detected by fractionation.

When anaesthetic chloroform containing 6 parts of acetaldehyde in 10,000 is agitated with an equal volume of water, the water extract fails to respond with Francois' reagent; therefore the test should always be applied to the sample direct, as given above, and no coloration should result even after 15 minutes in the case of anaesthetic chloroform. This method may, obviously, be made *approximately* quantitative, since the amount of aldehyde may be determined colorimetrically by comparison with standards, just as in the case of ethyl ether.³

Confirmation may be had of the presence of aldehyde by applying the test with 1 : 10 metaphenylenediamine hydrochloride solution. 10 cc. of the sample should afford no coloration, even after one hour's standing, after being thoroughly agitated with the test solution.

B. The Department of Chloroform with Nessler's Reagent.—The *Pharmacopoea Nederlandica*⁴ requires that 5 cc. of chloroform *ad narcosin* shall give no reaction

in 12 hours on shaking it with solid potassium hydroxide. Stengel (*Z. Oester. Apoth. Ver.*, 46, 279) claimed that no chloroform of the official specific gravity 1.485–1.490 will meet the requirements of the potassium hydroxide test of the Austrian pharmacopoeia. In Belgium it is required that chloroform shall impart no coloration to an equal volume of sodium hydroxide solution; potassium hydroxide is specified in Chili, Spain, and Mexico; and potassium hydroxide solution in Switzerland and France.

In the sixth revision of the *Pharmacopoeia of the United States* (1882) it was required that when a portion of chloroform was digested, warm, with a solution of potassium hydroxide, the latter should not become "dark colored."

It is true that pure chloroform is not visibly altered when heated with a solution of potassium hydroxide, although it is slowly acted on with formation of formate and chloride of potassium. In alcoholic solution this reaction occurs rapidly (see, in this connection, Desgrez, *Compt. rend.*, 125, 780; Thiele and Dent, *Ann.*, 302, 273); formic acid is produced by the secondary reaction of carbon monoxide on the alkali. The test with potassium hydroxide is not characteristic of the presence of acetaldehyde, however, being also indicative of contamination with acetone and extractive matter. A more decisive test is therefore necessary.

¹ For example, the potassium hydroxide used must contain over 80 per cent. KOH and *no water*, otherwise anaesthetic chloroform containing no aldehyde may give the coloration, owing to the oxidation of the alcohol in the chloroform. See Stengel, *Z. Allg. Oester. Apoth.-Ver.*, 46, 279.

² "On the Detection of Traces of Chloral in Chloroform," see Jona, *Giorn. Farm. Chim.*, 61, 57.

³ See Baskerville and Hamor, *THIS JOURNAL*, 3, 393, wherein the procedure of Francois (*Chem. News*, 76, 7) is discussed.

⁴ 1905, p. 90.

¹ Of the many samples of anaesthetic and commercial chloroform examined by the authors, only two contained excessive amounts of acetaldehyde. One of these, an unopened tin six years old, contained approximately 1 part of acetaldehyde in 3300; while the other, an unopened tin of chloroform manufactured in 1863, contained 1 part in 2000. Both of these samples also contained acetic acid, but the chloroform itself was unaltered. These findings support most convincingly the views already expressed as to the role of alcohol in preservation.

² Gay (*J. Pharm. Chim.*, [6] 4, 259) proposed that the sample be shaken with an equal volume of 10 per cent. silver nitrate solution; a white precipitate on standing indicates the presence of hydrochloric acid, and a black precipitate on boiling that of aldehyde, *formic acid*, or *acetone*. See also Scholvién, *Pharm. Ztg.*, 32, 686; Behal and François, *J. Pharm. Chim.*, [6] 5, 417.

³ This test, based on the reducing action of aldehyde on the "hydrated oxide" of silver, is given in the pharmacopoeias of Italy and Mexico.

⁴ Rusconi (*Arch. farmacol. sper.*, 8, 196) found that 0.1 per cent. of aldehyde may be detected in chloroform by means of sodium nitroprusside and $(\text{CH}_3)_2\text{NH}$, the test being made on the distillate.

⁵ Letheby (*Loc. cit.*) pointed out that aldehyde may be occasionally met with in chloroform. He considered it questionable if it occasions any injurious influence when it is inhaled with the chloroform, but indicated the irritating action of acetic acid. He recommended the "hydrated oxide of silver" and "liquor potassae" tests. Regnault (*J. Pharm. Chim.*, [4] 29, 402; see also *Mon. Sci.*, [3] 12, 262) stated that aldehyde may be detected by many of the tests for ethyl alcohol, and also by warming with potassium hydroxide, when its presence is indicated by a darkening in color. Scholvién (*Pharm. Ztg.*, 32, 686) found that a sample of chloroform, which, as regarded its density, boiling point, and reaction with both silver nitrate and sulphuric acid, satisfied the tests prescribed by the German Pharmacopoeia, possessed an odor of aldehyde. A piece of potassium hydroxide placed in the chloroform assumed a brown color, the chloroform itself becoming yellow in color. After treating the sample with alcoholic ammonia and gently distilling off the chloroform, the residue gave the characteristic odor of aldehyde-ammonia and a reaction with Schiff's reagent. Behal and François (*Loc. cit.*) stated that pure anaesthetic chloroform should not be colored by boiling with solid potassium hydroxide.

The Italian, Dutch and Austrian pharmacopoeias give this test for the presence of aldehyde. The chloroform should give no brown coloration.

tion when shaken with 5 cc. of water and 3 drops of Nessler's reagent—a comparatively stringent requirement,¹ for, while pure chloroform should, of course, give an absolute non-response with Nessler's reagent, since it is necessary to add alcohol for preservation, the test cannot be required wherein the reagent is used direct without dilution or other modification.

In order to determine the applicability of Nessler's reagent as a test for the presence of acetaldehyde in anaesthetic chloroform, the following experiments were performed, using 5 cc. of each sample and 5 cc. of Nessler's reagent U. S. P.:—

Sample and conditions.	Results.
1. Salicylid-chloroform, containing no detectable impurities; 0.25 per cent. pure ethyl alcohol.	Reagent assumed a faint opalescence after the mixture had been shaken and then allowed to stand 5 minutes.
2. Anaesthetic chloroform prepared from carbon tetrachloride and of full U. S. P. quality; 0.7 per cent. alcohol.	After 5 minutes, a turbidity was observed, but no coloration or precipitate.
3. A sample of anaesthetic chloroform prepared from acetone and complying in full with the requirements of the U. S. P.	Reagent assumed an orange opalescence after shaking and allowing to stand 5 minutes; after 10 minutes, the reagent became red colored.
4. An old sample of anaesthetic chloroform (48 years), which gave a marked reaction with François' reagent.	Reagent darkened immediately. After 5 minutes it possessed a dirty yellow color and a black precipitate was observed.
5. "Purified chloroform," of full U. S. P. grade; 0.9 cc. absolute alcohol in 100 cc.	After 5 minutes, the reagent possessed an opalescent orange color; it appeared turbid, but no precipitate settled out.
6. "Chloroform pure," of U. S. P. grade, and in addition conforming with the formalin-sulphuric acid test; 0.56 cc. absolute alcohol in 100 cc.	As in No. 5.
7. Anaesthetic chloroform prepared from chloral, and conforming with all requirements of the U. S. P. but the sulphuric acid test; 0.30 cc. absolute alcohol in 100 cc.	As in No. 5.
8. Anaesthetic chloroform conforming with all the requirements of the German Pharmacopoeia.	Red color at once; after 5 minutes, it became darker in color than No. 5.
9. Pure chloroform containing 1 part of acetaldehyde in 555.	Reagent assumed a brick-red color at once, but became black after several seconds; a heavy black precipitate after 5 minutes.
10. Pure chloroform containing an addition of 2 parts of acetaldehyde in 11,000.	Red color at once; a heavy brick-red precipitate after 5 minutes.
11. Ten cc. of pure chloroform containing an addition of 2 parts of acetaldehyde in 11,000; 10 cc. of water, and 5 drops of Nessler's reagent U. S. P.	Opalescent yellow color at once. After 5 minutes, the reagent possessed an opalescent orange-yellow color (turbid).
12. Ten cc. of No. 5; 10 cc. of water; and 5 drops of Nessler's reagent U. S. P.	No color at once, but a very faint yellow color after 5 minutes; the reagent was slightly turbid after agitation for 1 minute. The difference from the preceding was most marked.

From these general experiments, supplemented by

¹ Cf. Weigel, *Pharm. Centralh.*, 47, 400.

tests made on various other anaesthetic chloroforms, it was concluded that the test with Nessler's reagent is more delicate in this case than that with the reagent of Francois; and that while pure anaesthetic chloroform should behave as in Experiment 1, in our opinion it is sufficient to require that anaesthetic chloroform should comply with the following test: When 10 cc. of the sample 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 5 minutes, there should result no precipitate and the reagent should assume no coloration, although it may become opalescent or slightly turbid.

(To be concluded in the August No.)

LABORATORY STUDIES OF RENNIN.¹

I. A Study of the Properties of this Important Ferment, when Prepared by Different Methods. II. The Acceleration of the Action of Rennin by Phosphoric Acid. III. The Variation in the Length of Time Required to Curdle Different Specimens of Milk.

By A. ZIMMERMANN.

Received January 17, 1912.

I. KINDS OF RENNIN.

Rennin Precipitated by Sodium Sulphate.—The rennets are digested to complete solution at 110° F. After separation of the fatty matter and clarification of the solution, this is precipitated by adding 3 volumes of a saturated solution of sodium sulphate, at 104° F.; the precipitate is collected, pressed and then dried at a temperature not exceeding 110° F. The yield is greater than that obtained by sodium chloride, the bulk being made up by albumose bodies. This makes it of a lower strength, ranging from 1 : 30,000 to 1 : 40,000 in 12 minutes.

Rennin Precipitated by Sodium Chloride.—The clarified solution of the rennets is saturated with sodium chloride at 104° F. The rennin is collected, pressed, then dried at a temperature not exceeding 110° F. The yield is much smaller than with sodium sulphate, giving a rennin of a much higher strength, from 1 : 150,000 to 1 : 200,000 in 12 minutes.

Rennin in Scales (Granular Rennin).—Prepared by scaling the clarified solution of the whole rennets at a temperature not exceeding 110° F. When perfectly dry, the scales are forced through a 16-mesh sieve. The strength of this rennin is from 1 : 30,000 to 1 : 40,000 in 12 minutes.

Commercial Rennin.—There are two different forms of rennin upon the market: (1) Rennin in powder form, prepared from the sodium chloride product, powdered and diluted with sugar of milk, testing 1 : 30,000 to 1 : 40,000 within 12 minutes. (2) Granular rennin, prepared from the scales, which also tests 1 : 30,000 to 1 : 40,000 within 12 minutes.

Difference between Precipitated and Scales Rennin.—The precipitated rennets are diluted with more or less albumose substance. They are acid in reaction, as they carry the greater part of the acid from the solution during the precipitation. The scaled rennin contains the soluble products, peptone and albumose

¹ Presented at A. C. S. meeting at Washington, D. C., December, 1911

substances, formed during the process of digestion of the rennets by aid of hydrochloric acid, which it also retains and which gives to it its acid reaction.

The rennin by sodium sulphate is no longer manufactured for use in the pharmaceutical preparations, the most important of these being the Essence of Pepsin, which is much used as a vehicle for bromides; the presence of sulphates would make it incompatible with strontium bromide. The complete separation of the sulphuric acid from rennin is not easily accomplished: by the use of calcium chloride, the reaction requires several days, during which time the rennin loses its activity; with barium chloride, there is formed a nearly colloidal barium sulphate, extremely difficult of separation.

The sodium chloride product is not so permanent as the granular rennin and the sodium sulphate product in a glycerine-water solution in the form of glycerol, which is a most excellent solvent for making permanent solutions of this class of substances.

The following tests made with a glycerol containing both rennin and pepsin, upon milk kept refrigerated for 17 to 18 hours after the milking, shows the permanency of the different forms of rennin, each giving a strength of 1 : 2500 in the time indicated:

RENNIN AND PEPSIN GLYCEROL.

Kind of rennin.	NaCl pptd.		Na ₂ SO ₄ pptd.		Granular.	
	1	2	1	2	1	2
No. of milk.....	1	2	1	2	1	2
When prepared...	12 min.	12 min.	12 min.	12 min.	12 min.	12 min.
After 1 mo.....	30 "	25 "	12 "	12 "	12 "	12 "
After 2 mo.....	2.5 hrs.	2 hrs.	12 "	12 "	12 "	12 "
After 12 mo.....	3.5 "	3.25 hrs.	12 "	12 "	12 "	12 "
After 15 mo.....			12 "	12 "	12 "	12 "

The permanency of the rennin in solution seemed to be dependent upon phosphoric acid. This is contained in the rennets probably as a calcium salt, and during the digestion of these, for the preparation of rennin, the phosphoric acid is liberated by the hydrochloric acid used in the process. The granular scale and sodium sulphate product react for phosphoric acid, and in this they differ from the sodium chloride product, which appears to contain but very small quantities or none.

II. ACTION OF PHOSPHORIC ACID.

The addition of phosphoric acid in the proportion of 0.075 per cent. to milk, from individual cows or that mixed from the herd, has the effect of increasing the activity of the rennin very much. This applies to milk from 4 to 8 hours after the milking; as the milk gets older the rennin acts more rapidly, and with milk 2 days old preserved by refrigeration, the curd is formed within a few minutes without the need of any accelerant. The curd formed in milk from 4 to 8 hours old forms very gradually after the action of the rennin sets in and, when complete, is not nearly so firm as that formed in the presence of the phosphoric acid, which reduces the time of action to between $\frac{1}{10}$ and $\frac{1}{20}$.

Lactic, hydrochloric and oxalic acids also have an accelerating action upon rennin, but less than phosphoric acid. Lactic acid possesses about $\frac{1}{5}$, and the other acids about $\frac{1}{10}$ the activity of phosphoric acid. Lactic acid forms a firmer curd than hydrochloric or

oxalic acids, but not so perfect and firm a curd as is formed by the phosphoric acid:

COMPARATIVE ACTION OF RENNIN (R.) AND RENNIN ACCELERATED BY PHOSPHORIC ACID (R. P.).

Milk Specimen.	4-5 hrs. old.		17-18 hrs. old. ¹		40-42 hrs. old. ¹	
	R. Min.	R. P. Min.	R. Min.	R. P. Min.	R. Min.	R. P. Min.
1.....	60	1.75	9.5	1	4.0	0
2.....	35	1.5	3.5	1	3.0	0
3.....	62	2.0	7.0	1	2.5	0
4.....	40	1.5	8.0	1	2.0	0
5.....	42	1.75	9.0	1	3.0	0
6.....	63	2.0	5.0	1	1.5	0

The glycerol solution, 12 months old, prepared with sodium chloride precipitated rennin, which requires 3 to 3.5 hours to curdle 18-hour milk, curdles this same milk in one minute when accelerated by phosphoric acid.

III. VARIABILITY OF MILKS.

The length of time required to curd by the same specimen of rennin seems to be influenced by the length of time the milk is kept after the milking, as already noted under "Action of Phosphoric Acid." There is a slight difference in the degree of acidity of the milk, that which curds the quickest being slightly more acid. Milk which curds very quickly with rennin can be modified to require a greater length of time to curd, by varying its degree of acidity by addition of an alkali. This is shown in the following table:

Milk.	N NaOH.	Curd formed in
Cc.	Cc.	min.
75	0.0	0.5
75	0.6	0.5
75	1.2	13.0
75	1.5	None in 3 hrs.

Other investigators, Smeliansky² and Werncken,³ have noted the effect of acids (other than phosphoric) and alkalies upon the rennin coagulation of cows' milk, and these same investigators, with Van Dam⁴ and Gerber,⁵ have observed the influence of many other substances in this same direction.

The tendency of the milk to curd more quickly the longer it is kept after milking would appear to be of bacterial origin; but if this be the cause, how can we explain why a mixture of rennin and milk kept at 104° F. for several hours does not curd, while if the milk is kept at that temperature for several hours the addition of the same rennin causes very quick curdling? In the latter case the influence of bacterial growth is suggested, and in the first case we also have all the conditions to favor bacterial growth and hasten the curd forming, but such action is not perceptible.

Fuld and Wohlgemuth⁶ have found that cows' milk is more easily curdled after it has been frozen. According to Van Dam,⁷ when milk is heated the acidity increases. My observations in this direction have been with milk 18 to 20 hours after milking; when heated for 2½ hours at a temperature of 104° F., the

¹ Refrigerated.

² *Milchwirtsch. Zentr.*, **4**, 379-381; *Arch. Hyg.*, **59**, 187-215.

³ *Z. Biol.*, **52**, 47-77.

⁴ *Z. physiol. Chem.*, **58**, 295-330.

⁵ *Compt. rend.*, **66**, 552; **68**, 201-207; **145**, 577; **147**, 1320.

⁶ *Biochem. Z.*, **5**, 110-42.

⁷ *Milchwirtsch.*, **5**, 154-155.

acidity was raised from 30 to 40 per cent. in different specimens. With milk 2 hours after milking, kept at 104° F. for 2 1/2 hours, there was no change in the acidity.

The results of these investigations would indicate that acidity to within a limited degree influences the more rapid curdling of the milk by the rennin, but whether the increased acidity is directly of bacterial origin or due to a change in the acidity of the phosphates, will have to be proved by further investigation.

Standardized Rennin to Control Milk Used for Testing the Activity of Rennin.—To control the variability of milk for the assay of rennin it was found necessary to prepare a standard rennin to show whether the milk was fast or slow. This rennin was standardized by testing its action upon not less than 12 different specimens of milk, as daily supplied from a reliable source, and the average taken. Thus, if the rennin is standardized to 1 : 30,000 in 8 minutes, its use as a control with the rennin to be assayed readily shows whether the milk is fast or slow, and allowance is made accordingly. The rennin should be added to the milk as soon as it has the temperature of 104° F., for a longer time before the rennin is added makes it curd more rapidly.

Permanency of Rennin Solutions.—Aqueous solutions of rennin of a density 1.010, containing 0.20 per cent. by volume hydrochloric acid, lost 30 per cent. of their activity in one day at a temperature of 70° F. More concentrated solutions of a density 1.090 per cent., containing 1.30 per cent. by volume hydrochloric acid, were more permanent. Elevation of temperature causes more rapid destruction. The denser the solution, the slower the destruction at an elevated temperature.

Essence of Pepsin.—The results here obtained would suggest the use of the granular scaled rennin and of phosphoric acid in place of lactic acid in the preparation of essence of pepsin. Investigations concerning the making of a permanent rennin preparation are now under way.

BROOKLYN, N. Y.

MICRO-CHEMICAL TESTS FOR THE IDENTIFICATION OF SOME OF THE ALKALOIDS.

By EARL B. PUTT.

Received January 29, 1912.

Though the use of certain precipitants for detecting alkaloids has been quite general for a long time, the characteristics of the precipitates so produced do not seem to have received the study which they deserve.

Most schemes of analysis employ these general precipitants to detect the presence of alkaloids and then rely upon various color tests to identify any particular alkaloid, without subjecting the first precipitate to any further examination. If the color tests which are, at present, so extensively applied were always satisfactory and distinctive, there would be little value attached to any other system of identification. But most analysts are familiar with the fact that, in order to secure these color reactions so generally relied upon,

the alkaloids being tested must be in a fairly high state of purity, since the original tests were applied to pure alkaloids: that, in "shaking out" alkaloids by means of immiscible solvents, there is always a considerable amount of foreign matter present in the alkaloidal residue which interferes with many color reactions.

Then again it must be recalled that colorations produced with metallic and many other substances are reactions of the reagent employed and not of the alkaloid. An example of this may be cited in the tests for morphine and codeine with selenous acid.

Finally, the amount of material required to perform a series of color tests on an alkaloidal residue is frequently many times greater than the entire available sample.

A survey of the standard tests for alkaloids indicates that cocaine is the only alkaloid commonly identified by micro-chemical means. The characteristics of its precipitates with such reagents as chromic acid, platinic chloride and potassium permanganate are familiar to all toxicologists and are relied upon for identifying that alkaloid.

While but few alkaloids can be precipitated as easily and in such peculiar forms as cocaine, yet it is safe to predict that a number of very satisfactory tests may be employed in a similar manner for the identification of other alkaloids. With this idea in mind, the writer has been engaged, during the past two years, in an investigation of the precipitates produced by about forty of the alkaloids with some of the common alkaloidal reagents.

The method of procedure differs slightly from that usually employed, in that solution of the alkaloid is made directly on a microscope slide and not in a test tube or flask. In making a microscopic examination of crystals, it is entirely unnecessary to make a solution in a test tube and then use but a few drops for testing. It is also important whether a precipitate is produced in a test tube, the crystals filtered off and then placed on a slide or whether precipitation is made directly on the slide and the precipitate viewed at once through the microscope. The significance of this point will be shown later. A moment's consideration ought to show also that it is just as easy to work with a milligram of alkaloid dissolved in a drop of solvent on a slide as to prepare a 1-100 solution and then use only a drop of the dilution. Moreover, the practical analyst does not have available the large amounts usually prescribed for many of the tests and if he identifies a given alkaloid with a 10 mg. sample that is his good fortune.

In every case the method of procedure in precipitating the alkaloids was the same and essentially as follows: Using a teasing needle or glass rod, transfer a fragment of the alkaloid to a perfectly clean glass slide and drop upon it, from a burette, one drop of $N/10$ HCl. By tapping the end of the slide with the finger, sufficient agitation of the liquid is produced to effect solution of the alkaloid. When all is dissolved, add from a dropping bottle a drop of the appropriate reagent and, without stirring or otherwise

disturbing the mixture, place on the stage of a microscope and examine under the low power. In general, it may be said that the solution of alkaloid must be of such concentration that precipitation on the slide takes place immediately when the precipitant is added. By noting the rate of solution in the acid this may be readily determined in the first trial. If no precipitation takes place at once, set the slide aside protected from dust and make a new precipitation using not necessarily more alkaloid, but a smaller quantity of solvent, in order to obtain a more concentrated solution. In all cases except when using iodine as the precipitant it is advisable to use a slight excess of precipitant, *i. e.*, so that after precipitation the supernatant liquid has a distinct color of the precipitant. In general, it may be stated that when using iodine, only a fraction of a drop of solution should be added in order to secure a crystalline precipitate free from large masses of amorphous precipitate which obscure and prevent the coalition of compound crystals. The reagents used to secure the crystals shown in the accompanying photomicrographs were as follows: *N/10* iodine, 10 per cent. platinic chloride solution and 5 per cent. palladous chloride solution.

It is well to note that when crystallizing on a flat surface, there will often be fern-like crystal forms along the edge of the field which are due simply to evaporation of liquid and distortion due to the flat surface. The crystals shown in the accompanying photomicrographs were all formed within five minutes after precipitation took place.

ALKALOIDS PRODUCING CHARACTERISTIC CRYSTALS WITH IODINE.

Morphine (Plate 1).—Even the smallest drop of *N/10* iodine solution produces instantly a dense red-colored precipitate which when viewed at once appears perfectly amorphous under the microscope. Within about a minute, however, the agglutinated masses begin to separate and disclose shining red plates which overlap each other and often extend a third of the distance across the field. In some cases they assume a branch-like appearance but the individual plates can be clearly distinguished.

Codeine (Plate 2).—This alkaloid yields an amorphous precipitate at first as in the case of morphine, but the crystals eventually formed appear much more slowly. Always of a yellow color (never red) they first appear as little blade-like needles which slowly grow in size and send out little branches. The clusters finally formed are much smaller than those of dionin.

Dionin (Plate 3).—This alkaloid (ethylmorphine) is closely related to the above, which is methylmorphine, and as we might expect gives a precipitate very similar to codeine. Here again the crystals are yellow in color, but they are quickly formed, frequently at the first precipitation, and are much larger and more branching than those produced by codeine. If the solution of alkaloid is quite concentrated, a number of compound crystals are sometimes formed which, though much smaller, are very similar to the crystals

yielded by the alkaloid heroin with platinic chloride (Plate 14).

The other alkaloids of the morphine group, heroin, apomorphine and narcotine yield amorphous precipitates with iodine which do not become crystalline.

Atropine (Plate 4).—This alkaloid, though yielding oily, amorphous precipitates with a large number of

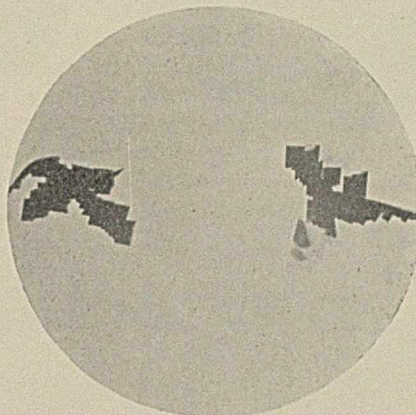


PLATE 1.

MORPHINE WITH *N/10* IODINE X 40.

reagents, forms quite readily a crystalline precipitate with iodine. When first precipitated, the field is simply filled with minute, red, oily globules. After about a minute, however, these little globules begin to elongate and within a few seconds after that process has begun, the entire field is covered with very small red crystals. The latter are fairly uniform in size and show a tendency to form small clusters, though they never unite to form large masses.



PLATE 2.

CODEINE WITH *N/10* IODINE X 40.

ALKALOIDS PRODUCING CHARACTERISTIC CRYSTALS WITH PALLADOUS CHLORIDE.

Morphine (Plate 5).—In a concentrated solution this reagent produces beautifully characteristic clusters of sheaves of crystals with morphine. They are light brown in color and in some cases form so dense a cluster as to appear almost spherical. If the solution is dilute, there is no precipitation at first, but if the slide is observed through the microscope, one may presently see an occasional cluster or bundle of crystals along the edge of the drop. These crystals thus observed along the edge are always much larger than

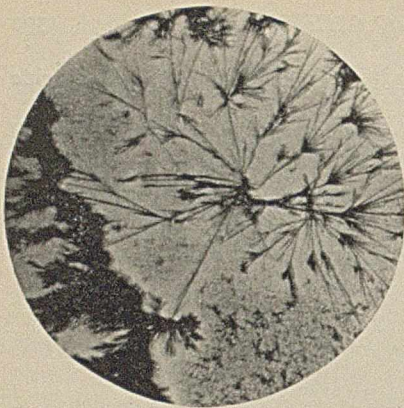


PLATE 3.
DIONIN WITH N/10 IODINE X 40.

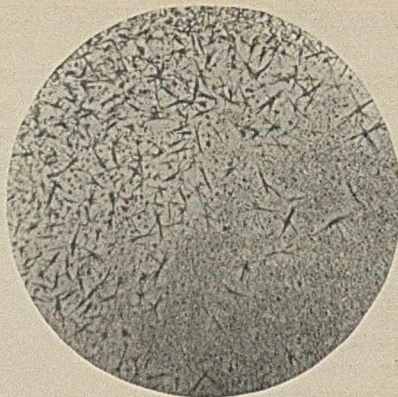


PLATE 4.
ATROPINE WITH N/10 IODINE X 40.

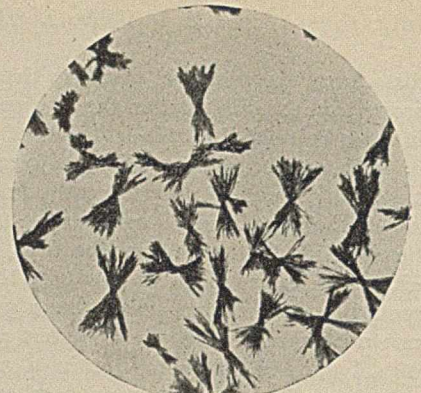


PLATE 5.
MORPHINE WITH PALLADOUS CHLORIDE X 40.

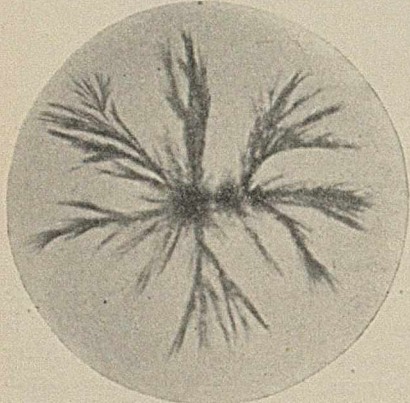


PLATE 6.
CODEINE WITH PALLADOUS CHLORIDE X 40.

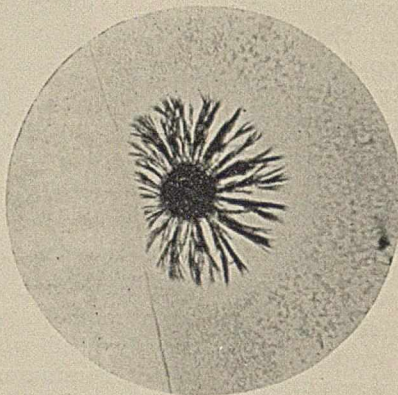


PLATE 7.
CODEINE WITH PALLADOUS CHLORIDE X 40.

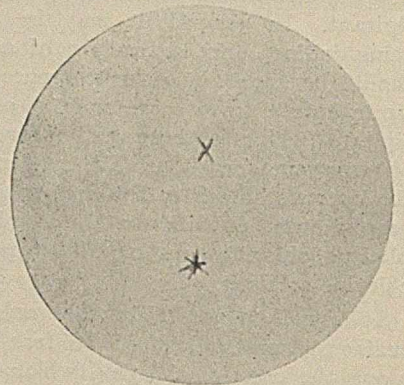


PLATE 8.
 β -EUCAINNE WITH PALLADOUS CHLORIDE X 40.

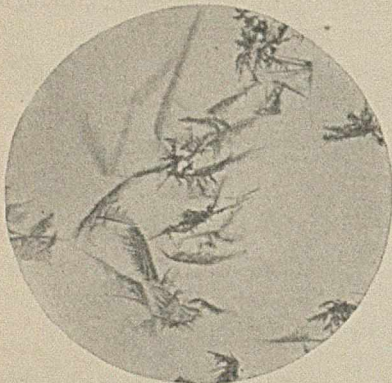


PLATE 9.
COCAINE WITH PLATINIC CHLORIDE X 40.

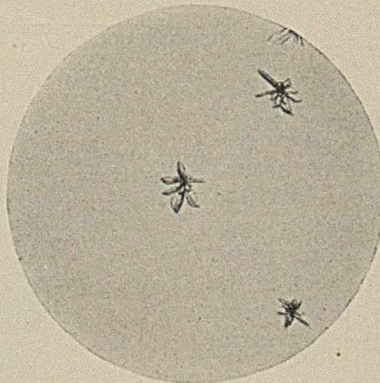


PLATE 10.
 β -EUCAINNE WITH PLATINIC CHLORIDE X 40.

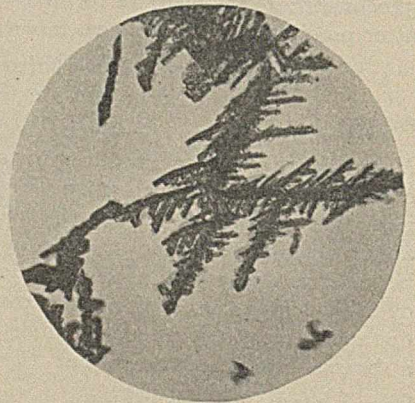


PLATE 11.
NICOTINE WITH PLATINIC CHLORIDE X 40.



PLATE 12.
ANTIPYRINE WITH PLATINIC CHLORIDE X 40.

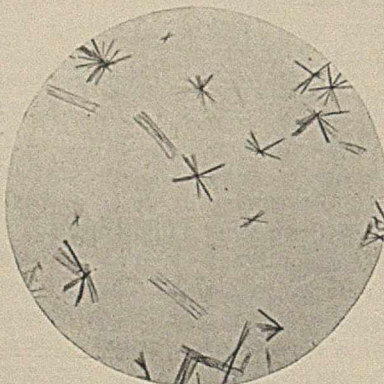


PLATE 13.
STRYCHNINE WITH PLATINIC CHLORIDE X 40.

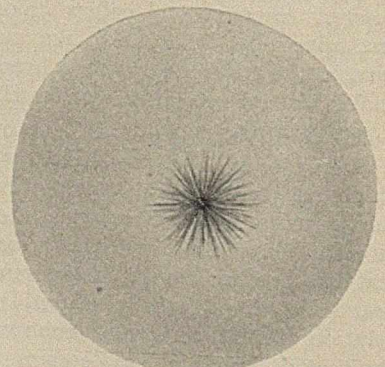


PLATE 14.
HEROIN WITH PLATINIC CHLORIDE X 40.

those formed in the center of the drop by reason of concentration due to creeping and evaporation. Whenever this first crystal makes its appearance, however, in this as in all other similar tests, it is usually but a few seconds till a number of other similar crystals make their appearance in other parts of the field. The first one is therefore a good index of the kind of crystal to follow. Though codeine sometimes forms a somewhat similar type of crystals, the latter rapidly grow in size and all tend toward the spherical form.

Codeine (Plates 6 and 7).—This alkaloid forms very peculiar crystals with palladous chloride which rapidly change in appearance. As first precipitated there appear a large number of light brown crystals which are clustered needles arranged in a spherical form very like the crystals of heroin with platinic chloride. This form is transient, however, and the crystals begin to grow in size and density till they assume the appearance shown in Plate 7. When the precipitate is not extremely dense, the crystal still continues to grow and needles become more divided and branching (Plate 6). The latter figure shows the compound crystal in its final form which is decidedly different from that first produced. The behavior of this crystal shows clearly the advantage of watching the development and growth of these crystals from the time the precipitation is first made.

Beta-Eucaine (Plate 8).—Though crystallization is relatively slow, this alkaloid forms highly characteristic crystals of a deep yellow color. The figure represents crystals formed from a concentrated solution. If they were permitted to remain undisturbed they would grow to a size almost twice that shown in the figure. The crystals are very distinct and seldom have more than eight branches.

ALKALOIDS PRODUCING CHARACTERISTIC CRYSTALS WITH PLATINIC CHLORIDE.

Cocaine (Plate 9).—This plate is introduced, not with the idea of presenting a new reaction, but for the purpose of emphasizing the importance of viewing alkaloidal precipitates when first formed. The accompanying photograph was taken immediately after the precipitant was added to the alkaloidal solution, and shows the highly characteristic, feathery crystals by which cocaine may be readily identified. But there is a vast difference in the appearance of these crystals at the end of even a few minutes after precipitation. They lose their delicate structure and while of course retaining a semblance of their former outline, they become more dense and show heavy spines where at first were only delicate feather-like processes. It is significant that while cocaine is the only alkaloid which produces these delicate, feathery crystals, yet other alkaloids also produce precipitates with platinic chloride which are very similar to the large heavy crystals into which the cocaine crystals are gradually transformed. A notable example of this is the alkaloid nicotine (see below).

Beta-Eucaine (Plate 10).—This alkaloid yields, with platinic chloride, crystals which resemble a cluster of little golden flower petals and are highly characteristic.

They do not in the least resemble those produced by the near relative of this alkaloid, cocaine. The precipitate, at first amorphous, slowly becomes crystalline and the crystals stand out in bold relief.

Nicotine (Plate 11).—The precipitate which this yields with platinic chloride is often so similar to a large dry crystal of cocaine under similar conditions that they can scarcely be distinguished. It is important to note, however, that the nicotine precipitate takes place only in neutral or faintly acid solution and is soluble in acids. The cocaine precipitate is of course insoluble. The point is well worth remembering when one is examining a preparation of tobacco for the presence of cocaine. When making quick precipitations one may frequently produce crystals with nicotine and platinic chloride as small as those shown in Plate 9, and on the other hand cocaine when precipitated with platinic chloride and the crystals allowed to become dry will often yield crystals very like those shown for nicotine (Plate 11).

Antipyrine (Knorr's) (Plate 12).—Though a synthetic compound which does not occur in nature, yet this well known artificial alkaloid yields, as one might expect, a precipitate with platinic chloride. The crystals are yellow and branching, often quite feathery in appearance.

Strychnine (Plate 13).—This alkaloid forms almost instantly with platinic chloride a great number of characteristic crystals. The peculiar chisel-shaped crystals of strychnine are present and these rapidly assemble to form a cluster. The interesting thing about them is that the clusters are scarcely formed till they suddenly fly apart again, leaving only a number of individual needles. When viewed under the microscope the crystals seem curiously unstable and active. The field is in constant motion with the union and dissolution of clusters. In order to secure a satisfactory photomicrograph, one must almost take a "snap shot." Such crystal forms could never be noted by viewing the dry crystals, filtered from an ordinary precipitation.

Heroin (Plate 14).—This alkaloid, diacetylmorphine, yields with platinic chloride crystals which are as characteristic as those for cocaine. The precipitate as first formed is perfectly amorphous and remains so for fully a minute. Within usually a minute or two, there appear at numerous places on the field, clear circular spaces in the amorphous mass in which are small clusters of needle-like crystals, one cluster in each space. The cluster grows quickly both in size and number of needles until it presents the appearance of a golden yellow spherical mass of spines. Frequently a chain of these clusters will extend across the field. Curiously enough, when the crystal has attained its full size, the needles begin to fly off from the main body as in the case of strychnine, but not so rapidly. These little spines keep splitting off, usually in pairs, until the whole cluster is disintegrated and finally there is nothing left of the original symmetrical cluster but its center, an orange yellow cube of platinic chloride.

The above test is infallible for this alkaloid and is

applicable to the extract obtained after subjecting the alkaloid to the usual "shaking-out" treatment with immiscible solvents, since heroin is not thus decomposed.

Of the common alkaloids which yield *amorphous* precipitates, under the above conditions, with palladium chloride may be mentioned the following: Apomorphine, physostigmine, nicotine, heroin, dionin, narcotine, hydrastine and arecoline.

Amorphous with iodine: Heroin, caffeine (neutral solution), alypin, emetine, narcotine and hydrastine.

Amorphous with platinic chloride: Morphine, atropine, quinine, coniine, codeine, hydrastine, dionin, alypin, aconitine, apomorphine and physostigmine.

With these and other reagents many of the alkaloids yield crystals which are fully as characteristic as those illustrated above. But these will serve to indicate the results which may be obtained.

In many cases, several distinct types of crystals are formed successively by the same precipitate, and such a series of changes has an additional value in determining the identity of any particular alkaloid.

A number of the above alkaloids have been identified by the above reagents in actual unknown samples, and all others have been subjected to the usual scheme of extraction and tests applied to the alkaloidal extract thus obtained. In every case, a satisfactory test was secured on the first extract without necessitating any further purification of the alkaloidal residue.

When not otherwise stated, the photomicrographs here shown were taken when the crystal had just attained its full size and before there was any appreciable evaporation of mother liquor from the slide.

Though the writer is fully aware that it is not customary to mix strong solutions in order to secure satisfactory crystallizations yet the method here employed minimizes the frequency of formation of rosette- or cluster-forms of needles, so common in concentration of an alkaloidal solution. It should be borne in mind, however, that many reagents will throw alkaloids out of solution, not by the formation of insoluble double salts, but by a "salting-out" action. Many of the slightly soluble alkaloids, such as strychnine, are thus easily precipitated when a drop of salt solution is added to the alkaloidal solution on the slide. When thus precipitated, the alkaloids show a pronounced tendency to assemble in needle clusters, and this behavior is not to be confused with the formation of a true double salt.

The tendency of a number of the alkaloids to form a series of crystal forms may explain, in part at least, the extreme variability of results obtained when volumetric solutions of alkaloidal precipitants are used for the quantitative estimation of alkaloids. If the solution of the alkaloid is fairly concentrated, most of the precipitate is amorphous and slowly becomes crystalline; if dilute, the tendency is toward a crystalline precipitate at once; and the two varieties of precipitate are not, of necessity, identical in composition.

DEPARTMENT OF PHARMACY,
NORTH DAKOTA AGRICULTURAL COLLEGE.

AN IMPROVED METHOD OF ASSAY FOR AROMATIC SULFURIC ACID.¹

By LINWOOD A. BROWN.

Received January 17, 1912.

During the examination of some samples of aromatic sulfuric acid, it was noticed that all the samples were running abnormally low in sulfuric acid, so much so that it made us think that possibly the method might be at fault. Consequently, we began some experiments on the method of assay for this preparation, the results of which are given in this paper, and which we believe will be of some interest to pharmaceutical chemists.

Aromatic sulfuric acid is a mixture of strong sulfuric acid, alcohol, tincture of ginger and oil of cinnamon, and is described by the U. S. P. as follows: "Should contain not less than 20 per cent. by weight, of absolute sulfuric acid, partly in the form of ethyl-sulfuric acid."

The consensus of opinion appears to be that ethyl-sulfuric acid is formed even at ordinary temperature when strong alcohol and sulfuric acid are mixed; also that it is hydrolyzed on heating with water or alcohol, but with the exception of Kastle and Frazer, no one seems to have studied its quantitative decomposition by hydrolysis.

It appears to be generally thought that the decomposition must be complete when heated with water, and it appears that the Revision Committee of the U. S. P. 8th held this opinion, for the present method of assay is based upon that theory. The first edition of the U. S. P. 8th, in the assay of this preparation required it to be boiled with 30 cc. water "for a few minutes;" the later editions, "with additions and corrections to June 1, 1907," extend this time of heating to 4 hours. Ethyl sulfuric acid is stated to be more easily decomposed than its salts, in fact the salts of this acid are considered as not being hydrolyzed on heating. This view is contradicted by the work of Kastle and Wilkie² in their work "On the

TABLE A.

No.	Time of heating.	Cc. of H ₂ O.	Per cent. H ₂ SO ₄ . U. S. P. Method.
1	4 hours	30	18.40
2	4 "	30	18.40
3	None	..	13.35
4	2 hours	30	15.44
5	4 "	30	16.81
6	6 "	30	17.83
7	8 "	30	19.02
8	4 "	30	16.81
9	4 "	60	16.46
10	4 "	90	16.35
11	4 "	120	15.77
12	4 "	150	15.53
13	4 "	300	14.81

TABLE B.

No.	Per cent.		Total H ₂ SO ₄ .	Gms. BaSO ₄ (direct).	Time of heating.	BaSO ₄ (addition).	Date of assay.
	free H ₂ SO ₄ .	H ₂ SO ₄ as ethyl-sulfuric.					
14	16.89	3.29	20.18				7/1/11
15	6.92	12.81	19.73				12/6/11
16	6.94	12.86	19.80				
17	6.95	12.59	19.54	0.1518	1 hour	0.0033	
18	6.98	13.05	20.03	0.1509	2 hours	0.0048	
19	7.00	12.99	19.99	0.1520	3 hours	0.0044	
20	6.94	12.82	19.76	0.1503	4 hours	0.0046	

¹ Presented at A. C. S. Meeting at Washington, D. C., December, 1911

² Unpublished—Thesis for B.S. degree, Ky. State Univ., 1904.

Decomposition of Barium Ethyl Sulfate." They, however, were studying the effect of the halogen salts upon the barium ethyl sulfate, which has very little bearing upon the conditions present in this paper.

The salts of ethyl sulfuric acid are soluble; even the barium salt is soluble, while any free sulfuric acid is precipitated as the sulfate, the barium ethyl sulfate remaining in solution. It is upon this feature that we have endeavored to work out a method for the determination of the total sulfuric acid in the aromatic sulfuric acid, U. S. P.

METHOD OF ANALYSIS.

After making up my standard sample of aromatic sulfuric acid, containing a known amount of sulfuric, I then assayed it by the U. S. P. method with the results shown in Exps. 1 and 2, and did not recover all of the sulfuric acid. Now, the next thing to do was to devise a method which would yield the total acid present. After a number of ideas were tested out, we finally decided upon the following method:

A sample of about 10 grams was weighed out and diluted with water to exactly 100 cc.; 10 cc. aliquots were taken and the total acidity determined by titrating against decinormal KOH, using phenolphthalein as indicator. This gave us the acidity due to free sulfuric acid and to ethyl sulfuric acid. The neutralized sample was then diluted to a volume of 100 cc., then quickly heated to boiling over a free flame, 2 cc. hydrochloric acid added, followed by an excess of barium chloride solution; the solution was boiled for an additional minute or two, then placed on the water bath and heated for one hour. The precipitate of BaSO₄ was filtered off, washed well, ignited and weighed.

CALCULATION OF RESULTS.

Grams BaSO₄ × 0.42 = grams H₂SO₄ in form of free sulfuric acid, divided by 0.0048675 = cc. of decinormal KOH required to neutralize free sulfuric acid.

Cc. N/10 KOH consumed in total acidity determination, minus cc. equivalent of free H₂SO₄ equals cc. N/10 KOH required to neutralize ethyl sulfuric acid.

As ethyl sulfuric acid is a monobasic acid, multiply the number of cc. for ethyl sulfuric by 2 × 0.0048675 × 10 × 100 and divide by weight of sample, equals per cent. of sulfuric acid in sample in the form of ethyl sulfuric acid.

Grams free sulfuric × 10 × 100, divided by weight of sample equals per cent. of free sulfuric.

This method was tried out on the standard sample, with the results shown in Exps. 14-16.

In samples that have been allowed to stand several months a small amount of the sulfuric acid is converted into the di-ethyl sulfate and which is not determined by this method; this, however, is very small, amounting to only about 0.4 per cent. H₂SO₄ in five months, under the conditions existing in the U. S. P. preparation.

In 1898, Kastle and Frazer, in an unpublished work (Thesis for Master of Science degree, Ky. State Univ.), studied the hydrolysis of sulfuric ethers, and came to the conclusion that ethyl sulfuric acid is hydrolyzed to a greater extent in concentrated than in dilute solutions.

Experiments 8-13 show the effect of dilution upon the hydrolysis of ethyl sulfuric acid, the time of heating being constant throughout the series.

Experiments 3-8 show the effect time of heating has upon the hydrolysis, the dilution remaining constant throughout the series.

In order to see what effect heating would have upon the barium ethyl sulfate, in separating the free sulfuric from the ethyl sulfuric acid in the proposed method, Experiments 17-20 were run as follows:

After the sample was neutralized by the standard alkali, rendered acid by hydrochloric and an excess of barium chloride added, the sample was heated on the water bath for 20 minutes, or just long enough to enable us to filter off the precipitated barium sulfate, after which the filtrates were heated for 1, 2, 3, and 4 hours longer, and any additional barium sulfate formed was filtered off and weighed up separate from the main bulk of the precipitate. Reference to Table B will show that practically no hydrolysis of the barium ethyl sulfate took place, as the small amount of barium sulfate obtained after heating remained fairly constant. The author believes that the additional amount of barium sulfate, thus obtained, was largely, if not entirely, due to the difficulty of removing the finely precipitated barium sulfate after only 20 minutes' heating, and not to any hydrolysis of the barium ethyl sulfate.

Table C shows the analysis (by both the U. S. P. and the proposed method) of some samples of aromatic sulfuric acid, as found in drug stores.

TABLE C.
Brown's method.

Experiment No.	Per cent.	Per cent.	Per cent.	Per cent.
	H ₂ SO ₄ .		free H ₂ SO ₄ .	
33,860	14.46	8.35	10.94	19.29
33,862	15.28	7.71	14.74	22.45
33,884	12.50	6.12	9.47	15.59
33,887	14.87	6.43	13.82	20.25
33,889	18.79	13.45	12.60	26.15
33,894	16.44	8.37	12.96	21.33
33,910	16.69	6.72	14.14	20.86
33,970	17.63	7.77	15.30	23.07
33,974	18.14	6.93	14.58	21.51

CONCLUSION.

1. The U. S. P. method of assay does not give the total amount of sulfuric acid present.
2. Ethyl sulfuric acid is hydrolyzed to a greater extent in concentrated than in dilute solutions.
3. The hydrolysis of ethyl sulfuric acid is not complete, even after 8 hours' heating, but does increase with the length of time of heating.
4. That a small amount of di-ethyl sulfate is formed after a few months in the aromatic sulfuric acid, and is not determined by either the U. S. P. or by the proposed method.
5. That the proposed method of assay gives more accurate results, closely approaching the theoretical amount of sulfuric acid present.
6. That the proposed method of assay shows the

amount of esterification that has taken place in the sample.

7. That barium ethyl sulfate is not hydrolyzed in dilute slightly acid aqueous solution, to any appreciable extent.

In conclusion, I wish to give credit to J. M. Humble for his assistance to me in conducting the experimental part of this work.

KENTUCKY AGRICULTURAL EXPERIMENT STATION.

A METHOD FOR ASSAYING SPIRITS OF CAMPHOR.

By ARTHUR T. COLLINS.

Received February 29, 1912.

Spirits of camphor can be assayed, and the percentage of camphor very accurately determined, by the use of the polariscope. It has been long known that camphor is optically active, some camphors rotating the plane of polarization to the right, and some to the left. The amount of this deviation will vary in camphors coming from different localities, or even from the same locality.

Most camphors are dextro gyrate, a 10 per cent. solution giving in a 200 mm. tube an angle of 8°, more or less. In order to know the percentage of camphor in a solution, it will be necessary to know the rotation angle of the particular camphor that was used in making up the solution. This can be done by taking 50 cc. or more of the spirits of camphor, and evaporating on a water bath; by this operation the camphor can be obtained free from alcohol or moisture. Of course there is a considerable loss of camphor, often as much as 30 to 40 per cent. but the camphor that remains has exactly the same rotation as the original.

The camphor obtained by evaporation on the water bath contains all the non-volatile impurities that were in the original solution, and in order to get rid of these, the camphor is transferred to a watch glass of about 7 or 8 cc. diameter, having for a cover a glass funnel of the same diameter—both funnel and watch glass having ground edges. The apparatus is placed over a low flame, and the camphor sublimed on to the funnel.

We have now the pure camphor that went to make up the original solution. This is made up to a 10 per cent. solution in a 25 cc. volumetric flask, and used as a standard for the determination of the camphor in the spirits of camphor in question. The method is very accurate and the entire operation may be accomplished in two hours time.

Using camphors from different sources made up to 10 per cent. solutions, the results are as follows:

	Rotation in minutes.	Per cent.
Sample A.....	482.8	9.94
Control.....	485.3	
Sample B.....	488.5	10.003
Control.....	488.3	
Sample C.....	492.5	10.01
Control.....	491.7	

If the original gum camphor has been impure, or if optically active substances have been added to increase the rotation, these may be found on the watch glass, after the camphor has been sublimed, and can then be weighed or investigated.

In case sugar has been added, this will be found by evaporating in a drying oven at a temperature of 105° C. After all smell of camphor is gone the sugar should be made up to volume with water, and the amount of rotation deducted from the optical rotation of the original spirits.

The entire method is as follows:

Polarize in a 200 mm. tube, making correction for temperature by adding 1/2 minute for every degree C. above 20° C., and deducting same amount below 20° C. Take the mean of 10 readings, place 50 cc. or more of the spirits in an evaporating dish on water bath, using cold air jet if convenient, to facilitate evaporation. Just before the camphor solidifies, stir with glass rod, so that it may become dry as soon as possible. When quite dry place on watch glass having funnel cover, over a low flame, with wire gauze between, and fitting closely to the bottom of the watch glass.

When the camphor is entirely sublimed, remove the pure camphor from the funnel, take 2 1/2 grams of this, make up with alcohol in a 25 cc. flask, polarize as in the first case; this is called the "control." The percentage is found by dividing the minutes of rotation of the control into minutes of rotation of the original sample, multiplied by ten.

SWARTHMORE, PA.

SUGGESTED MODIFICATIONS TO THE U. S. P. ASSAY OF OPIUM.¹

By R. NORRIS SHREVE.

Received January 17, 1912.

The Pharmacopoeia directs for the determination of Morphine, an aqueous extraction of the opium, concentration of these extracts, precipitations of the morphine from a weak alcoholic solution, and determination of the impurity in the precipitated morphine by weighing of the substance insoluble in lime-water. As thus carried out the method gives results that are not accurate. There are the following sources of error:

1. Incomplete extraction of the opium.
2. Retention of morphine by the mother liquor during precipitation.
3. Inaccuracies in the lime water method for determination of the impurities in the precipitated morphine.

INCOMPLETE EXTRACTION OF THE OPIUM.

The Pharmacopoeia directs for the extraction: Agitation every ten minutes (or continuously in a mechanical shaker) during three hours, followed by filtration, washing, re-agitation, and re-washing. In case of certain opiums this procedure will not exhaust the opium of its morphine as is shown in Table I.

Comment on Table I.—The three samples of opium were of Turkish grade and of a moderately fine powder. In every case ten grams were used for assay. Instead of determining the purity of the crude morphine by the lime water method as the U. S. P. directs, the more accurate but slightly longer Mallinckrodt

¹ Presented at the A. C. S. Meeting at Washington, D. C., December, 1911.

TABLE I.

No.	Outline of extraction, U. S. P. Method except as indicated.	Weight of crude precipitated morphine. Grams.	Purity of crude by Mallinckrodt re-assay. ¹ Per cent.	+ correction for solubility of morphine in U. S. P. mother liquors. Grams.	Pure morphine. Per cent.
Opium sample 1.					
1	In mechanical shaker for 8 hrs.	1.5875	94.6	0.052 0.024	0.076
	Marc of preceding reextracted.....	0.3185			
2	Extracted 3 times in shaker.....	1.909	93.0	0.0635	18.39
3	Opium triturated in mortar, then put in shaker; marc of preceding re-extracted.....	1.6265	94.6	0.060	13.02
		0.125			
4	Extracted shaker; Lamar ² modification applied.....	1.3125	88.7	0.055	19.16
5	Opium + 45% lime, extracted, acidified; Lamar modification applied.....	2.097			
Opium sample 2.					
6	In mechanical shaker for 8 hours.....	0.988	90.6	0.050	9.45
7	Duplicate.....	1.030	91.8	0.51	9.96
8	In very rapid shaker for 12 hours.....	1.623	89.3	0.060	15.11
Opium sample 3.					
9	In mechanical for 8 hours.....	0.914	91.3	0.051	8.86
10	Duplicate.....	0.960	91.1	0.051	9.26
11	In very rapid shaker for 8 hours.....	1.668	89.6	0.052	15.46
Opium sample 4.					
12	In mechanical for 8 hours.....	0.987	93.7	0.051	9.76
13	Duplicate.....	0.990	91.4	0.051	9.56
14	In very rapid shaker for 8 hours.....	16.55	90.6	0.052	15.51

¹ Proc. A. O. A. C. 23rd convention, Bur. Chem., *Bull.* 105, 128 (1906).

² *Am. J. Pharm.*, 71, 36 (1900).

re-assay was used. This re-assay is carried out as follows:

Morphine up to 2 grams is mixed with 0.5 gram of freshly slaked lime, and 18 cc. of water added, rotated occasionally during half an hour, filtered without suction (suction causes foaming), and washed with lime water until the filtrate weighs 35 grams; 3 cc. of alcohol added, flask rotated; 20 cc. of ether added, flask rotated again; finally 0.5 gram of ammonium chloride added, and the flask shaken for ten minutes; set aside for 2 hours (or over night) for the morphine to precipitate. Morphine filtered and washed, in the manner which the U. S. P. directs in case of the crude morphine. Correction for the morphine soluble in alcoholic mother liquors is determined by blank assay on pure morphine. The "+ correction for solubility of morphine in U. S. P. mother liquors" was obtained likewise by running a blank precipitation, but of course under the conditions parallel to the U. S. P. assay.

The opium of sample 1 was not completely exhausted of its morphine by the aqueous extraction, as is readily seen from Experiments 1 to 4 of Table I. However, in Experiment 5, which was a lime assay, the opium was exhausted as determined by test on the marc. The details of this experiment are as follows: 10 grams opium were mixed with 4.5 grams of lime, and triturated with 100 cc. water for several hours, filtered and washed with water sufficient to make filtrate measure 150 cc.; re-triturated and re-washed; filtrate acidified with dilute hydrochloric acid, concentrated, and inorganic matter, etc., thrown out by alcohol (Lamar Modification, *Loc. cit.*); alcohol evaporated and morphine precipitated as U. S. P. directs.

The opium of samples 2, 3 and 4 was exhausted of only about $\frac{2}{3}$ of its morphine by gentle mechanical shaking for 8 hours. By employing a mechanical shaker making three strokes a second, it was possible to exhaust the opium.

Such being the case with some opiums, I always

test the marc for completeness of extraction; for this, the following test is satisfactory: Wash the marc with an additional 100 cc. of water; evaporate the filtrate to about 2 cc., filter, add 4 cc. of washed ether, and ammonia to faint alkalinity. If the morphine was not all exhausted in the regular extraction, it will precipitate here in well defined crystals which give the characteristic color reactions. The precipitation is facilitated by scratching the inside of the test tube with a glass rod. I suggest that opium always be tested for completeness of extraction of its morphine, and that the Pharmacopoeia Revision Committee embody some such test as the one just given in the official method, with directions to repeat the assay using more vigorous shaking and more washing in case the test shows morphine in the marc. This repeating will be generally necessary, as by the time the result of the test is obtained the morphine in the assay will have been precipitated, since it is not worth while to wait for a test which will indicate morphine in the marc in only an occasional opium.

In case of the U. S. P. powdered opium, the substances used by the manufacturers to standardize the opium often retard the extraction of the morphine, so that in assay of opium of this kind, it is especially necessary to apply tests to determine completeness of extraction. Because of this difficulty of extracting some opiums, an aliquot part method for the assay of this drug is not advisable as one could never be sure of the relative amount of morphine in that part taken for assay.

RETENTION OF MORPHINE BY THE MOTHER LIQUORS DURING PRECIPITATION.

It is well known that the alcoholic mother liquors employed during the precipitation of the morphine hold in solution some of the morphine. This has been pointed out by many workers especially in the co-operative work on opium assaying, done during the leadership of the Bureau of Chemistry.

The amount of pure morphine retained by solvents present when the morphine is precipitated in the

U. S. P. assay is easily obtained by dissolving one and one-half grams of morphine in 5.5 cc. *N/1* sulfuric acid and water sufficient to weigh 20 grams; then precipitate under the conditions of the U. S. P. Table II gives results of such blank precipitations.

TABLE II.

No.	Amt. of morphine taken.	Amt. of morphine recovered.	Amt. of morphine retained by mother liquors.	Temperature during precipitation.
	Grams.	Grams.	Gram.	Centigrade.
1	1.500	1.459	0.041	0°
2	1.500	1.443	0.057	20°
3	1.500	1.428	0.072	26°
4	1.500	1.426	0.074	26°

Comment on Table II.—In case of No. 4, instead of dissolving the morphine in 5.5 cc. of normal acid, there was used 16.5 cc. to ascertain if the decrease of free ammonia and the increase of ammonium salts would have an appreciable effect on the morphine retained; the result shows no effect. The length of time for precipitation was over night, though for the blanks themselves one or two hours is sufficient.

The corrections for solubility of morphine in Table I were determined by such blanks run parallel to the opium precipitation. There is no doubt, however, that the extractive matter in opium has an influence on the amount of morphine thus retained. To obtain some evidences on this point the following experiments were conducted:

Two assays were run: No. 1 on 10 grams of opium in the regular way; No. 2 on 100 grams of opium, using 10 times the quantities of solvents, etc. Both assays were precipitated under the same conditions: No. 1 gave 1.624 grams of crude morphine, re-assaying 80.2 per cent. pure and, hence containing 1.302 grams pure morphine; No. 2 gave 16.007 grams of crude morphine, re-assaying 81.1 per cent. pure, and hence contained 13.0 grams pure morphine. Thus both gave the same percentage of morphine.

The mother liquors of No. 2, the 100 grams assay, were analyzed for morphine by this method: Made slightly acid, evaporated, mixed with excess of slaked lime and the cake exhausted of its morphine. The lime water filtrates were extracted with benzole to remove non-phenolic alkaloids, then acidified, evaporated to small volume, alcohol added to throw out inorganic matter, filtrates plus washings heated to drive off alcohol. Now morphine completely extracted with amyl alcohol, after making alkaline; amyl alcohol extracted with 10 per cent. sulfuric acid, and morphine precipitated by ammonia. The purity of this morphine was determined by Mallinckrodt re-assay: result, 1.15 grams of morphine alkaloid which remained dissolved in the mother liquors. This corresponds to 0.115 gram for regular U. S. P. mother liquors. A parallel blank on pure morphine indicated a correction of 0.069 gram, so it is apparent that in this case the extractive plus the solvent present held back considerably more morphine than is represented by the dissolving power of the solvents themselves.

This analysis of the U. S. P. mother liquors was very tedious, yet it should be carried on the mother liquors of assays from a number of different opiums before we can say just how much morphine is retained in the precipitation mother liquors. The

chloroform alcohol method of Eaton¹ could probably be used and would be simpler.

Of course it would be better to use an immiscible solvent method for the assay of morphine and thus avoid altogether this retention of the morphine in the mother liquors of the U. S. P. assay. I have successfully used an amyl alcohol extraction, but the method is tedious and long. It gives results agreeing with the modified U. S. P. method as was used for the assays of Table I.

The chloroform alcohol extraction method of Eaton looks very promising, but I would suggest, because of the difficulty in extracting opium, that instead of an aliquot part extraction of the opium, a complete lime extraction be employed. This indeed works very nicely, and to carry it out I mix with the opium 40 per cent. of its weight of lime and extract with lime water. Furthermore it would be advisable to collect a sufficient quantity of the morphine from the evaporation of the chloroform alcohol, and compare the purity by titration against the accurate Mallinckrodt re-assay (run with blank to determine morphine in the mother liquors).

INACCURACIES IN THE LIME WATER METHOD FOR DETERMINATION OF THE IMPURITIES IN THE PRECIPITATED MORPHINE.

These inaccuracies were pointed out by Kebler in the above-mentioned coöperative work under direction of the Bureau of Chemistry. My experience has been that the lime water method gives results that are from 3-7 per cent. higher than the truth, the error varying with the nature and amount of impurity with morphine. This variation in the impurity depends on the sample of opium and the treatment it has been subjected to, such as temperature during and upon the conditions of the assay.

The only satisfactory method for the determination of the purity of crude morphine in the U. S. P. and similar assays is the Mallinckrodt re-assay. Two objections have been brought against this method, namely (a) time involved, (b) correction for morphine in mother liquors.

In the hands of several chemists, whom I have observed, the extra time necessary over that required by the lime water method is the 15 or 20 minutes it takes to filter and wash the precipitated morphine from the re-assay. On the other hand it is neither essential to use counterbalanced or tared filter papers for filtration of the crude morphine, nor is it worth while to dry the crude morphine. After washing the crude morphine, suck it nearly dry, and then remove it to a small Erlenmeyer flask for solution in excess of lime, and filter through the same filter paper.

The corrections for morphine dissolved in the re-assay mother liquors can readily be obtained from blanks on pure morphine. This correction varies with temperature and slightly with individual manipulation. After a series of corrections for the conditions are determined, it is no longer essential to run a blank as the variations under ordinary conditions are relatively small. Table III gives a series

¹ *Bur. Chem., Bull.* 137, 188 (1910).

of blanks for different temperatures. The morphine used was purified by twice crystallizing from Columbian spirits and the alkaloid obtained by precipitating a solution of sulfate of morphine.

TABLE III.

No.	Amt. of morphine. Grams.	Amt. of morphine recovered. Grams.	Amt. of morphine retained by mother liquor. Gram.	Temperature during precipitation. Centigrade.
1	1.500	1.482	0.018	17°
2	1.500	1.481	0.019	22°
3	1.500	1.4745	0.0255	27°
4	1.500	1.474	0.026	29°

CONCLUSION.

We have discussed (1) the difficulty of completely extracting morphine from opium; (2) the amount of morphine retained by the alcoholic mother liquors of the U. S. P. method; (3) the determination of the purity of the crude precipitated morphine.

It is suggested (1) that a test always be applied to determine the completeness of the removal of the morphine; (2) that a correction be added for morphine dissolved in the mother liquors of the U. S. P. opium assay, and that provisionally a blank on pure morphine be made to determine this correction; (3) that the Mallinckrodt re-assay be used to determine the purity of the crude morphine.

It gives me pleasure, in connection with this paper, to acknowledge my indebtedness to the Lamar Chemical Works and to the Mallinckrodt Chemical Works.

LAMAR CHEMICAL WORKS,
NEWARK, N. J.

A NOTE ON THE DETERMINATION OF THE DIGESTIVE VALUE OF PAPAIN.

By J. R. RIPPETOE.

Received January 11, 1912.

H. T. Graber in a recent article (THIS JOURNAL, Dec., 1911, p. 919) gives a method for determining the digestive value of papain, using fine ground steak in 0.3 per cent. hydrochloric acid solution and comments as follows: "Some manufacturers claim that the test should be conducted in an alkaline media and that egg albumen should be used instead of raw beef; but to me this seems as absurd as to claim that pepsin should be tested upon starch in an alkaline media."

For several years this laboratory has employed a method for determining the digestive value of papain using egg albumen in an alkaline media. It might be of interest to note some results obtained by this method.

Method.—Prepare egg albumen as directed under pepsin assay U. S. P. 8th revision. Introduce into a 4-oz. wide-mouth flint bottle 40 cc. of a 0.1 per cent. sodium hydroxide solution and add 10 grams of the disintegrated albumen; stopper the bottle and shake vigorously until the albumen is broken up. Then add the papain in fine powder and mix by shaking gently for 15 seconds. Place the bottle in a water bath previously heated to 52° C. and digest at this temperature for 6 hours, removing the bottle every 10 minutes and shaking gently for 15 seconds. At the end of this period transfer the mixture to a 100 cc.

graduated stoppered cylinder, rinse the bottle with water, add the rinsings to the mixture and make the volume up to 70 cc. with water. Set the cylinder aside and after standing for 1 hour read off the volume of the deposit. The deposit may be read a second time after standing 16-18 hours (over night) which seems to give more positive results, especially if the volume is large.

The results of the assay of five samples by the above method are recorded in the following tables:

TABLE I.

Sample.	Deposit read after standing	
	1 hr. Cc.	16 hrs. Cc.
Blank.....	52.0	43.0
A 0.1 gram papain.....	26.0	18.0
A 0.2 gram papain.....	8.0	8.0
B 0.1 gram papain.....	41.0	31.0
B 0.2 gram papain.....	36.0	18.0

The blank consisted of 10 grams of the disintegrated albumen in 40 cc. of the alkaline solution without the addition of papain and was carried through the digestion and agitation in the same manner as the tests containing the papain.

Sample A was assayed in an acid media using 0.2 grams of papain in fine powder with the results as shown in Table II:

TABLE II.

	Deposit read after standing	
	1 hr. Cc.	16 hrs. Cc.
0.1 per cent. HCl solution.....	16.0	20.0
0.2 per cent. HCl solution.....	30.0	30.0
0.3 per cent. HCl solution.....	32.0	30.0

TABLE III.

	Deposit read after standing	
	1 hr. Cc.	16 hrs. Cc.
C 0.1 gram papain.....	15.0	12.0
C 0.2 gram papain.....	3.0	5.0
D 0.1 gram papain.....	25.0	23.0
D 0.2 gram papain.....	13.0	12.0

TABLE IV.

	Deposit read after standing	
	1 hr. Cc.	16 hrs. Cc.
C 0.1 gram papain.....	2.0	3.0
C 0.2 gram papain.....	0.8	1.0
E 0.1 gram papain.....	5.0	5.5
E 0.2 gram papain.....	1.0	1.5

It might be said that Sample A, Table I, had twice the digestive value of Sample B, since the deposit from 0.1 gram A was the same as the deposit from 0.2 gram B, reading after 18 hours.

The results shown in Table II indicate that some digestion takes place in 0.1 per cent. HCl but 0.2 or 0.3 per cent. inhibits the action of the ferment.

The variation in the volume of the deposit obtained with Sample C, as shown in Tables III and IV, is possibly due to the varying composition of the albumen of the eggs used, and suggests the advisability of using a standard sample of papain for comparison when making an assay of an unknown sample upon egg albumen.

The method is also applicable for determining the digestive value of pineapple juice. A sample of dry

pineapple juice, using 1 gram of dry juice, neutralized with sodium hydroxide, to 10 grams of the albumen in 35 cc. 0.1 per cent. sodium hydroxide solution, with 3 hours' digestion, left a residue of 2 cc., reading after 18 hours, while a blank read 41 cc.

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THE BROMINE AND IODOMETRIC METHODS FOR THE VOLUMETRIC DETERMINATION OF CRESOL.¹

By C. M. PENCE.

Received January 17, 1912.

Of the several methods suggested for the volumetric determination of phenol, the bromine method has received the most consideration, and in almost every instance where bromine has been used an attempt has been made to substitute iodine in its stead.

The popularity of the bromine method is no doubt due to two causes: First, to the fact that it answers the demand for a reliable method in the determination of the first member of the series, namely, phenol; second, to the ease in manipulation resulting from the use of the Koppeschaar bromine solution.

Now cresol is the next member of the homologous series; however, it presents, upon treatment with bromine solution and acid, problems quite different from that of phenol. Since commercial cresol is a mixture of the three isomeric phenols *o*-, *m*- and *p*-cresol, the presence of the CH₃ group in the different positions necessitates the formation of compounds structurally unlike and empirically the same, and also causes, in the case of meta cresol, the formation of compounds both structurally and empirically different from those formed by *o*- and *p*-cresols. In 2,4,6-tribrom phenol brom, the bromine occupies both the *o*- and *p*-positions. Now in the case of *o*- and *p*-cresol the CH₃ group occupies the *o*- and *p*-positions and only dibromcresol and dibromcresol brom compounds can be readily formed since the CH₃ group is more difficult to replace by free Br than is a hydrogen atom. However, the CH₃ group is slowly replaced and prolonged standing (several days) results in formation of tribromphenol brom—W. Autenrieth and F. Beuttel² have recently published the results of an extensive investigation along this line.

Meta cresol forms tribrom-*m*-cresol brom since the CH₃ group is not in the position that the Br atom would occupy.

H. Ditz and F. Cedivoda³ have proposed a bromine method for cresols depending upon the difference in speed of reactions between bromine and *m*-cresol on the one hand and bromine and *o*- and *p*-cresols on the other. If either *o*- or *p*-cresol is mixed with a known excess of bromine solution, acidified with (1:1) hydrochloric acid and agitated for 1 min., on adding KI and titrating with thiosulfate it will be found that each molecule of *o*- and *p*-cresols has

absorbed 2 atoms of bromine. Under the same conditions each molecule of *m*-cresol will absorb 3 atoms of bromine. Now if acidification is effected by concentrated sulfuric acid, the solution shaken for five minutes and insoluble matter removed by filtration, 3 atoms of bromine will have combined with each molecule of *o*- and *p*-cresol, 4 atoms with each molecule of *m*-cresol.

The above method depends for its success upon definitely fixed conditions; namely: time, strength of acid, excess of bromine, etc. F. Russig and G. Fortmann⁴ have criticized this method and H. Ditz⁵ has replied at length.

The present study of the reaction of bromine and iodine upon the different cresols was made for the purpose of finding which of the cresols were amenable to assay by processes which do not require previous knowledge concerning the percentage of product, that is, by processes dependent upon the formation of definitely fixed, comparatively stable, final products; namely: compounds containing three atoms of bromine in combination.

Samples of the individual cresols were redistilled and volumetric solutions prepared from the distillates, small amounts of *N*/₂ NaOH being added to facilitate solution. Aliquot portions of these solutions were used in the several determinations.

The results appearing in the tables are based upon the formation of dibromcresol brom and tribrom compounds on the one hand and diiodo compounds on the other.

ORTHO CRESOL.									
No.	Cc. Ortho cresol.	Cc. <i>N</i> / ₁₀ Br.	Cc. H ₂ O.	Cc. Conc. HCl.	Time of standing.	Cc. 20% KI.	Cc. Conc. HCl.	Time of standing.	Results. Per cent.
1	20	50	175	5	20 min.	10	—	1 1/2	94.45
2	20	50	175	5	1 1/2 hrs.	10	—	1 1/2	103.5
3	20	50	175	5	1 1/2 hrs.	10	—	2 1/2	102.7
4	20	50	175	5	1 1/2 hrs.	30	—	3 1/2	101.1
5	20	50	275	5	1 1/2 hrs.	20	—	2	100.98
6	20	50	275	5	1 1/2 hrs.	20 ¹	—	2	100.68
7	20	50	275	5	1 1/2 hrs.	20	—	14	99.78
8	20	50	275	5	1 1/2 hrs.	30	—	2	99.98
9	20	50	275	5	1 1/2 hrs.	30	—	3 1/2	100.17
10	20	50	275	5	1 1/2 hrs.	30	—	4 1/2	99.95
11	20	75	275	5	1 1/2 hrs.	20	—	2	109.4
12	15	50	275	5	1 1/2 hrs.	30	—	18	105.15
13	10	50	275	5	1 1/2 hrs.	30	—	18	106.85
14	15	50	275	5	3 hrs.	30	—	5 min	113.3
15	15	50	275	2.5	5 hrs.	30	—	18	106.9
16	10	50	275	2.5	4 hrs.	30	5	20	93.4
17	15	50	275	2.5	5 hrs.	30	5	40	86.22

No.	Ortho cresol. cc.	<i>N</i> / ₁₀ I. cc.	g. CH ₃ COONa 3H ₂ O.	Time of standing.	Procedure.	Per cent. Result.	Excess <i>N</i> / ₁₀ I. cc.
18	25	50	5	30 min.	Diluted, added 5 cc.	93.66	±25
19	25	50	5	1 1/4 hrs.	CHCl ₃ , titrated with	100.04	±25
20	25	50	5	14 hrs.	<i>N</i> / ₁₀ thiosulphate,	100.71	±25
21	25	50	9	1 hr.	using starch as in-	99.93	±25
22	25	50	9	2 hrs.	dicator	100.1	±25

Ortho cresol does not readily form a stable dibrom-*o*-cresol brom or a tribrom compound as is evidenced in Exp. 1. However, upon 1 1/2 hours' stand-

¹ Read at A. C. S. meeting at Washington, D. C., December, 1911.

² "Ueber die Bestimmung des Phenols, Salicyl alkohols, der Salicylsäure und *p*-oxybenzoesäure als Tribrom phenol brom" (Autenrieth and Beutel), *Archiv der Pharm.*, 1910, 112.

³ "Reactions of Bromine with Phenol and the Cresols, a Process for Calculating the Composition of Mixtures Thereof" (Ditz and Cedivoda), *Z. angew Chem.*, 1899, 873 and 897. Abstr.—*Analyst.*, 25, 74.

⁴ "Estimation of Cresol" (Russig and Fortmann), *Z. angew. Chem.*, 1901, 157-60. Abstr.—*J. Chem. Soc.*, 1901, II, 289.

⁵ "Estimation of Cresol" (H. Ditz), *Z. angew. Chem.*, 1901, 160-5. Abstr.—*J. Chem. Soc.*, 1901, II, 289.

³ Heated to 40° C. after addition of KI.

ing more than sufficient Br is absorbed for the formation of these compounds and the addition of 10 to 30 cc. of 10 per cent. KI with from 1½ to 3½ hours' standing does not result in the liberation of the bromine necessary for the formation of either dibrom-*o*-cresol or a tribrom compound as would occur if reaction proceeded in a manner strictly analogous to phenol (Exps. 2, 3, and 4).

Now a greater dilution results in the absorption of a smaller quantity of bromine but results are still too high, Exps. 5 and 6. Increased standing after addition of 20 cc. 20 per cent. KI causes a reversal with practically theoretical quantities of bromine absorbed, the time of standing being materially reduced upon increase in the quantity of KI (Exps. 7, 8, 9 and 10).

An increase in concentration of bromine in contact with *o*-cresol as is effected by larger quantities of Br solution or a decrease in the quantity of cresol solution results in the absorption of much more than the theoretical quantity of bromine and even upon prolonged standing in contact with increased quantities of KI, suitable reversal does not take place (Exps. 11, 12, 13, 14 and 15).

The effect due to increase in the quantity of acid is very marked. When bromine is liberated by one-half the usual quantity of concentrated HCl sufficient reversal does not take place after addition of KI (Exps. 14 and 15). However, when an additional 5 cc. of concentrated HCl are added at the same time as the KI, the reversal causes far less than theoretical quantities of bromine to remain in combination (Exps. 16 and 17).

Thus it will be seen that practical results dependent upon the formation of a dibromcresol brom or tribrom compound can not be obtained except by definitely fixing the several conditions of the experiment in pursuance of which a previous knowledge of the percentage of *o*-cresol is required.

Now when iodine acts upon *o*-cresol, diiodo-*o*-cresol is formed. The reaction is reversible and sodium acetate is added to unite with the hydriodic acid produced by the substituting iodine, thereby causing the reaction to proceed to completeness (Exps. 18, 19, 20, 21 and 22). In this case, the reaction ends with the formation of the diiodo compound, hence it is made the basis of the following method for the determination of *o*-cresol.

Dissolve 2-2.5 g. *o*-cresol in distilled water containing about 10 cc. *N*/10 NaOH to facilitate solution. Dilute to 1000 cc. Withdraw 25 cc. portions and place in a 500 cc. glass stoppered receptacle. Add to the receptacle approximately 9 grams sodium acetate and then 50 cc. *N*/10 I solution. Let stand 1 hour, dilute with 100-200 cc. distilled water, add a few cc. of CHCl₃ to dissolve the precipitated diiodocresol and titrate with *N*/10 thiosulphate, using starch as an indicator.

1 cc. *N*/10 I = 0.002681 g. *o*-cresol.

Meta cresol does not rapidly form tribrom-*m*-cresol brom with the subsequent formation of tribrom-*m*-cresol upon standing in contact with KI

META CRESOL.

No.	Cc. Meta cresol.	Cc. <i>N</i> /10 Br.	Cc. H ₂ O.	Cc. Conc. HCl.	Time of standing.	Cc. 20% KI.	Cc. Conc. HCl.	Time of standing.	Result.
1	20	50	-	5	1 min.	10	-	1 hr.	97.9
2	20	50	-	5	½ hr.	10	-	2 hrs.	98.48
3	20	50	-	5	1 hr.	10	-	1 hr.	99.2
4	20	50	-	5	1½ hrs.	10	-	2 hrs.	99.9
5	20	50	175	5	½ hr.	10	-	2 hrs.	99.6
6	20	50	175	5	1½ hrs.	10	-	2 hrs.	100.07
7	20	50	175	5	3 hrs.	10	-	18 hrs.	99.93
8	20	50	175	5	6 hrs.	40	-	18 hrs.	99.81
9	15	50	175	5	6 hrs.	10	-	5 min.	101.11
10	15	50	175	5	6 hrs.	10	-	½ hr.	100.5
11	15	50	175	5	6 hrs.	10	-	½ hr.	100.2

No.	Cc. Meta cresol.	Cc. <i>N</i> /10 I.	g. CH ₃ COONa 3H ₂ O.	g. NaHCO ₃ .	Time of standing.	Procedure.	Result.	Per cent.
12	25	40	9	-	1 hr.	Diluted, added about 5 cc.	118.5	
13	25	40	-	0.5	1 hr.	CHCl ₃ and titrated	122.0	
14	25	40	-	2.0	1 hr.	with <i>N</i> /10 thiosulphate, using starch	130.0	
15	25	50	-	2.0	2 hrs.	indicator.	155.0	
16	25	50	9	-	2 hrs.		152.0	

(Exps. 1, 2 and 3). If the *m*-cresol solution stands 1½ hours in contact with the bromine and then 10 cc. 20 per cent. KI are added and solution is allowed to stand 1 to 2 hours, all the cresol is converted into tribrom-*m*-cresol (Exp. 4).

Dilution permits a more rapid reaction which almost completes itself in ½ hour. The addition of KI causes a complete reversal even though the time of standing in contact with free bromine has been much prolonged (Exps. 5, 6, 7, 8, 9, 10 and 11).

It is thus apparent that *m*-cresol may be determined by a conversion into the tribrom compound.

Upon the other hand, when iodine¹ acts upon *m*-cresol in the presence of sodium acetate or sodium bicarbonate, a diiodo compound that may be made the basis of calculation is not produced. More than the theoretical quantity of iodine is absorbed (Exps. 12, 13, 14, 15 and 16).

PARA CRESOL.

No.	Cc. Para cresol.	Cc. <i>N</i> /10 Br.	Cc. H ₂ O.	Cc. Conc. HCl.	Time of standing.	Cc. 20% KI.	Cc. Conc. HCl.	Time of standing.	Result.	Per cent.
1	20	50	275	5	1 hr.	10	-	2 hrs.	81.1	
2	20	50	275	5	4½ hrs.	10	-	18 hrs.	95.73	
3	20	50	-	5	4½ hr.	10	-	18 hrs.	76.35	
4	15	50	275	2.5	3 hrs.	10	-	5 min.	97.34	
5	15	50	275	5	1½ hrs.	30	-	18 hrs.	89.73	
6	10	25	200	2.5	3 hrs.	10	-	18 hrs.	101.8	
7	10	25	200	2.5	3 hrs.	20	-	18 hrs.	101.75	
8	10	25	200	5 hrs.	3 hrs.	10	-	18 hrs.	97.7	
9	10	25	200	2.5	8½ hrs.	10	-	16 hrs.	104.6	
10	10	25	200	2.5	4 hrs.	30	5	20 hrs.	84.94	
11	10	25	200	2.5	5 hrs.	30	5	40 hrs.	82.90	

No.	Cc. Para cresol.	Cc. <i>N</i> /10 I.	g. CH ₃ COONa 3 H ₂ O.	Time of standing.	Procedure.	Result.	Excess.
12	25	30	9	1 hr.	Diluted, added 5 cc.	98.81	25
13	25	30	15	1 hr.	CHCl ₃ , titrated with	99.56	25
14	25	40	9	1 hr.	<i>N</i> /10 thiosulphate,	99.75	25
15	25	50	9	1 hr.	using starch as in-	99.75	25
16	25	50	9	2 hrs.	dicator.	99.75	25

¹ "Preparations of Iodo Derivatives of Phenol" (E. Richard), *J. Pharm. Chem.*, 1902, 15 [5] 217-221. Abstr.—*J. Soc. Chem. Ind.*, 1902, 423. "New Class of Iodated Phenols" (Messenger and Vortmann), *Ber.*, 22, 2312-2322. Abstr.—*J. Chem. Soc.*, 1889, 1150.

Para cresol absorbs bromine much more slowly than either of the other cresols. Under similar experimental conditions, 4 $\frac{1}{2}$ hours' standing in contact with free bromine results in absorption of only 95.73 per cent. of the theoretical quantity (Exps. 1, 2, and 3). If concentration of free bromine is increased and the usual quantity of HCl decreased one-half, the bromine in combination exceeds the amount necessary for the formation of a dibrom-*p*-cresol brom or tribromcresol compound and 18 hours' standing does not result in sufficient decomposition even though the quantity of KI is doubled (Exps. 4, 5, 6, 7, 8 and 9).

However, an increase in both HCl and KI results in a most pronounced reversal¹ which is due to the decomposition of dibrom-*p*-cresol brom into dibrom-*p*-cresol (Exps. 10 and 11).

Here again the result is directly dependent upon conditions and previous knowledge is necessary on part of the operator.

Now when iodine reacts with *p*-cresol in presence of the condensing agent, sodium acetate, diiodo-*p*-cresol is formed in theoretical quantity if sufficient time is allowed for reaction to complete itself.

This reaction is made the basis of a method for the determination of *p*-cresol (Exps. 12, 13, 14, 15 and 16). The procedure is exactly the same as that given under *o*-cresol.

SUMMARY.

1. Usual bromine methods for determination of cresol depend upon fixed conditions presupposing a previous knowledge on the part of the operator, and while they may be of service they do not satisfy the demand for a desirable method.

2. Tribrom-*o*- and *p*-cresol brom compounds can not be formed in a manner analogous to the production of 2,4,6-tribrom phenol brom. Dibromcresol brom compounds are formed and finally tribromphenol brom; however, *o*- and *p*-cresols can not be determined volumetrically by a conversion into these compounds.

3. Meta cresol is determined by a conversion into tribrom-*m*-cresol.

4. Ortho and para cresols form diiodo compounds, and this reaction is made the basis of a method for their determination.

5. Meta cresol does not yield diiodo compounds under the same conditions; hence, cresol U. S. P. or any mixture containing *m*-cresol can not be determined by a volumetric iodine method.

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THE ACCURATE VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID IN PHOSPHATE ROCK.

By JOHN G. FAIRCHILD.

Received January 30, 1912.

The method of determining the phosphoric acid content of phosphate rock here described is a modification of Pemberton's caustic alkali titration, which

has the great advantage of being quicker than other volumetric or gravimetric methods. The difficulty experienced in the use of the Pemberton method has been invariably a low result compared with that obtained by the standard method of weighing the phosphoric acid as magnesium pyrophosphate. After close observation of the successive operations whereby the yellow precipitate is dissolved in an excess of standard alkali and this excess titrated after addition of a few drops of phenolphthalein, it was noticed that the final end point was considerably delayed, and this was the more marked the greater the amount of phosphoric acid present or the larger the aliquot parts taken.

In the belief that if this behavior of the indicator toward phosphoric acid could be overcome the method would be very accurate, the suggestion of Sutton² was adopted, namely, to precipitate out the phosphoric acid with barium chloride in excess before titrating the excess of alkali. The results stated below show how the method is improved by this modification.

In the first place low results being obtained in dealing with phosphate rocks by standardizing the alkali solution against microcosmic salt in the old way, it was thought possible that the other salts in the rock solution interfered with the titration. A rock solution whose phosphoric acid content was accurately determined gravimetrically was taken as the standard. The average of four results (32.69, 32.82, 32.88 and 32.93) obtained by using different aliquot² parts of a 2 gram solution was found to be 32.83 per cent. P₂O₅. Double precipitations were made after weighing the first precipitate, any calcium sulfate or silica being removed by its solution in sulfuric acid with alcohol. The second weights were only 0.1 to 0.3 mg. less, so that this correction could be disregarded.

The next step was to take an aliquot part, preferably 0.1 gram, add 20 cc. of strong ammonia (sp. gr. 0.90), make acid with 1 : 1 nitric acid, and add slowly 25 cc. of warm molybdate solution (about 40° C.). The temperature of formation of the yellow precipitate here is most important, the limits being 45° to 55° C. After shaking for five minutes the precipitate is let stand till cool, then filtered through a 9 cm. No. 590 S. & S. paper and washed, once with a 2 per cent. nitric acid solution and then with a 2 per cent. potassium nitrate solution till the washings cease to redden blue litmus. Paper and precipitate are then transferred to the original flask and dissolved in an excess of standard alkali; diluted slightly with cold water; three drops of phenolphthalein solution are added and one drop of methyl orange (to give a sharper end point). Excess of alkali is then titrated with standard acid, either nitric or hydrochloric. Next, about 8 cc. excess of alkali are again added and 10 cc. of a 10 per cent. solution of neutral BaCl₂, which is usually sufficient to precipitate all the phosphate, the molybdate, and also any carbonate. The important feature is the elimination of the phosphate. After again titrating the excess of alkali the two readings show 32.6 cc. and 33.1 cc. The results of several

¹ *Volumetric Analysis*, 9th Ed., p. 113.

² Pipettes used were standardized to the flask.

¹ "Zur Quantitativen Bestimmung des Phenols und Parakresols in Gemischen derselben und ihre Anwendung auf den Harn," *Pharm. Zentralhalle*, 1911, 1288.

determinations gave this difference of 0.5 cc. Dividing the amount of P_2O_5 present, 0.03283 gram, by 32.6 and by 33.1 gives two values per cubic centimeter, namely, 0.001007 and 0.000992 gram P_2O_5 , a difference of 1.5 per cent.

Again, taking the value per cubic centimeter as 0.001007 gram P_2O_5 and multiplying this by 33.1, the correct number of cubic centimeters required for 0.1 gram of the standard rock solution, the percentage of P_2O_5 found is 33.33, which is 0.51 per cent. too high in P_2O_5 , or a 1.5 per cent. actual error corrected by the use of $BaCl_2$.

A solution of microcosmic salt was then prepared by dissolving 2.088 grams in some water containing 40 cc. 1 : 1 nitric acid and diluting to 500 cc. Several portions of 25 cc., equivalent theoretically to 0.03546 gram P_2O_5 , were taken and their content, determined gravimetrically, was found to be 0.03575 gram P_2O_5 . Exactly the same value was found by using 50 cc. of solution. A volumetric determination was now made on 25 cc., which required 35.5 cc. of alkali, barium chloride not being used. Excess of alkali was again added with 10 cc. of $BaCl_2$ and the excess titrated. The result of the second titration was 36.0 cc. Multiplying the value of the alkali solution previously obtained against the standard phosphate rock we have $36.0 \times 0.000992 = 0.03571$ gram P_2O_5 , which is the exact amount taken for analysis. If the first burette reading is used we have $35.5 \times 0.000992 = 0.03522$ gram P_2O_5 , a difference of 0.5 per cent. of P_2O_5 , or 1.5 per cent. actual error, as before.

Although this calculation proves that microcosmic salt can be safely used in standardizing the alkali solution, still, in order to show more strongly that such salts as calcium nitrate have no effect on the titration figure, sufficient pure dry calcium carbonate was added to the nitric acid solution of the microcosmic salt to form tricalcium phosphate with all the phosphoric acid. The same aliquot portions were taken, precipitated, and titrated with these results: without $BaCl_2$, 35.5 cc.; after addition of $BaCl_2$, 36.0 cc. These check the results first obtained.

The value of the alkali solution having in this way been fixed very accurately, analyses of a series of eight phosphate rocks (from different localities in order that all probable variations might occur in the composition of the rock solution) were made in the regular way by both volumetric and gravimetric methods. Two grams of the rock powder were put with a little water in a small covered casserole and digested on the steam bath with 40 cc. of 1 : 1 nitric acid for 20 minutes or more. The filtered solution

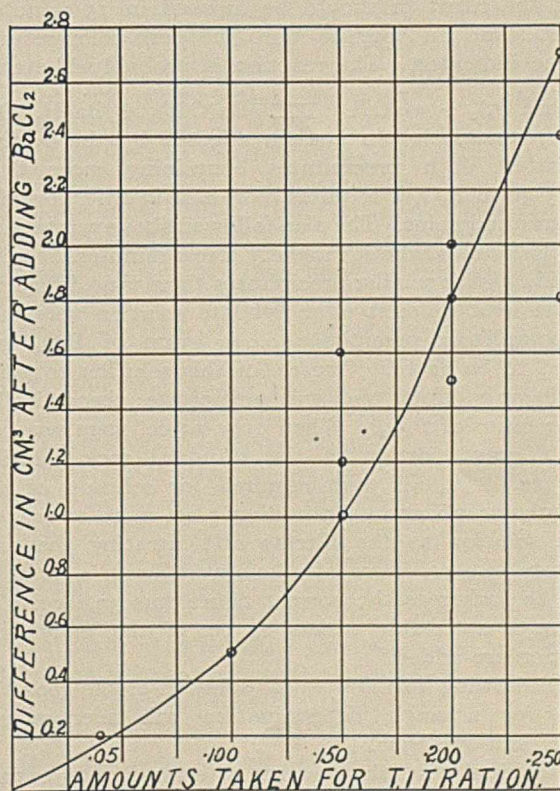
Volumetric, per cent.	Gravimetric, per cent.	Differences.
31.68	31.70	-0.02
25.42	25.74	-0.32
31.79	31.99	-0.20
14.40	14.34	+0.06
24.83	24.67	+0.16
20.66	20.42	+0.24
24.43	24.49	-0.06
37.82	37.93	-0.11
		Sum, -0.25

Average difference = 0.03 per cent.

was made up to 200 cc., a portion amounting exactly to 0.1 gram being taken for the volumetric and 0.5 gram for the gravimetric determination. In the preceding table will be found the results of single determinations.

Examination was next made of the insoluble residues. Four of these were combined and the papers were ashed in a large platinum crucible and fused with sodium carbonate. Silica was removed by evaporation of the acidified solution in a porcelain dish, the residue taken up with hot 1 : 1 nitric acid, and test made for P_2O_5 . Only a trace was found. The papers of the second four were ashed, the silica volatilized with HF and H_2SO_4 , the HF being practically all expelled by repeated evaporation on the steam bath. After oxidation with HNO_3 , filtration, addition of ammonia and about 10 grams of NH_4NO_3 , the P_2O_5 found after dividing by 8 was 0.05 per cent. Several other tests have been made of residues insoluble in hot dilute nitric acid and only once was as much as 0.10 per cent. found, the usual result being no more than a trace.

The curve below shows the effect of $BaCl_2$ on the titration when increasing amounts of phosphate solution are used.



These are the actual percentages:

Portions (gram).....	0.04	0.100	0.150	0.200	0.250
With $BaCl_2$	33.02 ¹	32.84	32.84	32.84	32.84
Without $BaCl_2$	32.50	32.34	32.14	32.14	32.01

The following results compare the two methods just described, the old method of weighing the yellow precipitate direct, and Blair's method² of reducing the molybdic acid followed by titration with $KMnO_4$.

¹ Single determination. About 0.2 per cent. high. See curve.

² *Analysis of Iron*, 6th Ed., p. 92.

The factor used for P_2O_5 in the ammonium phosphomolybdate was 0.03782. The yellow precipitate was washed well with 2 per cent. nitric acid and dried in a porcelain Gooch crucible at $125^\circ C.$ to constant weight.

Weighed as ammonium phosphomolybdate.		
	Gram.	Per cent. P_2O_5 .
Portion taken.....	0.250	32.66
Fresh sample.....	0.500	32.70

REDUCTION METHOD.		
Portion taken.		
Gram.	Per cent. P_2O_5 .	
0.025	32.94	
0.050	32.94	
0.050	32.51	
0.050	32.51	

Blair's reduction method¹ gives accurate results when extreme care is taken to wash the yellow precipitate entirely free from the molybdate precipitant. Inasmuch as the portion taken here is very small, any slight difference in cubic centimeters of $KMnO_4$ used is multiplied by a large factor four times the factor for the caustic alkali titration. A difference of 0.35 cc. on a 0.05 gram portion gives a difference of 0.40 per cent. in P_2O_5 content.

It is important to bear in mind that the barium phosphate precipitate hydrolyzes rather rapidly, so that the titration should be finished in 15 minutes. If let stand an hour or more the pink color returns to the indicator. The reaction is probably like this:

$$\ddot{B}a_2(\ddot{H}P\ddot{O}_4)_2 + 2\ddot{H}O\ddot{H} \rightleftharpoons \ddot{B}a(\ddot{O}H)_2 + \ddot{B}a(\ddot{H}_2P\ddot{O}_4)_2$$

The phenolphthalein is then affected by the barium hydrate. With precipitates containing more than 0.035 gram P_2O_5 it requires more care in order to strike the true end point. The plan followed above was to close the flask and shake it violently a few minutes, keeping it cold. With smaller precipitates there is no difficulty.

The least amount of molybdate solution necessary to completely precipitate 0.030 gram of P_2O_5 was found to be 20 cc. One cc. of this solution contains 0.048 gram MoO_3 and will precipitate, theoretically, 0.002 gram of P_2O_5 . When only 15 cc. were used on a 0.1 gram portion of the standard rock solution 25.5 cc. of alkali were required for solution of the phosphomolybdate. On adding 5 cc. more of molybdate solution to the filtrate and titrating the precipitate, 7.2 cc. more of alkali were used, a total of 32.7 cc., whereas the correct figure was 33.1 cc. To insure a noticeable excess 25 cc. of the molybdate solution are added.

By allowing 20 minutes for solution of the rock the time for a single determination will average not more than one hour.

As a final test, the amount of error due to expansion of the standard solutions was fixed. A standard alkali solution was transferred to a 100 cc. flask up to the mark and its temperature taken. The solution was then heated exactly 10° and the rise in volume noted on the neck of the flask. This increment was then withdrawn by a pipette and its value found by running in from a burette enough to reach the top mark again. This difference due to $10^\circ C.$ was found to be 0.2 cc., an error altogether negligible.

¹ Factor $MoO_3 : Fe$, 0.85714.

In conclusion, it is seen that the greatest accuracy possible by the gravimetric method is 0.50 per cent., or 0.15 per cent. of the P_2O_5 content, and it varies to 0.75 per cent., or 0.25 per cent. P_2O_5 . The accuracy of the caustic alkali method is a trifle over 1 per cent. actual error, or a difference of 0.30 per cent. P_2O_5 in the rock.

STANDARD SOLUTIONS.

Caustic Alkali.—31 grams of the C. P. soda sticks dissolved in water and diluted to 2 liters: 1 cc. equals about 0.001 gram P_2O_5 . The small amount of CO_2 present, about 0.12 per cent., is negligible.

Nitric Acid.—Practically a 2 per cent. solution which is diluted till 1 cc. equals 1 cc. alkali solution.

Phenolphthalein.—A 1 per cent. alcoholic solution.

Methyl Orange.—A 0.1 per cent. solution.

Molybdate Solution.—100 grams MoO_3 , 144 cc. NH_4OH (sp. gr. 0.90), and 271 cc. H_2O ; 489 cc. HNO_3 (sp. gr. 1.42) and 1.148 cc. H_2O .

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THE DETERMINATION OF TOTAL MANGANESE IN SOILS.

By ROSS A. GORTNER AND CLAYTON O. ROST.

Received January 25, 1912.

INTRODUCTION.

It is a well-known fact that the gravimetric estimation of small quantities of manganese, such as occur in rocks or soils, is highly inaccurate even when great care is used. The inaccuracy may be caused by a number of factors, including incomplete separation from the iron and aluminium, incomplete precipitation, and contamination of the precipitate by other substances. These errors, because of the small amounts of manganese present, can not be depended on to balance each other.¹ The usual method which is now employed is to determine the manganese colorimetrically after oxidation to permanganic acid. Various means of effecting this oxidation have been employed. The oldest method is the oxidation of the manganese in nitric acid solution by the addition of lead peroxide.² This material proved unsatisfactory owing to the necessity for the removal of the excess of the lead peroxide, which settled very slowly.

Acting on the suggestion of Marshall,³ Walters⁴ substituted ammonium persulfate for the lead peroxide. All of Walters' determinations were made either on steel, pig irons or blast furnace cinders. This method was later adopted by Hillebrand⁵ and Washington⁶ for the determination of total manganese in rocks.

Essentially the method consists in decomposing the rock powder in a platinum basin by means of hydrofluoric and sulfuric acids, expelling the excess of hydrofluoric acid by repeated evaporation with small amounts of sulfuric acid, evaporating almost to dryness, diluting with 1 : 1 nitric acid, filtering, and

¹ See Hillebrand, *Bull.* 422, 116, U. S. Geol. Survey.

² Pichard, *C. R. acad. sci.*, Dec. 30, 1872.

³ Marshall, *Chem. News*, 83, 76 (1901).

⁴ Walters, *Ibid.*, 84, 239 (1901).

⁵ *Loc. cit.*

⁶ Washington, "The Chemical Analysis of Rocks," Wiley and Sons, N. Y., 1910.

oxidizing the manganese to permanganic acid by the addition of ammonium persulfate. The permanganic acid solution is then diluted to a known volume and the color read against a solution of known strength in a colorimeter.

In applying this method to Nebraska soils, following the detailed directions of Washington¹ we have found that in many cases we could not obtain concordant results on duplicate determinations, the variation between duplicates being sometimes as much as two hundred per cent. Brinton² has already noted that in some iron ores the treatment with sulfuric and hydrofluoric acids does not give complete extraction of the manganese, and we have found that this is the case with all of the soils which we have investigated. In most of these soils, three, and in some cases four, extractions with hydrofluoric and sulphuric acids were necessary before all of the manganese was obtained in solution. Inasmuch as each extraction requires nearly three hours, it will be seen that to accurately determine manganese in soils by this method is a very tedious operation. We have, therefore, endeavored to devise a method which is much more rapid, more accurate, requires less attention, and eliminates all fumes of hydrofluoric acid or sulfur trioxide. The smaller amount of platinum required in the process is also a decided advantage.

As an oxidizer we have used sodium bismuthate instead of ammonium persulfate, inasmuch as it gives a better oxidation, always giving the true permanganate color while the persulfate oxidation often produces a reddish tint that is difficult to read accurately. Blair³ and Brinton⁴ seem to recognize the superiority of the "bismuthate" oxidation by stating that "for samples containing not over 2 per cent. of manganese the bismuthate is the most accurate method known." Walters⁴ states that the persulfate oxidation does not always progress smoothly for when the salt is dry "the reaction is very incomplete and irregular and not to be depended on", a fact that is not mentioned in the description of the method by Hillebrand or Washington. By moistening the persulfate much more concordant results are obtained, but we have found that the bismuthate is much more reliable than the persulfate. In some instances we were unable to oxidize all of the manganese by means of ammonium persulfate but when these same solutions were reduced with sulfurous acid and reoxidized with bismuthate the correct percentage of manganese was obtained. The bismuthate method has the added advantage over the persulfate in that it is not necessary to add silver nitrate to catalyze the reaction.

EXPERIMENTAL.

The Estimation of Manganese in Soils by Walters' Method.—The soil, which had been ground to pass through bolting cloth of 0.1 mm. mesh, was treated with hydrofluoric and sulfuric acids as described by

Washington¹ and the manganese determined in the extract. The first part of Table 1 shows the results which were obtained on eight different soils. Soil number 3490 was selected to determine whether or not all of the manganese was rendered soluble with one extraction, and it was found that in some instances four extractions were necessary to completely remove all traces of manganese. In those samples where several extractions were made, the total amount of manganese obtained was nearly a constant, but even in these there is too great an error for exact work, for, although the maximum difference between duplicates is only 0.010 per cent., this error represents almost ten per cent. of the total manganese present.

The Estimation of Manganese in Soils by our Method.

—One gram of soil is intimately mixed with four grams of manganese-free, dry, sodium carbonate and fused in a 20 cc. platinum crucible over a blast lamp until the melt is quiet, usually after about ten minutes' fusion. The liquid mass is then poured into a platinum basin and the basin rotated in order to obtain the melt in a thin film, thus providing for more rapid solution. The melt and the crucible are then treated with about 100 cc. of distilled water and heated on a water bath in either a platinum or a porcelain dish² until the fused product is completely disintegrated. The crucible is then removed from the dish, any adhering solution washed off, and the mixture acidified with 130 cc. of 35 per cent. (by weight) sulfuric acid³ and diluted to 250 cc. Should there be a heavy precipitate of silica at this point it is advisable to filter, using a Büchner funnel and filtering by suction. This is seldom necessary, however, for in most cases the silica does not precipitate to any extent, but merely produce a slight opalescence which does not interfere with the permanganate readings. One hundred cc. of this solution are then placed in a beaker and from 0.25 gram to 1 gram of sodium bismuthate added, depending on the quantity of manganese present. We have found that 0.25 gram is sufficient where the manganese content does not exceed 0.20 per cent. The oxidation mixture is then heated to boiling and the boiling continued until the liquid has the true permanganate tint. If there is any red coloration the boiling has not been continued long enough. The solution is then cooled and read in a colorimeter or Nessler's glasses against a standard solution of permanganic acid which has been prepared by reducing a solution of potassium permanganate in 20 per cent. sulfuric acid by the cautious addition of sulfurous acid, and reoxidizing with bismuthate. This standard solution should contain about 0.2 mg. of MnO per 10 cc. From the ratios thus obtained the quantity of manganese in the original sample

¹ *Loc. cit.*

² Glass should not be used inasmuch as the alkali might attack the glass and dissolve out some of the manganese which is present in most laboratory glass, including Jena apparatus. See Gortner, *Am. Chem. J.*, 39, 157 (1908).

³ This excess of sulfuric acid is employed inasmuch as the oxidation progresses more rapidly and basic bismuth salts do not precipitate. The same results may be obtained when half of this quantity of acid is used, but the oxidation requires several minutes' boiling and the permanganic acid solution must be filtered through asbestos in order to free the solution from precipitated bismuth salts.

⁴ *Loc. cit.*

² Brinton, *THIS JOURNAL*, 3, 237 (1911).

³ Blair, *J. Am. Chem. Soc.*, 26, 793; also *Chem. Anal. of Iron*, 7th Ed., p. 121.

⁴ *Loc. cit.*

is calculated. After a little practice, the complete operation can be carried out in an hour and a half, so that in this respect alone the method is greatly to be preferred.

When duplicate determinations are desired only one fusion is necessary, for two separate oxidations may be taken from the total 250 cc. In the data which are given in the last column of Table 1 each figure represents a separate fusion and oxidation, and in the sixteen determinations, representing duplicate fusions on eight different soils, the maximum difference between duplicates amount to only 0.002 per cent. No determinations were discarded in compiling this table.

TABLE 1.—PERCENTAGE OF MnO FOUND BY WALTERS' METHOD AS DESCRIBED BY WASHINGTON, AND BY OUR NEW METHOD.

Exp. No.	Soil No.	Walters' method, MnO in extractions I-IV.				Total.	Authors' method.
		I.	II.	III.	IV.		
1	3490	0.082	0.020	0.004	trace	0.106	0.109
2	3490	0.080	0.027	0.005	?	0.112	0.111
3	3490	0.060	0.042	trace	?	0.102	
4	3490	0.095	0.013	trace	?	0.108	
5	3490	0.095	0.013	trace	?	0.108	
6	3490	0.064	0.016	not			
7	3490	0.046	0.029	determined			
8	3486	0.045		not determined			0.107
9	3486	0.052					0.105
10	3487	0.018					0.111
11	3487	0.028					0.110
12	3488	0.020					0.111
13	3488						0.112
14	3489	0.025					0.120
15	3489	0.031					0.119
16	3491	0.044					0.123
17	3491	0.044					0.125
18	3483	0.060					0.096
19	3483	0.060					0.098
20	3459	0.033					0.067
21	3459						0.067

SUMMARY.

1. We have found that Walters' method for the determination of small quantities of manganese, as described by Washington and Hillebrand, is not applicable to Nebraskas soils, but that in some instances four extractions on a one-gram sample with hydrofluoric and sulfuric acids were necessary before all of the manganese was obtained in solution.

2. We have found that when such soils are fused with sodium carbonate and the solution of this melt is acidified with sulfuric acid and oxidized by means of sodium bismuthate, that all of the manganese is oxidized to permanganic acid, and may easily be estimated colorimetrically.

3. We claim for this method greater rapidity, absence from irritating fumes, less danger of loss by spattering, more ease of operation in unexperienced hands, duplicate determinations on one sample of soil, and much greater accuracy.

ALTERING THE COMPOSITION OF INDIAN CORN BY SEED SELECTION.¹

By L. H. SMITH.

Received January 8, 1912.

In a paper presented before the American Chemical Society in 1899 Dr. C. G. Hopkins reported a line of experiments undertaken at the Illinois Experiment Station to influence the composition of the corn

¹ Presented at A. C. S. Meeting at Washington, D. C., December, 1911.

kernel by selection and breeding. At that time the experiments had been under way only about two years, but already results had been obtained sufficiently pronounced to indicate the possibility of changing the composition of the corn kernel as regards protein, oil and carbohydrates. In fact, in his conclusion the author remarks that "while it may require ten or twenty years' work to enable one to form a very definite opinion as to the extent to which it is possible to influence the chemical composition of corn, it is believed that the data thus far obtained may be of practical and scientific value."

Since the time this statement was made this investigation has been continued and twelve years' work has been added to these experiments. No further report, however, has been given to this Society, and in view of this fact it was thought that the members would be interested to learn regarding the present status of the work.

Inasmuch as the general purpose of the investigation and the methods of carrying it out have been given already quite fully in the above-mentioned paper and elsewhere (see *Bull.* 128, Illinois Agricultural Experiment Station), it will be the present plan to mention only as much of this matter as is necessary to an intelligent understanding of the results, the chief purpose being to give a brief résumé of the results up-to-date.

Stated briefly, the proposition involved in this investigation was to take a variety of corn and through selection and breeding try to influence the composition of the grain in four different directions, namely: 1, Increase the protein content; 2, Decrease the protein content; 3, Increase the oil content; 4, Decrease the oil content.

Through a preliminary study involving the analyses of a good many samples of different ears and parts of ears the principles of the selection were established. It was found that there is considerable variation among different ears with respect to composition, while the kernels within a single ear are comparatively uniform; that is to say, the ear can be taken as the unit of selection and this gives the working basis. Thus the method is to take two or three rows of kernels lengthwise of the ear as a sample for analysis. If the ear proves to be suitable for seed the remaining kernels are planted.

Starting in 1896 with a variety then known as Burr's White, 163 ears were chosen and analyzed, determinations being made for protein, oil, ash and carbohydrates. According to the percentage of the constituents, four lots of these ears were picked out with which to start the four respective breeding plots, a high protein plot, a low protein plot, a high oil plot, and a low oil plot. Each ear was planted in a separate row, the different plots being isolated in order to avoid contamination from cross pollination. From the harvest a large number of ears were analyzed from each plot, and based upon these results ears were selected for seed with which to plant the respective plots the following year.

This general plan, with a few minor changes of

detail, has been followed year after year until we now have the results for 14 generations (the samples for the fifteenth generation have not yet been analyzed). In this manner four different strains emanating from the same variety have been derived. It has been extremely interesting to watch their gradual evolution. This may be shown in outline by the following tabular arrangement:

BREEDING FOR HIGH AND LOW PROTEIN.

Average per cent. protein in crop each generation.

Year.	High protein.	Low protein.	Difference.
1896	10.92	10.92	0.00
1897	11.10	10.55	0.55
1898	11.05	10.55	0.50
1899	11.46	9.86	1.60
1900	12.32	9.34	2.98
1901	14.12	10.04	4.08
1902	12.34	8.22	4.12
1903	13.04	8.62	4.42
1904	15.03	9.27	5.76
1905	14.72	8.57	6.15
1906	14.26	8.64	5.62
1907	13.89	7.32	6.57
1908	13.94	8.96	4.98
1909	13.41	7.65	5.76
1910	14.87	8.25	6.62

BREEDING FOR HIGH AND LOW OIL.

Average per cent. oil in crop each generation.

Year.	High oil.	Low oil.	Difference.
1896	4.70	4.70	0.00
1897	4.73	4.06	0.67
1898	5.15	3.99	1.16
1899	5.64	3.82	1.82
1900	6.12	3.57	2.55
1901	6.09	3.43	2.66
1902	6.41	3.02	3.39
1903	6.50	2.97	3.53
1904	6.97	2.89	4.08
1905	7.29	2.58	4.71
1906	7.37	2.66	4.71
1907	7.43	2.59	4.84
1908	7.19	2.39	4.80
1909	7.05	2.35	4.70
1910	7.72	2.11	5.61

In considering these data attention should be called to the fact that environmental conditions exert an influence upon the protein as well as the oil content and a study of these results reveals some pronounced seasonal effects. By having a "high" and a "low" plot of each, however, we obtain a check which enables us to eliminate these seasonal effects to some extent. Thus the last column of the table showing the difference in per cent. each year furnishes the best information of the real progress due to heredity.

Without going further into a detailed discussion of the figures we may say by way of summary that starting with a variety of corn of average composition it has been possible by 14 years of breeding to increase the protein content from 10.92 per cent. in the original, to 14.87 per cent. in the crop of 1910, at the same time by selection in the opposite direction, to decrease this constituent to 8.25 per cent. Even more striking changes than these have been produced in the oil content. The oil has been increased from 4.70 per cent. in the original to 7.72 per cent in the crop of 1910 while at the same time in another strain it has been decreased to 2.11 per cent.

In other words, out of a single variety of corn two strains have been developed of which one is

now nearly twice as rich in protein as the other, and two other strains have been developed, the one of which is now more than three times as rich in oil as the other.

The question arises as to the effect of this selection upon the composition of parts of the plant outside of the kernel. This matter has been studied by analyzing each year different plant parts in the various strains. Without entering into any discussion of the results it may be stated in a general way that as yet we have been able to find no pronounced changes in the composition of other parts of the plant resulting from the changes produced in the grain.

Another practical question always arises in this connection, and that is regarding the effect of this selection upon productive qualities. It may be said that in spite of the rigorous selection for special characters to which this corn has been subjected, the yields in these four strains have, in general, been quite well maintained. Selection for high protein seems to have been accompanied in this instance by a somewhat diminished yield as measured by bushels of corn per acre. If, however, we place it upon the basis of pounds of protein per acre our high protein strain is sufficiently higher in percentage, so that it yields more protein per acre than the ordinary varieties growing alongside it in the productivity tests.

COLLEGE OF AGRICULTURE,
UNIVERSITY OF ILLINOIS.

RELATION OF ACTIVE POTASH TO POT EXPERIMENTS.¹

By G. S. FRAPS.

Received March 25, 1912.

By the term "active potash" we mean that soluble in $N/5$ nitric acid. This solvent has been in use for some time for extracting the more soluble potash and phosphoric acid from the soil. As pointed out in a previous article, the quantity of phosphoric acid extracted is related to the results of pot experiments on the soil. Similar experiments will here be reported on potash.

Pot experiments with representative Texas soils have been made at this station for seven years. The experiments have been carried on under diverse conditions, sometimes not favorable to the best growth of the plants. The plants were grown in Wagner pots containing 500 grams soil, applications of fertilizer being made to the various pots. The pots were kept in houses covered partly or completely with canvas, in order to moderate the temperature. A crop is regarded as very deficient if it is only 50 per cent. or less, of the completely fertilized crop. If less than 90 per cent., it is considered deficient (D). If between 90 and 110 per cent., it is considered as not deficient (S). If over 110 per cent., it is considered that the fertilizer injures the crop (T). The crop without potash (PN) is always compared with the crop with potash (PNK).

Relation of Deficiency to Active Potash.—The 172 soils studied have been divided into groups according to their content of active potash. The following

¹ A full account of this work will be published as *Bulletin 145* of the Texas Experiment Station.

table shows the percentages of deficient crops, D and DD, and of those injured by potash T.

The percentage of deficient crops decreases with the quantity of active potash in the soil. The percentage of injured crops increases with the quantity of active potash in the soil.

TABLE I.—RELATION OF ACTIVE POTASH TO NUMBER OF DEFICIENT CROPS.

Active potash in soil. Parts per million.	Percentage deficient. (DD and D).	Percentage injured. (T).
0-50	86.7	7
50-100	55.1	17
100-150	54.3	16
150-200	39.1	17
200-300	37.5	31
300-400	42.6	25
400-600	15.0	46
600-800	18.0	44

Relation to Weight of Crop.—The weight of the crop without potash divided by the weight with potash, expressed in percentages, shows the relative effect of the potash on the growth of the plant. The average figures for 403 crops are given in Table II.

TABLE II.—RELATIVE SIZE OF CROP WITHOUT AND WITH POTASH.

Active potash in soil in parts per million.	Percentage PN/PNK.
0-50	67
50-100	79
100-150	84
150-200	91
200-300	100
300-400	98
400-600	101
600-800	116

The effect of fertilizer potash on the weight of the crop decreases with the active potash in the soil. When the active potash exceeds 200 parts per million, the fertilizer potash effects no increase, on an average.

Relation to Potash Content of Crop.—The average potash content of (a) the corn crop and (b) the kaffir and sorghum crop, is given in Table III.

TABLE III.—RELATION OF ACTIVE POTASH OF SOIL TO POTASH CONTENT OF CROP.

Active potash in parts per million.	Percentage of potash.	
	Corn crop.	Kaffir and sorghum crop.
0-50	1.38	0.78
50-100	1.70	0.93
100-150	2.29	0.89
150-200	2.55	1.45
200-300	3.65	1.68
300-400	3.53	1.72
400-600	3.83	2.44
600-800	4.31	1.79

The potash content of the crops increases with the active potash content of the soil.

Relation of Active Potash to Total Potash Removed.—The average and maximum quantity of potash re-

TABLE IV.—RELATION OF QUANTITY OF POTASH REMOVED BY ALL CROPS TO ACTIVE POTASH OF SOILS.

Potash in soil. Parts per million.	Potash removed by crops in parts per million of soil.	
	Average.	Maximum.
0-50	29.3	53.4
50-100	37.2	143.3
100-150	51.0	176.2
150-200	80.9	249.6
200-300	120.1	434.6
300-400	156.9	354.8
400-600	119.4	295.8
600-800	206.9	380.8

moved by the crop which received no potash is given in Table IV.

The average quantity of potash removed by the crop increases with the active potash content of the soil.

SUMMARY AND CONCLUSIONS.

1. The average percentage of crops deficient in potash decreases with the active potash in the soil.
2. The average percentage of crops injured by potash increases with the active potash in the soil.
3. The effect of fertilizer potash on the weight of the crop decreases as the active potash content of the soil increases.
4. The percentage of potash in the crop increases as the active potash in the soil increases.
5. The total potash removed by the crop from the soil increases as the active potash content of the soil increases.

AGRICULTURAL EXPERIMENT STATION,
COLLEGE STATION, TEXAS.

THE DETECTION OF FORMIC ACID IN FRUIT PRODUCTS.

By F. L. SHANNON.

Received March 22, 1912.

In *Bull. 195*, of the Dairy and Food Department of the State of Michigan, the author called attention to the fact that formic acid was being used in this country as a preservative of fruit products.

It has been the general belief among chemists, for some time, that some preservatives other than the ones ordinarily found were being used in the preservation of fruit products, and investigations have been made in various laboratories throughout the country for the purpose of determining the identity of the substance used. Owing to its use in Germany, a number have suspected formic acid and have built up their investigations with that substance in mind, but because of the unsatisfactory and indirect methods of identification it has been difficult to reach a positive conclusion.

A search of the literature on the subject revealed the fact that the detection of formic acid did not depend upon its isolation and subsequent identification, but mainly upon the indirect method of its reducing power, principally upon silver nitrate and mercuric chloride solution. For example, the older literature states that formic acid is a constant constituent of many plant and animal products, a statement based on the fact that when they are subjected to steam distillation some substance is obtained in the distillate which reduces silver nitrate and mercuric chloride solution. However, in view of recent investigations along this line, it seems that this whole subject of the natural occurrence of formic acid needs further study, as it has been found possible to subject a host of substances which were known to contain no formic acid, to steam distillation and obtain a distillate which gave a pronounced reduction with both silver nitrate and mercuric chloride solution. From none of these substances, however, has it been possible to isolate and identify formic acid as such. Therefore, it is evident that we are not justified in designating as formic acid every substance obtained by steam dis-

tillation which reduces silver nitrate and mercuric chloride solution. It was found, for example, that when phosphoric acid was subjected to distillation, the distillate possessed the reducing properties generally ascribed to formic acid. Furthermore, in a number of methods in which the formic acid recovered by steam distillation is neutralized using phenolphthalein as indicator, the indicator itself was found to have a reducing action on mercuric chloride.

One of the most satisfactory indirect methods for the detection of formic acid is based on its reduction to formaldehyde by means of magnesium and dilute sulphuric acid. Fenton¹ has shown that carbonic acid may be reduced in the same way, but Bacon² has called attention to the fact that this is of theoretical importance only, there being no danger of confusing the two in practice. However, every step in this method must be carried out with absolute precision, or erroneous conclusions may be drawn.

The qualitative method as applied to the products used in this investigation is as follows: To about 200-500 cc. of the syrup or crushed fruit in a two-liter, long-necked round bottom flask provided with a Reitmeier bulb, add about 50-100 cc. of water. Subject to steam distillation, collecting the distillate (usually about 2500 cc.) until it ceases to give an acid reaction with litmus. Exactly neutralize the distillate with $N/1$ NaOH, using litmus as an indicator. Evaporate on a steam or water bath to about 50 cc., transferring from the large evaporating dish to smaller ones as the volume decreases. Transfer to an Erlenmeyer flask, provided with a glass tube about three feet long as an air condenser, add a few pieces of pure magnesium ribbon or wire and a slight excess of dilute sulphuric acid and set in a cool place for one hour, adding dilute sulphuric acid through the tube from time to time as the reaction ceases. Transfer the liquid to a suitable distilling flask and collect the first ten cc. of the distillate, which will contain most of the formaldehyde, if the original syrup contained formic acid.

There are a number of methods published for the detection of formaldehyde and nearly every analyst has his favorite test. However, the methods which proved the most satisfactory in this work were, Leach's Method,³ Phloroglucinol Method,³ Rimini's Method,³ and the Resorcin Method of the United States Pharmacopoeia. A positive reaction with *these four tests* was considered conclusive evidence of the presence of formaldehyde.

CRYSTALLOGRAPHIC IDENTIFICATION.

Inasmuch as practically all methods for the detection of formic acid previously reported are indirect methods depending upon the decomposition of the formic acid or upon its reducing powers, it seemed desirable to attempt the isolation of formic acid in the form of an insoluble salt.

The usual procedure in determining the identity of an organic acid in plants is to prepare some readily crystallizable salt, sparingly soluble in water. Of the

various formates the lead salt crystallizes readily without water of crystallization, is very stable and requires 63 parts of water for solution. The formation and identification of lead formate would therefore constitute a direct and positive proof of the presence of formic acid. After numerous attempts the following procedure was adopted:

Steam distil about 1000-1200 cc. of the syrup as in the first operation, collecting the distillate (2500-3000 cc.) in a receiving flask to which about 5 cc. of lead cream has been added. (This is made as follows: Precipitate a solution of lead nitrate with potassium or sodium hydrate in the presence of phenolphthalein until a faint pink color appears. Wash by decantation 8-10 times.) Shake the flask occasionally and as the lead hydrate is dissolved add a few cc. more, until all of the formic acid is combined. Concentrate the liquid in a large dish on a steam or water bath to about 50 cc. Filter and transfer to a suitable crystallizing dish and set aside in a desiccator. If formic acid was present in the original material, needle-like crystals of lead formate will form. Wash the crystals with absolute alcohol, to remove any lead acetate which may be present, spread on filter paper and dry. To the dry crystals apply the following tests:

- (a) Aqueous solution will reduce $AgNO_3$ upon warming.
- (b) Aqueous solution will reduce mercuric chloride solution upon warming.
- (c) Aqueous solution will reduce platinum chloride upon warming.
- (d) To a portion of the crystals in a dry test tube add sulphuric acid and warm. Carbon monoxide is generated which will burn in the tube with a blue flame when ignited. Further note that the lead formate is not discolored.
- (e) Transfer some of the crystals to a small distilling flask, treat with concentrated phosphoric acid and distil. The distillate, which is formic acid, will react as follows:

1. Acid to litmus and acid taste.
2. Reduces silver nitrate on warming.
3. Reduces mercuric chloride on warming.
4. Reduces platinum chloride on warming.
5. Is reduced to formaldehyde by magnesium and dilute sulphuric acid.

As previously mentioned it was found that when phosphoric acid and water alone were distilled, the distillate would reduce silver nitrate and mercuric chloride solution. Therefore, before test (e) was carried out the phosphoric acid was subjected to distillation until it no longer gave a distillate that would reduce silver nitrate or mercuric chloride. The crystals of the lead compound were then added and the distillation continued.

Although the chemical evidence that the volatile acid obtained from the fruit products used in this investigation is conclusive, it was thought desirable to submit the crystals to Dr. Edward H. Kraus, Professor of Geology and Mineralogy, University of Michigan and he reports as follows:

¹ *J. Chem. Soc. London*, 1907, 91, 687.

² *Circ.* 74, U. S. Dept. Agric., Bur. of Chem.

³ *Bull.* 107, 185, U. S. Dept. Agric., Bur. of Chem.

"The crystals, which were examined crystallographically, were obtained by slow crystallization from an aqueous solution of the material furnished by Fern L. Shannon, State Analyst, Lansing, Michigan. They are prismatic in habit and about 2-3 mm. in length and of slightly yellowish color. All crystals were clear and transparent. Although the crystals were in general doubly terminated, readings were made only upon the faces of the prism zone, the end faces being extremely small and, hence, difficult of adjustment. The images obtained were very good, considering the size of the crystals.

"The measured angles, compared with the values given by Plathan,¹ for lead formate are as follows:

	Kraus.	Plathan.
$m : m$ (110) : (110)	$73^{\circ} 26'$	$73^{\circ} 28'$
$m : m$ (110) : (110)	$53^{\circ} 17\frac{1}{2}'$	$53^{\circ} 16'$

"This comparison shows that the agreement in the values for this material and those given by Plathan for lead formate are exceedingly close.

"Parallel extinction was observed upon all the faces examined. The indices of refraction are higher than that of methylene iodide, as determined by the Becke and the Schroeder van der Kolk methods.

"The above crystallographic-optical properties, together with the fact that a distinct reaction for lead is easily obtained upon the plaster tablet with the blowpipe, indicates conclusively that the substance examined is lead formate."

To further substantiate the proof a number of fruit syrups that were known to contain no added formic acid were subjected to steam distillation, and an attempt made to separate a lead compound. In some instances a few crystals were obtained, but at no time would the crystals give the characteristic tests for lead formate.

It would seem then that the formation of formaldehyde coupled with the formation of lead formate and their subsequent identification would furnish a conclusive and positive proof of the presence of formic acid.

The author desires to take this opportunity to thank Dr. Edward H. Kraus for his cooperation in this work.

MICHIGAN DAIRY AND FOOD DEPARTMENT,
LANSING.

THE DETECTION OF PRUSSIAN BLUE IN TEA.

By FRED WEST.

Received January 26, 1912.

In this test advantage is taken of the well known blue color reaction between Prussian blue and a solution of oxalic acid.

Grind about 15 grams of the tea to be examined, in a mortar, and pass through a 20-mesh sieve, neglecting the few stems which resist comminution.

Procure five squares of plate glass 15 X 15 cm. each; upon each plate place an 11 cm. circular filter, as thin as procurable and having a smooth surface.

Saturate each filter with test solution oxalic acid, U. S. P., removing any air spaces under filter.

The well wetted filters are now to be sprinkled with the ground tea. This is best performed by sifting the tea from the sieve, holding it about 30 cm. above the plates, which should lie flat. Sprinkle filters well but avoid overlapping the particles of tea.

Allow the filters to dry on the plates in the air. When thoroughly dry remove filters from plates and brush off tea with a stiff brush.

The presence of Prussian blue is indicated by bright blue spots, best seen with the aid of a hand glass, and where large particles of the Prussian blue have rested, the color radiates and spreads through the filter fiber.

If smooth filters are not procurable, rough ones may be used, but a second glass plate should be clamped over the filter to press the particles of tea against the fiber. This necessitates the use of gentle heat to dry the plate.

Comparison of the amount of color in different samples may be observed by noting the total number of spots to each sample, using five plates to each one. Difficulty in counting spots on the filters can be overcome by using a Wolffhuegel counting plate and a large hand lens.

As the natural coloring matter in tea does not stain the filters in the presence of the oxalic acid, this gives a clear white field upon which any blue spots will show very clearly. The blue spots on the filters are fairly permanent and the filters may be attached to the report sheets for reference.

SAN FRANCISCO, CAL.

LABORATORY AND PLANT

FACTORS DETERMINING THE CAPACITY OF A FILTER PRESS.

By C. ALMY, JR., AND W. K. LEWIS.

Received March 18, 1912.

Very little information can be found in the literature regarding the flow of a liquid through a filter cake. Hitherto the popular assumption has been that the rate of flow is, up to a certain point, directly proportional to the pressure and inversely proportional to the thickness of the cake. The object of this investigation has been to establish more accurately the relationships existing between the rate of flow, pressure, and thickness of cake; relationships which, as will

¹ Groth, *Chemische Kristallographie*, 1910, 3, 16.

be shown, can for any particular sludge be expressed by a simple mathematical equation.

For this purpose we used a chromium hydrate sludge made by reducing dichromate with glucose and precipitating with sodium carbonate. The filter press was a six inch corner-feed laboratory press. It was of course impracticable to measure the thickness of the cake during the progress of a run, but as the volume of filtrate at any time is obviously proportional to the thickness and is an equally significant value in filtration, this figure has been substituted throughout this work in both plots and equations.

Six runs were made, at 100 lbs., 75 lbs., 50 lbs., 25 lbs., 10 lbs. and 5 lbs. pressure per square inch re-

TABLE I.¹

100 lbs.			
Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
1' 15"	600	14' 30"	2400
2' 55"	1000	18' 20"	2700
6' 00"	1500	22' 35"	3000
8' 20"	1800	27' 30"	3300
11' 15"	2100	32' 50"	3600

TABLE II.

75 lbs.			
Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
2' 15"	800	15' 35"	2300
4' 00"	1100	19' 40"	2600
6' 10"	1400	24' 25"	2900
8' 45"	1700	29' 30"	3200
11' 55"	2000	35' 30"	3500

TABLE III.

50 lbs.			
Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
45"	400	16' 00"	2200
2' 00"	700	20' 25"	2500
3' 45"	1000	25' 20"	2800
6' 00"	1300	30' 50"	3100
8' 50"	1600	37' 05"	3400
12' 10"	1900	42' 35"	3600

TABLE IV.

25 lbs.			
Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
40"	300	17' 40"	2100
2' 00"	600	22' 35"	2400
3' 55"	900	28' 10"	2700
6' 30"	1200	34' 25"	3000
9' 40"	1500	41' 35"	3300
13' 20"	1800	49' 05"	3575

TABLE V.

10 lbs.			
Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
2' 05"	500	21' 10"	2000
7' 35"	1100	27' 10"	2300
11' 20"	1400	34' 10"	2600
15' 55"	1700	42' 30"	2900

TABLE VI.

5 lbs.			
Time.	Vol. of filt. Cc.	Time.	Vol. of filt. Cc.
1' 50"	400	20' 45"	1800
5' 20"	800	27' 25"	2100
10' 10"	1200	35' 25"	2400
14' 55"	1500	41' 55"	2600

spectively. Two half-inch distance frames were used giving two cakes $\frac{5}{8}$ " thick with an area of about 35 sq. in. These runs were all made on the same day with the same sludge, experience having shown us that in order to get comparable results this is absolutely essential. It is impossible to exactly duplicate conditions on two different days, and furthermore the character of the sludge itself has unquestionably been shown to alter very materially on standing.

The sludge which was kept thoroughly agitated was pumped into the frames by hand, and the time recorded for every 100 cc. of filtrate (see Tables I-VI).

From the data in these tables, the six curves in figure 1 were plotted. By means of these curves, the rate of flow was graphically determined at frequent intervals and plotted against the volume of filtrate as before. It is evident that the rate of flow is, as

¹ To economize space, only a small number of the recorded values have been given in this and in the following tables.

expected, some function of both the volume of filtrate and the pressure. With the object of ascertaining whether the rate was a power function of the volume of filtrate, in which case the relationship could be expressed by the equation,

$$R = f \frac{P}{V^n}$$

the logarithms from these curves were plotted as shown in figure 2.¹ It will be seen that with the exception of the 100 lb. run, these are all parallel straight lines for the greater part of their length, showing that up to the break, the rate of flow for a constant pressure is a power function of the volume of filtrate or thickness of cake.

The unexpectedly quick rate of flow for the first part of the 100 lb. run is a phenomenon that was always observed at high pressure and is difficult to satisfactorily account for. Presumably it is due to the fact that the sludge, rushing into the frames with increased velocity, does not at first pack evenly over the surface of the filter cloths but forms small channels through which the liquid flows more readily. It should be mentioned incidentally that a pressure of 100 lbs. is so high that it could not be used in practice on account of the probability of obtaining a cloudy filtrate.

The break in the curves which occurs after approximately 2000 cc. of filtrate have come over represents the point at which the distance frames become completely filled with the precipitate. If more sludge be pumped in, it gets tightly packed around the inlets with the result that the entire filtering surface of the cloths is no longer effective and consequently the rate of flow decreases. As would be expected, this point occurs somewhat later with the higher pressure than with the low, since at high pressure the capacity of the frames is increased on account of the greater compression of the precipitate.

With the idea that the rate of flow might possibly be a power function of the pressure as well as of the volume of filtrate, we plotted the rate for a constant volume (1000 cc.) against the pressure, and taking the logarithms as before, obtained the straight line shown in figure 3. This indicates that such is actually the case, or to express the relationships mathematically,

$$R = K \frac{P}{V^n}$$

where R is the rate of flow in cubic centimeters per minute, V is the volume of filtrate in cubic centimeters, and K is a constant. For the series of runs above described, the calculated values of m , n and K will be found to be 0.270, 0.810 and 13,600, respectively, giving as the equation for the rate of flow at any volume of filtrate or pressure,

$$R = 13,600 \frac{P^{0.27}}{V^{0.81}}$$

From this equation, it is strikingly evident that instead of the rate of flow being directly proportional to the pressure as has hitherto been generally supposed,

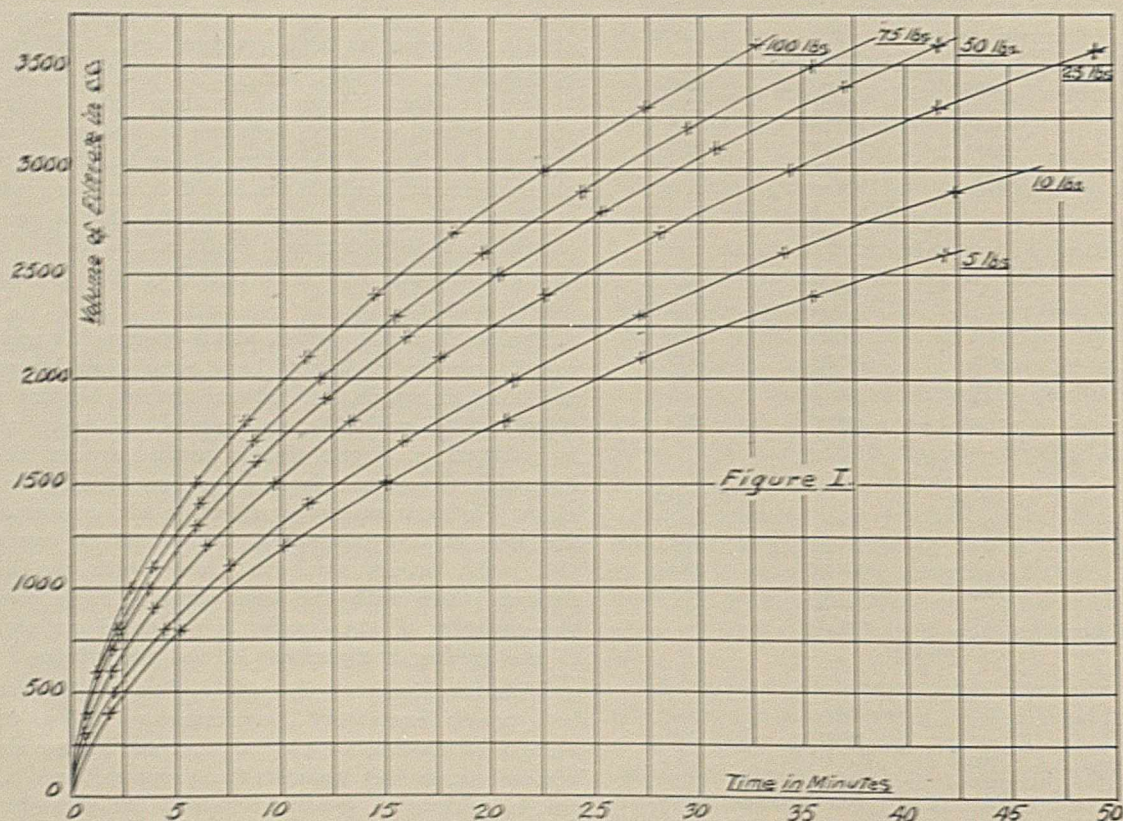
¹ As each of these runs was carried out at a constant pressure, $f(P)$ is, of course, a constant, and the equation becomes $R = K/\sqrt[n]{V}$. Taking the logarithm of each side gives us $\text{Log } R = K - n \text{ Log } V$.

it is for this particular sludge proportional to only approximately the fourth root of the pressure. Assuming, as is probable, that the rate of flow through a filter cake is analogous to that through fine capillary tubes where the rate is directly proportional to the pressure and to the square of the radius of the openings, this low coefficient is readily explained by the nature of the sludge here used. Owing to its non-crystalline character, it is very easily compressed, and consequently with the same amount of precipitate in the frames, at the higher pressure the passages through the cake would be expected to be considerably smaller than at the lower pressures. If this explanation is correct, then with a sludge containing a more granular precipitate the pressure coefficient should more nearly

carried out inside of two hours on a small laboratory press such as was used in this investigation with results which may be depended on to closely approximate those of actual practice.

EFFECT OF VISCOSITY.

In commercial filtration, the viscosity is, as a rule, a pre-determined factor which cannot be varied at will. But it is very possible that the viscosity effect may be of considerable importance in determining the rate of washing, where the washing medium is usually less viscous than the original filtrate. Reasoning from the analogy already observed between flow through a filter cake and flow through capillary tubes, it would be expected that the rate would be inversely proportional to the viscosity.¹ To determine



approach unity, and work to determine this point has already been started in this laboratory.

A study of these results makes it clear that all the problems in filter press design can readily be solved by their aid. The equation for the rate of flow having been established as

$$R = K \frac{P^m}{V^n}$$

it is only necessary to determine experimentally the values of K , m , and n , to be able to calculate the rate at any pressure or thickness of cake desired. From work that is at present being carried on in this laboratory, and from other data already on hand, it is known that these values vary very greatly with the nature of the precipitate, but for any particular sludge they are constant. To determine these values for industrial application, it is necessary to make only two trial runs at different pressures, and it is our opinion that these runs may be

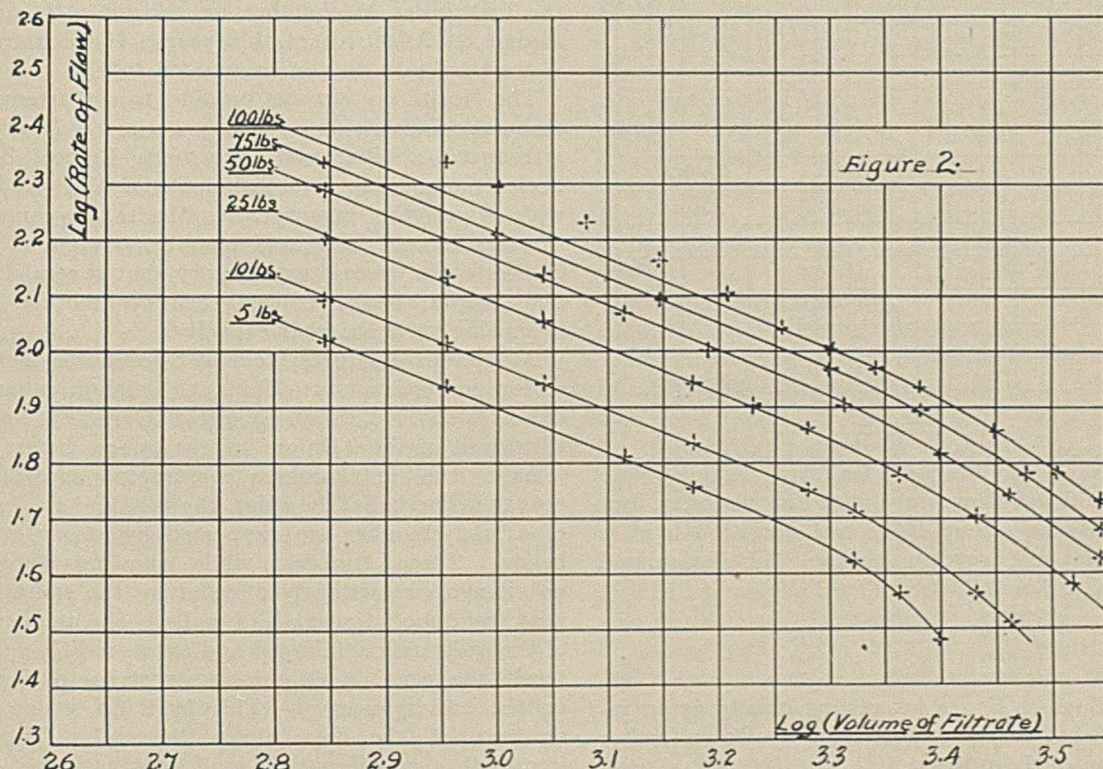
this point, and also to ascertain whether the viscosity has any effect on the pressure and volume coefficients, the two runs described below were undertaken.

These runs for determining the effect of viscosity were exactly the same, except that the amount of precipitate varied. An indefinite amount of sludge (about a liter and a half for the first run and a half liter for the second) was pumped into the frames at 25 lbs. pressure, and then filtrate alone was pumped through until the rate of flow became constant. By referring to Run No. 4, the volume of filtrate to which this rate corresponds can be readily ascertained. The filtrate was now diluted one-half with water and again pumped in until the rate was constant. Without changing the solution entering the press, the pressure was dropped to 5 lbs. and then raised

¹ The flow through a capillary tube is equal to $\frac{r^4 P}{8 \mu l}$, where r is the radius of the tube, l is the length, P the pressure, and μ the viscosity of the liquid. (Lamb, "Hydrodynamics," p. 544.)

again to 25 lbs., the rate being recorded for each pressure. The discrepancy which will be noticed existing between the rates at 25 lbs. before and after dropping the pressure is probably due to channels forming through the sludge when the pressure was relieved, and on this assumption the second rate has been accepted as the more comparable to the other values. Finally in the same manner, pure water was

explanation advanced for the low coefficient previously encountered, for in this case where the pressure is simply lowered and raised again without the addition of any more precipitate, it would not be expected that the size of the small openings through the cake would alter materially; consequently the rate of flow would follow the law for flow through capillary tubes where it is directly proportional to the pressure.



pumped in, and the rates of flow determined as before at 25 lbs. and 5 lbs. pressure.

From these runs, the following data were secured:

	Run A. Cc.	Run B. Cc.
Rate of flow with filtrate (at 25 lbs.)	87	167
Volume of filtrate corresponding to this rate as determined from Run No. 4	1515	675
Rate with diluted filtrate at 25 lbs:		
Before dropping pressure	92.3	174
After dropping pressure	100	175
Rate with diluted filtrate at 5 lbs.	20	35
Rate with pure water at 25 lbs.	109	180
Rate with pure water at 5 lbs.	21.5	36
Absolute viscosity of filtrate ¹	0.0124	
Absolute viscosity of diluted filtrate	0.0109	
Absolute viscosity of pure water	0.0096	

From these figures, the rate of flow is apparently approximately proportional to the viscosity as was expected, but owing to the fact that on account of the change in conditions experienced on dropping the pressure, the rate with straight filtrate is not strictly comparable to the other rates; too much faith should not be put in this conclusion in the absence of further confirmatory evidence.

It will be noticed that the rate of flow at 25 lbs. pressure is in every case just five times that at 5 lbs.; in other words, the pressure coefficient has become equal to one. This is directly in accordance with the

¹ Viscosity determinations were made according to Gurney's method. (See *J. Am. Chem. Soc.*, 34, 24.)

The values for the volume coefficient (n) as calculated from these runs are:

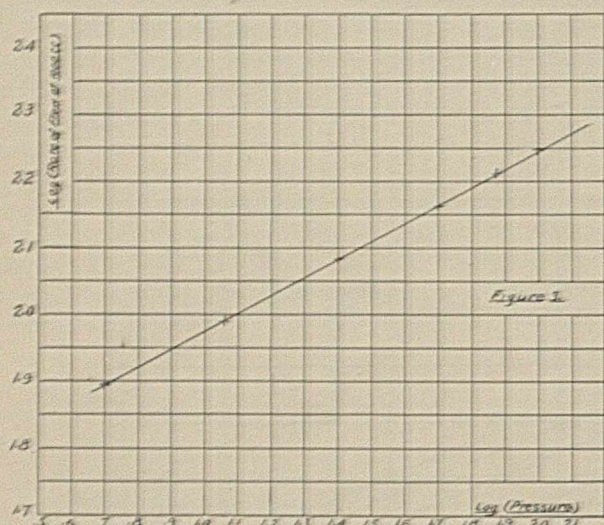
	n .
Straight filtrate	0.810
Diluted filtrate	0.692
Pure water	0.621

It must be understood that these figures are not to be considered anything but relative, since their absolute accuracy depends, of course, on the correctness of the value for the volume of filtrate which was taken from Run No. 4—a run made with a different batch of sludge. But though the above calculated figures for n are for this reason possibly considerably in error, nevertheless the relationship between them is correct, which is all that is essential. Comparing these values with the absolute viscosity of the solution, it appears that the volume coefficient is roughly proportional to the viscosity. This relationship is brought out by the following table:

	Viscosity.	n .	Viscos. n .
Straight filtrate	0.0124	0.810	0.0153
Diluted filtrate	0.0109	0.692	0.0158
Pure water	0.0096	0.621	0.0155

The reason for this unexpected relationship is very difficult to see, and it is unquestionably true that too much emphasis should not be laid upon results from preliminary experiments such as these. But it is hoped that by pointing out this apparent

proportionality, other investigators will be led to try more exhaustive and accurate experiments which will afford an explanation for the phenomenon.



From the equation $R = K \frac{P}{V^n}$, it would be expected that K would vary inversely with the viscosity, but the effect of the above-mentioned variation in n is so great that the reverse is true. The calculated values of K are as follows:

Viscosity.	K .
0.0124	1310
0.0109	635
0.0096	410

These values of K are interesting chiefly as an indication of what may be expected to develop on further investigation of the subject.

The purpose of this article is twofold: First, to point out that, despite the popular theory, the rate of flow of a liquid through a filter cake is not as a rule directly proportional to the pressure and inversely proportional to the thickness of cake, but can be expressed by the equation $R = K \frac{P^m}{V^n}$, in which the constant and coefficients can be quickly and easily determined; and secondly, by outlining some preliminary experiments carried out in this laboratory to stimulate further investigation which will be able to explain the very interesting and unexpected relationships which apparently exist between the viscosity of the filtrate and the values of n and K .

RESEARCH LABORATORY OF APPLIED CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON.

IMPROVED SULPHURIC ACID CHAMBERS.¹

By THOMAS H. NORTON.

While visiting the extensive works of the Union Fabrik Chemischer Produkte at Kratzwieck, near Stettin, I was afforded an opportunity to examine minutely two series of sulphuric-acid chambers recently constructed by the company. These are regarded as embodying the most advanced ideas of the day.

¹ Special report to Bureau of Manufacturers, Department of Commerce and Labor.

On October 10, 1910, three of the nine chamber plants were destroyed by fire. In planning for rebuilding, the director decided to adopt the essential features of the so-called Moritz system of chamber construction, as not only promising economy in future cost of production, but also offering exceptional facilities for rapid replacement of the missing units, even during the winter season. He was able to use the first series of chambers on March 15th and the second on April 4th of this year. The construction of the third unit did not begin until July.

The Moritz system was brought to the attention of technical chemists about four years ago. It was first introduced at Wasquetal, northern France, by the Société anon. des Etablissements Eyken et Leroy, with which the inventor, R. Moritz, is connected. The results obtained in a chamber system of 4,500 cubic meters were so satisfactory that several French and Belgian works utilized the new method when increasing their chamber capacity.

At present a large system of 8,000 cubic meters is under construction at Hainaut, Belgium, a smaller one of 4,000 meters at Elberfeld, Germany, and the third unit of the "Union" works (5,200 meters).

As a rule, in chambers constructed according to prevalent methods, the sides, the top, and the bottom of a lead chamber are supported by strong wooden beams. These timbers, while showing externally no change, are seriously affected by the radiation of heat from the adjacent lead walls. The temperature of the walls may attain 90° and even 100° C., and as a result the wood rapidly loses its strength, becomes brittle, and is warped. This leads to a dangerous strain upon the flaps along the walls. They are frequently torn off and the wall loses its shape. This tendency is heightened by the great difference between the coefficients of expansion of lead and wood. The thoroughly dry timber offers also an undesirable amount of very combustible material, as shown by the extensive fire at Kratzwieck in 1910 and the conflagration at the Wasquetal works in 1907.

Much more serious, however, is the increased corrosion of the lead chambers, due to the use of wooden supports. Those portions of the lead walls adjacent to the timber supports are prevented from radiating heat freely. This retards the oxidizing reaction in the immediate vicinity, while allowing the lead to be corroded more rapidly. Careful measurements of the thickness of the wall in different parts of a lead chamber, after the fires mentioned, showed that the portions of wall screened by a timber were on an average half a millimeter thinner than other sections of the chamber. This was in spite of the fact that the timbers were separated by spaces of 8-10 cm. from the lead walls.

An additional disadvantage results from the more rapid corrosion of the lead behind a beam, as leaks occur thereby most frequently at points where the repairs are difficult to execute. In some few works iron instead of wooden beams have been introduced. This obviates the distortion of the chamber walls, due to the warping of the wood, but does not diminish

the trouble arising from rapid corrosion and the difficulty in carrying out repairs.

With regard to the bottom of chambers, observation shows that corrosion is very pronounced along the lower edge, where the lead is bent upward. Here a zone of about 6 inches is peculiarly liable to rapid attack; and the same is true of the lower part of the side walls, which form the hydraulic joint. The direct cause of this quick corrosion is the thick flooring of wood necessary to support the weight of the acid, by retarding the radiation of heat from the surface of the lead.

The tops of chambers are ordinarily flat. The lead sheets are attached by flaps to overhead beams or hung upon iron rods or tubes. In both cases the same disadvantages exist as have been previously mentioned. A flat roof also favors the accumulation of dust, which in turn retards radiation. As a rule it is a matter of great difficulty to clean thoroughly the ordinary flat roof of an acid chamber.

The prevalent method of attaching the various sections of a lead chamber to its supports prevents almost entirely any uniform expansion of the different parts. In consequence of the heavy weight of the lead, and of the uneven expansion, there is a constant tendency toward strain about the flaps, and cracks that are exceedingly awkward to mend appear along the soldering lines.

All of these defects of the customary construction seem to be avoided in the Moritz chambers. The essential feature of such a chamber unit is a strongly built skeleton of structural iron, enclosing the chambers, which are suspended from overhead beams. The skeleton serves also as a support for the roof.

The main columns of this skeleton, which bear the weight of the roof, have been constructed in some cases of concrete or masonry. Preference is, however, given to iron, as involving less time in preparation and assuring greater strength. A tile roof is used. The outer walls of the structure are built of brick, laid between the upright columns. The bricks are placed edgewise, so that the walls are exceedingly light, 2.36 inches in thickness. No windows are required. An abundant use of panels of wire-net glass and of ordinary glass tiles in the roof affords all needed light. Some additional light and abundant ventilation are assured by numerous series of openings in the brick walls, the bricks being arranged in a lattice-like manner at distances of 3.937 inches from each other. Such an arrangement suffices to keep out snow and rain, while affording a maximum of air circulation for cooling purposes.

At Kratzwieck two units are located side by side, separated from each other by an aisle about 4 feet wide, and under a single roof. In other forms of construction there is a separate roof over each unit.

Great ingenuity is displayed in the manner of suspending the chambers from the skeleton framework. At intervals of 31.5 inches along the top edges (27.5 inches on the end sides) hooks of half-inch iron are attached firmly to the lead sheets. These hang by iron rods (1.57 by 0.24 inches) from the T girders

overhead, and thus insure a complete, unhindered exposure of the side walls to the cooling action of the air. There is, however, a further addition necessary, in order to obviate any danger from expansion or contraction. Along the walls, likewise at distances of 31.5 inches (or 27.5 inches on the end walls), vertical flaps are soldered on tightly. Light iron rods, round or flat, pass through these, and are connected above with the pendant supports, while below they are attached, by means of spring hooks, to the upturned edge of the chamber floor. They give a ribbed appearance to the chamber walls and increase the cooling surface. While imparting a certain amount of rigidity, and preventing undue swelling outward, or inward depression, they still permit of free play for ordinary contraction, or the reverse, without any undue strain falling upon the soldered fastening of the ribs. The effectiveness of this rib construction is heightened by numerous horizontal connections, by means of iron rods, with the skeleton frameworks.

A similar principle is applied in the case of the top of a chamber. Here there is also a ribbed construction, and hooks at frequent intervals are connected by round iron bars with the girders overhead. All exposed iron parts are carefully protected from corrosion by a special paint.

In the shape of the chamber top we encounter one of the most striking innovations of the Moritz system. It is of a semicylindrical form to prevent the accumulation of dust, while avoiding "dead corners" inside the chamber, and their liability to frequent repairs, and assuring a more perfect circulation of air about its upper surface.

The lead floor of the chamber rests upon an under floor of iron plate 0.197 inch in thickness, and this in turn is supported by brick columns about 8 feet high. In some instances the constructors have used wood or ferro-concrete. In all cases, however, the upturned edge of the floor consists of iron plate, bent underneath to a distance of 9.8 inches. This is to insure the most rapid cooling at the weakest point in the construction of a chamber, where corrosion is most pronounced, and repairs involve a complete stoppage of manufacture. An identical method is used in supporting the lead mantles of the Glover and Gay-Lussac towers. Details are naturally much simpler, on account of the smaller size of the towers. Each tower shows eight vertical ribs.

There are certain theoretical considerations connected with the use of the rounded roof that deserve mention. In addition to the advantages attendant upon this particular shape, the inventor claims that it is a powerful factor in equalizing temperature, and consequently in insuring uniform chemical activity and production in all parts of a chamber. While there is little movement of air over a flat roof, there is, on the contrary, an active current over the surface of a curved roof, thus bringing about a more rapid cooling. In a chamber of rectangular construction the hotter gases accumulate at the top. With a curved roof the volume of such gases is reduced to a minimum. They are constantly drawn off by the

gyratory movement of the chamber's contents, due to external cooling, and descend steadily downward along the walls. An instance is cited from the observations made at Wasquetal upon the temperatures at three different points in the first chamber of a plant. Under similar conditions of external temperature, with the same pyrites, the same ovens, and the same towers, the temperatures observed at the three points in a rectangular chamber were 90° , 88° , and 86° C. In the chamber with curved top, which replaced the former, they were 75° , 75° , and 74° C. The more rapid cooling and the close approach to uniformity are noteworthy. The director of the works at Kratzwieck is, however, of the opinion that a more gently curved roof is quite as effective as one of semicircular shape and more desirable from several standpoints. In the plant now under construction he plans to modify this feature.

At the outset it must be noted that the cost of construction, per unit of cubic chamber space, is higher than by the old method. At Kratzwieck the additional cost was found to be about 33 per cent. This figure would vary according to local factors.

There seems to be no doubt of the manifest economy in space, frequently an important factor where chemical works are hampered in their development by lack of sufficient available area for building. At Kratzwieck the two units already built on the Moritz system occupy but two-thirds of the area formerly covered by three separate units before the fire. Yet these two units produce more sulphuric acid than the three units that were destroyed.

The next important economy is in the amount of nitric acid required to produce the maximum effect in the lead chambers. The newly erected plant of the "Union" yields daily about 7 kilograms of acid (50° Baumé) per cubic meter of chamber space. Formerly, at this rate of production, 0.7–0.8 kilogram of nitric acid (36° Baumé) was consumed for each 100 kilograms of chamber acid of the above strength. This consumption has now fallen to very nearly 0.5 kilogram. It is to be noted that 0.9 kilogram is a very common figure in German acid works. In 1900 the average consumption was 1.4 kilograms in American acid works burning pyrites. This loss of nitric acid is an important item in the cost of producing sulphuric acid. In Germany it constitutes 4–8 per cent. of the total cost. It is obvious that a saving of 1 or 2 per cent. in this direction constitutes a notable economy. The inventor guarantees a maximum loss of 0.6 kilogram where chambers are producing 7 kilograms daily per cubic meter. It may be mentioned in this connection that in the "Union" system water in the form of spray is admitted to the chambers in summer and in the form of steam during the winter.

Apart from the direct saving on the daily cost of production, the director of the "Union" works is confident from his study of the plant during the few months that it has been in operation that there will be ultimately a very material saving in the item of depreciation, through the prolonged life of the chambers, and the ease and simplicity with which any necessary eventual repairs can be executed.

A MODIFICATION OF THE FRARY ELECTRODYNAMIC STIRRING DEVICE.

By J. M. KNOTE AND W. R. WORK.

Received March 14, 1912.

The use of a solenoid for the rapid determination of metals in the electrolytic way was proposed by Frary (*Journal of the American Chemical Society*, November, 1907, and in other publications). He employed the usual form of solenoid which is a coil of copper wire cylindrical in shape and hollow, and enclosed in an iron case. The beaker containing the electrolyte is put into the hollow space in the center of the coil and a current passed through the electrolyte in the usual way. At the same time a current through the solenoid produces a magnetic field in the region of the beaker which in conjunction with the electrolyzing current causes a rapid circulation in the electrolyte.

The disadvantages of this form of apparatus are that the electrolyte is not in sight and an inspection of the electrodes during the process of electrolysis is not easy. The solution becomes quite hot and in some common determinations this is not desirable. The use of a cooling coil complicates the apparatus.

MODIFICATION.

By actual measurements the magnetic field produced by a solenoid was shown to be practically as strong at the top of the coil as it is at any point in the interior, and an inch above the top it still amounts to 40 per cent. of this strength, gradually decreasing as the distance increases, as shown by Fig. 1. The lines

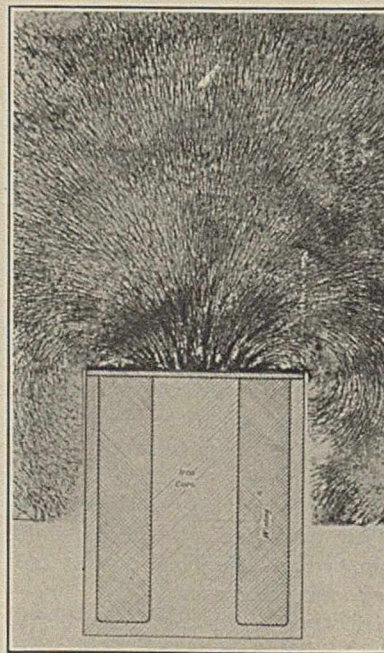


FIG. 1.—VERTICAL SECTION THROUGH SOLENOID AND DIAGRAM OF MAGNETIC FIELD ABOVE IT.

of force which constitute the field pass without hindrance through glass, paper, wood, brass, etc., so it is a simple matter to put the coil of the solenoid around an iron core, cover the top with a suitable material and place the beaker containing the electrolyte on it. By using electrodes with bent stems a very simple

and convenient electrode holder can be used in conjunction with this form. Both electrodes are fastened to a small block which is raised with one hand while the wash bottle is used with the other.

The objection might be raised to our modification that on account of the strong field at the bottom of the beaker and the weak one at the top, most of the stirring would be at the bottom. It is true that the vigorous stirring does originate at the bottom, but on account of the free circulation, the upper part of the solution gets all the stirring necessary. In any event the solenoid stirring does not produce the commotion in the solution caused by a mechanical stirrer but nevertheless results can be obtained quickly. The average strength of the magnetic field measured in the region of the beaker is 700 gauss.

RESULTS.

(Frary has described in detail the speed and accuracy obtained by the use of a solenoid in electrolytic work.)

The four solenoids shown in Fig. 2 have been in use in the Chemical Department of the Pittsburg Testing

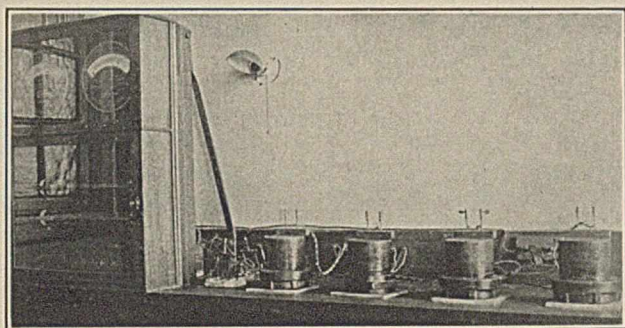


FIG. 2.—SOLENOIDS WITH MOVEABLE ELECTRODE HOLDERS IN POSITION.

Laboratory for several months and are very satisfactory for the large variety of determinations we are called upon to make. We recognize the merits of the various forms of apparatus proposed for mechanical stirring but prefer our present equipment. We find it much more satisfactory than the stationary gauze electrode alone where a variety of determinations are to be made.

With stationary gauze electrodes in 125 cc. of solution containing about one gram of copper we allowed three amperes to pass for fifty minutes in order to be sure all the copper had been deposited. With the solenoid the same amount of copper is deposited in thirty minutes under the same conditions using the same electrodes. With a higher current the results can be obtained in less time.

PITTSBURGH TESTING LABORATORY,
CARNEGIE TECHNICAL SCHOOLS.

THE UNDERWRITERS' LABORATORIES EXTRACTION APPARATUS.

By HENRY J. CARY-CURR.

Received April 16, 1912.

It has been found necessary in certain lines of extraction work to devise for routine work a method that is both rapid and convenient, such, for example,

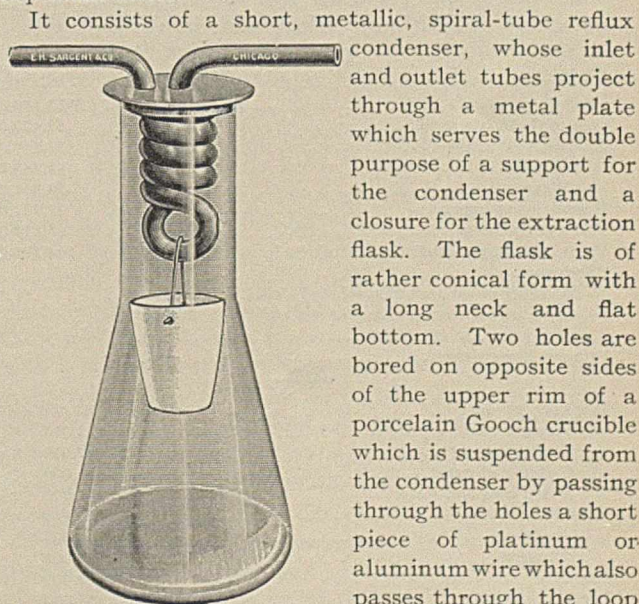
as the determination of certain extractable constituents of rubber insulation on wire, etc. In such a case the moisture content (generally less than one-half of 1 per cent.) is a negligible factor in the determination and may therefore be overlooked except in special cases where it is especially desired. Based on this ground the Chemical Department of the Underwriters' Laboratories at Chicago have spent several years in developing methods and apparatus to be used in a standard procedure for chemical tests of rubber compounds used on wires and cords.

Any form of extraction apparatus may be used, but it must conform to the following specifications: (1) "The extraction cup shall be surrounded by the vapor of the solvent at its boiling point." (2) "The condensed solvent shall fall directly on the sample." (3) "The outlet from the extraction cup shall be at the bottom only." (4) "No rubber or cork stoppers shall come in contact with the solvent." (5) "Sample shall be put directly into extraction cup without the use of a paper thimble—a disc of filter paper or its equivalent at the bottom of the cup being depended upon to hold back the solid part of the sample."

Following the manipulations of the above-mentioned methods it becomes necessary to extract into a tared flask which must be reweighed and which must therefore be of proportions and style suitable for admission to the bows and pans of an ordinary analytical balance.

Rapidity and efficiency of condensation together with ease of manipulation and installation as well as simplicity of construction and therefore low cost of maintenance and replacement were other points to be considered.

To meet these requirements a new apparatus has been devised and thoroughly tried out and is of exceptional merit.



It consists of a short, metallic, spiral-tube reflux condenser, whose inlet and outlet tubes project through a metal plate which serves the double purpose of a support for the condenser and a closure for the extraction flask. The flask is of rather conical form with a long neck and flat bottom. Two holes are bored on opposite sides of the upper rim of a porcelain Gooch crucible which is suspended from the condenser by passing through the holes a short piece of platinum or aluminum wire which also passes through the loop at the bottom of the condenser. The charge having been placed in the neck of the flask, the condenser and crucible are placed in the neck of the flask, the water connections made and when a good flow of water has been

established, heat is applied to the flask and the action is carried on automatically.

The evaporated solvent is condensed on the spiral coil and drops into the crucible, passing through the sample into the flask where it is again volatilized and the cycle is repeated.

As the whole apparatus is only 6" high and 3" wide it takes up the minimum of space, and where much work of this character is done a battery of extractors and flasks can be arranged on a hot plate or water

bath of very small dimensions, say two rows of ten or more flasks, in which case the bath can be furnished with a set of spring clips to steady the flasks when one of the set is removed. The water flowing from one condenser to the other only one inlet and one outlet is needed.

Copies of the Standard Methods alluded to above may be obtained from the Underwriters' Laboratories of Chicago; the apparatus from E. H. Sargent & Co., of Chicago.

CHICAGO.

ADDRESSES

THE PRESENT STATUS OF THE GAS INDUSTRY AND ITS OUTLOOK.¹

By CHARLES E. MUNROE.

When speaking of the gas industry our mind naturally reverts to those public service corporations that are manufacturing gas for distribution and sale, and it is interesting to note that we are almost touching the centenary of their origin, an event which has proved of such importance in the development of civilization and in making life in dense communities feasible, and relatively secure, as to be worthy of commemoration; for, although, following Murdoch's demonstration at Redruth, in Cornwall, England, in 1792, several isolated plants for lighting houses and factories were built and operated, the gas industry as we now regard it, with its central producing plant connected by mains and services with a multitude of consumers began when, in April, 1812, a Royal Charter of Incorporation was granted to the Chartered Gaslight and Coke Company of London, England.

In the United States, although isolated plants of an experimental nature are recorded as having previously been erected at Newport, R. I., and Richmond, Va., this industry began with the chartering of a gas company in Baltimore, Maryland, in 1816.

GAS INDUSTRY.

Number of establishments.....	1,296
Capital.....	\$915,537,000
Cost of materials used.....	52,428,000
Salaries and wages.....	33,316,000
Salaries.....	12,385,000
Wages.....	20,931,000
Miscellaneous expenses.....	27,757,000
Value of products.....	166,814,000
Value added by manufacture (products less cost of materials)	114,386,000
Employees:	
Number of salaried officials and clerks.....	13,515
Average number of wage earners employed during the year.....	37,215
Primary horsepower.....	128,350

PRODUCTS.

Total gas produced.....	2150,835,793,000	cu. ft.
Straight coal.....	219,985,253,000	" "
Straight water.....	1,726,082,000	" "
Carbureted water.....	79,418,486,000	" "
Mixed coal and water.....	40,775,283,000	" "
Oil.....	8,688,860,000	" "
Acetylene.....	225,186,000	" "
All other.....	216,643,000	" "
Coke.....	2 82,049,683,000	bu.
Tar.....	2 92,152,938,000	gal.

¹ Address before the Division of Industrial and Engineering Chemistry, Annual Meeting A. C. S., Washington, December, 1911.

² In addition, 27,558 thousand cubic feet of straight coal gas, 13,070 thousand cubic feet of acetylene gas, 44,347 bushels of coke, and 38,370 gallons of tar were produced for sale by establishments engaged primarily in the manufacture of other products.

The present status of this industry in the United States is approximately set forth in the preceding table, wherein the statistics given are those collected by the Bureau of the Census for the year ending December 31, 1909; they show to what enormous dimensions this industry has grown in this country in less than one hundred years.

In presenting these statistics I must, as I have on several previous occasions, call your attention to the limitations placed on census statistics, in common with all other bookkeeping statistics, growing out of the necessity for keeping each category carefully separated.

Thus while in the foot-note there is given the statistics for those establishments that manufacture "artificial gas for sale" as a subsidiary product, there is not included in the table or foot-note the natural gas produced for sale, since this is not manufactured, nor the blast furnace gas or producer gas, since while these are manufactured they are not produced for sale but are consumed by the establishments manufacturing them. Likewise, though the by-products coke oven gas produced for sale is included in the statistics of the table when such establishments are primarily engaged in producing gas for sale, yet the gas from the larger number of by-product plants, and also the coke and tar produced by them, is not included in the table since these products are chiefly consumed by the establishments of which they form a part. Such gas, however, as has been sold by these last mentioned establishments to gas companies appears in the table by value, though not by quantity.

A comprehensive treatment of all gas industries would include the statistics for gas from all these sources, and I hope to be able later to present them.

It is to be noted that the Chartered Gaslight and Coke Company and the Baltimore Gas Company made coal gas by the destructive distillation of bituminous coal. The table includes water gas, mixed coal and water gas, oil gas, and acetylene gas in addition to coal gas. In quantity, carbureted water gas exceeds them all, and if the straight water gas together with that used in compounding the mixed gas be also regarded, water gas greatly exceeds in quantity all other gases combined. There may be some little surprise at finding acetylene gas and oil gas carried in this account for they are not usually thought of as being handled by public service corporations, yet to-day there are a considerable number of smaller

communities having central acetylene plants, and as this condition carries these acetylene statistics into this account, other returns for acetylene, shipped in containers, are combined with them. Oil gas is more remotely connected with this category, for it is almost wholly, if not completely, sold in containers, but nevertheless it is more closely connected with this account than any other opened on the Census books, and hence is placed here. Besides, since the product is largely supplied to railway coaches, and thus enters as a factor in interstate commerce, the companies are quasi-public.

The history of the gas industry is a record of continued struggles. As Walton Clark has said: "The conception of a system of illumination comprehending a central source, and radiating lines of conduits; the measurement and recording of the service rendered as rendered, and the absolute and immediate control by the served of the time, period and measure of service, was as bold and startling as has occurred in the mind of man." The product was early known to possess poisonous, properties and to form explosive mixtures with the atmosphere. Its manufacture was promptly observed to create nuisances. For fifty years its most potent competitors in the field of artificial illumination were tallow, wax, and sperm oil, and the producers, conveyors and merchandizers of these materials were active in proclaiming the evils and dangers attending gas lighting, and opposing its introduction and growth. Because of its advantages outbalancing its disadvantages and because of many inventions, through which these evils and dangers were reduced and its benign characteristics improved, it eventually overcame these competitors and outstripped them, only to be met by petroleum and petroleum refining which, through the many forms of lamps devised for the burning of its products, gave cheap and brilliant illumination.

Fortunately about this time, through the ingenuity of Tessie du Motay and of T. S. C. Lowe, the manufacture of water gas and especially carbureted water gas was made commercially practicable. Moreover, in 1856, Perkin had made his discovery of mauve. In 1867 Kekulé published his classic memoir which stimulated the utilization of coal tar. The Bunsen burner had become known and its value demonstrated. About this time the value of ammoniacal salts as fertilizers began to be recognized and in consequence, the tar and ammoniacal liquor began to assume commercial value, and, thus protected and fostered, the gas industry flourished and grew side by side with its competitor petroleum, and even fed upon the latter in that the cheaper petroleum distillates were successfully adapted to the carbureting of the water gas.

But in 1879 Edison gave to the world the first practical incandescent electric lamp and in a short time the commercial feasibility and advantage of this method of illumination became so markedly apparent that the gas industry was thought to be doomed. Yet a series of events regvanized it and put fresh life into it. First in importance was the invention by Auer von Welsbach in 1886 of the incandescent

gas mantle which he attached to the Bunsen burner and which had been so perfected by 1892 that the use of these mantles became so widespread that approximately 100,000,000 of them were manufactured in the year 1903, and a larger number annually since then. In 1881 the Siemen's regenerator was adapted to the Coppeé oven and the general type of by-product oven since styled Otto-Hoffmann was produced. In 1882 the Knab-Carvés oven was developed into the Semet-Solvay by-product oven, and through these and subsequent improvements in the designs and methods of operation of the by-product ovens and their accessories the cost of the manufacture of gas became greatly reduced. Moreover, by the adaption of the Bunsen principle by Fletcher, in 1883, and others, to burners of various kinds, gas heating became feasible, and the use of gas as a source of heat and power, as well as of light, promoted the growth and extension of the industry.

But the perfection of methods for low cost generation and distribution of the electric current and its utilization as a source of light, heat and power for almost every condition under which these forms of energy are employed for domestic, manufacturing and community purposes, has gone on in the last ten years with continued acceleration so that the gas industry to-day finds itself menaced at every point by this competitor, and in the power field finds the gas engine completely outranked in simplicity and certainty of operation, and cost of up-keep, by the electric motor. Wisely, most of the larger gas corporations have protected themselves by combining the generation and distribution of electricity with the manufacture and distribution of gas, thus removing a dangerous competitor from the field, while at the same time gaining an intimate acquaintance with each industry and keeping informed of the state of each art and the attitude of the community toward each product.

I sympathize with the owners of gas securities who anticipate a great shrinkage in the values of their holdings, but I cannot believe the chance of this occurring in the near future to be so likely as some may fear. It is true that to hold the field where active competition with electricity may arise or to prevent this competitor from entering the field, the price of gas must be reduced; but the profit can be maintained by reducing the cost of its production; this simply means, in most instances, the introduction of better, and in most cases, now known methods and devices, and in a more scientific management of the enterprise.

A first step may be taken in the employment of the chemical engineer to observe and check with his thermocouples, his burettes, and reagents, the operations of gas making and purification, and the character of the by-products and their derivatives at every stage of the operations. The expense involved in the employment of a wise and accomplished chemical engineer cannot fail to prove to be a profitable investment.

A second step may be taken in the reduction of heat losses whereby a saving may be effected in the fuel account, and the efficiency of the operators im-

proved, for this is a feature in the manufacturing operations which, until recently, has been almost universally overlooked.

A third step may be taken in the more complete recovery of the by-products and their more complete utilization. This will lead to a more diversified industry and demand a larger measure of chemical knowledge and experience. It may be of interest to recall, what has already been recorded in our literature, that one gas establishment in the United States has, in addition to producing coke, tar and ammonium salts, entered on the manufacture of cyanides. But it tries the patience of the chemist to see the sulfur and other compounds going to waste in the purifying material when they can be usefully employed for so many different purposes.

A cheapening of cost throughout may be effected by the introduction of more modern plants. There is not time in which to go into details of the several systems but I may refer to the by-product coke ovens as having, through the size of their units the following advantages; the introduction of mechanical methods for handling coal and for charging and discharging the ovens; the ability to successfully make use of coals not before classified as gas coals; the better recovery and utilization of the by-products; and the cheaper production of gas. A difficulty in their use lies in the fact that they are primarily coke producers and that they can be employed profitably only where, as at blast furnaces, there is an assured market for this coke at a reasonable price. When, in 1906, I was engaged in the study of this industry I found its progress arrested by an inability to dispose profitably of the tar. It is worthy of note that in the interval that has elapsed, the proof of the value of coal tar as a binder for road material has been so well demonstrated, and the "good roads movement" has met with such acceptance, that an active market has been made for coal tar and the building of by-product coke ovens has proceeded while the outlook for the disposal of tar from gas works has improved. Beginning with the by-product plant at Everett, Massachusetts, gas from such plants has been distributed for sale when they were conveniently adjacent to large consuming communities, and to a market for the coke, but a combination of these prerequisite conditions is not common.

Fortunately there have now been devised, both by Koppers and by the Semet-Solvay Company, gas ovens which combine with the proved advantages of the by-product oven a method of utilizing such a portion of the coke in further manufacture that most neighborhood markets can absorb the residue at a good price. So far as I am aware the Semet-Solvay oven is yet undemonstrated but the Koppers gas oven has been built and operated and it has been ready to contract to put gas made in this oven into the holder at a cost of but 6.3 cents per thousand cubic feet. At such a cost gas can for a long time yet compete with electricity.

The development of flameless incandescent surface combustion may fortify the gas industry. The ap-

plications of gas by this means to domestic uses, manufacturing and metallurgical purposes and to the generation of steam, are most impressive. This discovery and invention is now being subjected to severe scrutiny and test and if it proves to be what it now appears to be, it is expected to be of more benefit to the gas industry than Welsbach's invention of the incandescent gas mantle.

Moreover, the recovery of the sulfur whose loss in the past has been mentioned and deplored seems now commercially possible since means for its utilization, which have been demonstrated as feasible and operative in the laboratory are now being tested on a commercial scale in the factories, Burkheiser's recovery process being operated in connection with the Flemalle Grande coke ovens near Liege, Belgium, while Walther Feld's rival process is being employed at the gas works in Königsberg, Germany. Both aim to produce ammonium sulfate from the ammonium compounds in the gas liquor and the sulfur compounds obtained from the coal. Feld's process is of special interest to the theoretical chemist in that the formation of the commercial product sought and the saving of the useful matter accomplished is effected through the aid of the tetrathionates and the controlling under manufacturing conditions of the reactions through which they are formed and those into which they will enter.

An unexpected competitor to the gas industry in its commercially successful utilization of its by-products is the alcohol industry which produces as a by-product enormous quantities of slops, the major portion of which have gone to waste, for it is found that through the action of the enzyme, amidase, upon the diamido acids present in these distillery residues, ammonia and propionic acid are formed. Being an enzymatic reaction no expensive or complicated plant and no difficult or dangerous manipulation is required in the process. This process, known as the Effront process, produced at the Nesle distillery, from the molasses vinasse, resulting from the production of 100 liters of alcohol, 35 kilos of ammonium sulfate and 35 kilos of the fatty acid; and from the beet-root vinasse representing 100 liters of alcohol it produced 16 kilos of ammonium sulfate and 12-14 kilos of fatty acid. In the process, the diamido nitrogen was completely converted into ammonia, no amines or ammonia compounds resulting.

The competition from this quarter is prospective but it is not likely to materialize immediately. For the consolation of the afflicted manager of gas works it may be said that the microorganisms and their enzymes may be commercially employed in the resolution of some of his troubles. Very properly the denser and more progressive communities are forbidding him to discharge his polluted effluents into the adjacent water courses. I imagine nothing can be more enraging than to be thus enmeshed, but these microscopic bodies may be put under his command to not only so purify these effluents that they become quite innocuous, but to also give such a commercially valuable return in the product as to almost if not quite repay the cost of the operation.

CURRENT INDUSTRIAL NEWS

SELENIUM GLASS.

Selenium, to the extent of about 11,000 lbs. annually, is produced by three American firms from the anode muds in electrolytic copper refining. The demand, which is not large, is practically limited to manufacturers of red glass and red enameled ware; but while the use of selenium as a means of coloring glass was patented twenty-one years ago by F. Welz (*Ber.*, 25, 819), very little has been published on selenium glass. It is for this reason that the paper by Fritz Kraze in *Sprechaal*, 45, No. 14, 214-6; No. 15, 227-8 (1912) is of great interest to the glass manufacturer; accordingly, it is abstracted at some length.

Welz used selenium or a compound of selenium and cadmium sulphide for the production of rose, red and orange colored glasses (see, in this connection, *Eng. Min. J.*, December 18, 1897, 731); but an enquiry in the "Fragekasten" of the *Sprechaal* showed Kraze that these mixtures were not yet satisfactory. He gives as a good composition for coral-red corresponding to Kaiser-red glass (see *Sprechaal*, 1911, 707): 100 kg. sand, 20 kg. soda, 8 kg. potash, 7 kg. lime, 0.5 kg. borax, 13 kg. cryolite, 300 grams selenium, 700 grams cadmium sulphide, and 230 grams sulphur. Similarly, for a transparent yellow-red glass, 200-300 grams selenium and 60 grams uranium oxide with 100 kg. sand, 12 kg. soda, 16 kg. potash, 20 kg. minium, and 10 kg. limestone, are recommended. The use of selenium and uranium oxide in the manufacture of orange-yellow glass, was patented in 1893. Uranium-selenium glass shows a green color in reflected light, while it is yellow-red in transmitted light (cf. uranium glass).

Spitzer patented a process for the red coloration of glass by the use of selenites and selenates (*Ber.*, 27, 777). These compounds are more suitable than metallic selenium, since they are more stable in the heat of the furnace, and are in consequence less likely to become lost through volatilization and oxidation. New shades of color are obtained by the use of selenium and selenium compounds with gold (*Ibid.*, 28, 195), or with silver, opacifying metallic oxides and certain minerals, such as cryolite, fluorspar, various phosphates, etc.

Even if elementary selenium is incorporated into the glass batch, it dissolves in the clear fusion without producing any coloration; doubtless it is oxidized and exists in the form of dioxide in a colloidal state. A reducing agent is necessary if a red selenium glass is to be obtained. Arsenic trioxide will effect the reduction of selenium compounds dissolved in glass, and the same reaction occurs with corresponding amounts of powdered charcoal or in fusion in a reducing atmosphere. With glasses fused with sodium selenate, Kraze always obtained a red coloration following an addition of arsenic trioxide corresponding to the reduction to selenium.

"All formulas including saltpeter for red selenium glass are absurd;" in fact, the use of saltpeter "does not seem to apply even in lead glass colored with selenium" (*Sprechaal*, 1911, 142), for there will always be an oxidation of the selenium present, giving rise to ineffective selenium (colorless dioxide) and occasioning considerable loss. Kraze failed to obtain a color with a batch of the following composition: 100 kg. sand, 15 kg. potash, 15 kg. soda, 12 kg. marble, 6 kg. minium, 3 kg. saltpeter, and 125 kg. selenium.

Kraze concluded that if the red color of selenium glass is due to the separation of red elementary selenium, then there must result an evolution of hydrogen upon treating the glass with concentrated hydrofluoric acid. Investigation showed a simultaneous formation of hydrogen selenide, which could only be attributed to the presence of a selenide in the glass examined. No. 1 of the experiments given below.

Glasses decolorized by means of selenium possess an unusual

clearness and brilliancy. The use of selenium as a decolorizing agent (sodium selenate is generally used) is claimed in German Patents 63,558, 78,565, and 88,615. Careful experiments have shown (see Miskowsky, *Keram. Rundschau*, 18, 457) that the ratio of ferrous oxide to decolorizing agent is 1 : 0.000208 for selenium, which acts as a decolorizer by producing a complementary color which "covers" the green tint imparted to glass by iron oxides. (Selenium-manganese is now being marketed in the United States as a glass decolorizer.) Kraze found that the undesirable red tint, due to too much selenium in decolorized glasses, was removed when arsenic was added to the molten glass, which showed that arsenic acted as a reducing agent.

In the experiments made by Kraze, the following types of glass were placed in a Seger oven in chamotte crucibles and mixed with sodium selenate or selenium:

No. I.	1.7	K ₂ O	CaO	9.8	SiO ₂	
No. II.	1.7	Na ₂ O	CaO	9.8	SiO ₂	
No. III.	1.18	Na ₂ O	CaO	6.94	SiO ₂	
No. IV.	1.53	K ₂ O	CaO	5.4	SiO ₂	
No. V.	1.53	K ₂ O	BaO	5.4	SiO ₂	
No. VI.	1.53	Na ₂ O	BaO	5.4	SiO ₂	
No. VII.	1.53	K ₂ O	ZnO	5.4	SiO ₂	
No. VIII.	1.53	Na ₂ O	ZnO	5.4	SiO ₂	
No. IX.	1.49	K ₂ O	CaO	9.8	SiO ₂	
No. X.	1.49	K ₂ O	BaO	9.8	SiO ₂	
No. XI.	1.49	K ₂ O	ZnO	9.8	SiO ₂	
No. XII.	1.49	K ₂ O	PbO	9.8	SiO ₂	
No. XIII.	1.49	K ₂ O	CaO	9.3	SiO ₂	0.5 B ₂ O ₃
No. XIV.	1.49	K ₂ O	CaO	9.47	SiO ₂	0.33 P ₂ O ₅
No. XV.	1.49	K ₂ O	CaO	9.3	SiO ₂	0.5 SnO ₂
No. XVI.	1.49	K ₂ O	CaF ₂	0.3	Al ₂ O ₃	9.8 SiO ₂

According to the calculation of the mixtures of types I-XVI, all contained 100 parts by weight of quartz, in order to measure the proportion of added selenium recommended by Schuster & Wilhelmy A.-G. for the production of rose-colored glass. According to this firm, 300-350 grams sodium selenate or 100-120 grams elementary selenium are used with 100 kg. sand.

No. I.—The crude mixture contained by weight: 100 quartz, 40 potash, 17 limestone. Of this mixture 157 grams were fused with 0.3 gram sodium selenate. On the first run, 3 hours after heating the Seger oven, the glass was still colorless. It was then treated with 0.5 gram arsenic, and after 30 minutes another test was made. The result was a completely fused glass with a very faint red color. This molten glass was next well-stirred and 1 hour after the previous test was found to be colored red. After another hour the color remained unchanged. It was next mixed with 0.6 gram more arsenic, which produced a deep red color; and, in 15 minutes, with the addition of another gram of arsenic, the color remained unchanged. This experiment showed that the red colored selenium separated out under strong reducing influences, the color increasing until the completion of reduction.

No. II.—An equal molecular weight of soda was substituted for potash; and the mixture contained 100 grams quartz, 31 grams calcined soda, and 17 grams lime. This time 0.5 gram selenium was added. After 2 hours, the glass was colorless; the addition of arsenic an hour later gave no result, and the glass finally became greenish without any noticeable red tint. These experiments showed that the soda-lime glass was unsuited for selenium coloring; the formation of a colored sodium selenide had not taken place. The green color observed was traced to dissolved ferrous silicate, resulting from the iron rod employed in stirring.

No. III.—This corresponded to a glass composition according to Tscheuschner and was selected in order to try a high-alkali glass: 100 grams quartz, 30 grams calcined soda, and 24 grams calcium carbonate were fused with 0.3 gram sodium selenate. After 3 hours, the glass was incompletely fused, very opaque,

but clearly rose-colored, being even stronger than No. I before the addition of arsenic. The glass became slightly transparent 30 minutes later, but the red color had disappeared; after another half-hour there still remained some unfused matter, but otherwise the glass was clear, although it possessed a greenish tint. An addition of 0.5 gram arsenic was now made, and the result was a clouded and intensely green colored glass; the green color persisted until clear fusion. Another addition of 0.5 gram arsenic gave a pale but still green glass. These fusions showed, as in the case of No. II, that soda-lime glass was hardly suited for selenium coloring, even though the greater lime content as compared to the soda present, was somewhat favorable for coloring at first. The increase in depth of the green color after the addition of arsenic was ascribed to a reduction of ferric silicate.

No. IV.—100 grams quartz, 65 grams potash, and 31 grams calcium carbonate were fused with 0.5 gram selenium. The iron oxide (from the rod) altered the red color of the selenium. An addition of 0.5 gram arsenic brightened the glass, and further additions served to produce ferrous oxide, the green color of which, with the red color of the selenium, produced the decolorization. The cold glass was bright yellow-brown, although it had a rose tint.

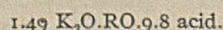
No. V.—The batch contained 100 grams quartz, 65 grams potash, and 60 grams barium carbonate, making a glass which fused easily: 0.5 gram selenium was added, and before fusion an addition of 1.5 grams arsenic was made. After 2 hours, the glass was bright and possessed a coffee-brown color and a rose shade. After 30 minutes, 1 gram arsenic was added, whereupon the glass rapidly became colorless, with only a weak brown tint. Further additions of arsenic produced a green color. The arsenic had finally caused a complete reduction of ferric oxide to ferrous oxide and consequently a green color; the selenium had been volatilized, although probably barium selenide was formed to a certain extent.

No. VI.—The batch contained 100 grams quartz, 50 grams calcined soda, 60 grams barium carbonate, and 0.5 gram selenium. The addition of arsenic was made as in No. V. The first result was an orange-brown, crystalline glass; after another addition of arsenic (1 gram), it became colorless. The complementary effects of the colors entered in here, for on repeated additions of 1 gram arsenic, the glass became very green colored.

No. VII.—The fusion was made with 100 grams quartz, 65 grams potash, 25 grams zinc oxide, and 0.5 gram selenium. After 2½ hours, the glass was clear and of a deep brownish yellow color. The addition of arsenic failed to produce a change in color after 15 minutes; a second addition gave rise to a yellowish gray tint; and a third addition caused no change but a slight brightening. Kraze was led to believe that zinc selenide was formed in this experiment.

No. VIII.—100 grams quartz, 50 grams calcined soda, 25 grams zinc oxide, and 0.5 gram selenium. The results obtained were similar to those in No. VII, except that the clarification occurred after 3 hours and the color changes were different. After the first addition of arsenic, the color change was to yellow, and further additions effected no change in color and only a slight clarification. A red tint was never noticed.

The following tests were decidedly more acid than the preceding and the glasses were similar to potassium glasses of the type:



In the previous tests the acids entered into the composition solely as silica; in the following difficultly fusible, acid glasses were experimented with for comparison.

No. IX.—This was a composition for Bohemian crystal glass taken from Hohlbaum's "*Zeitgemässe Herstellung, Bearbeitung und Verzierung des feineren Hohlglases.*" The batch of 100 grams quartz, 35 grams potash, and 17 grams calcium

carbonate was fused with only 0.1 gram selenium. Three hours after heating the furnace, test 1 showed no unfused parts and was deep brown; 2 hours after, tests 2 and 3 possessed the same color. The addition of 0.5 gram arsenic, however, caused a change to a pretty red (test 4). The rose color did not change after ¾ hour (test 5), and even remained after repeated additions (2.5 grams) of arsenic (test 6). Even after 30 minutes later, following an addition of arsenic (0.5 gram), no change in color was observed. The results of this experiment showed that the desired color had been obtained with very small amounts of selenium (0.1 gram). Hence the results agreed with those of No. I, for the measured addition of sodium selenate (40 per cent. salt) used in the latter corresponded to 0.12 gram selenium; but glass No. I, with less silica, did not assume a rose color so rapidly as No. IX. Therefore, it seems that the acid content of the glass plays an important part in developing the red color. Nevertheless, it must not be considered that sodium selenate requires more energetic reduction for red coloring than selenium.

Kraze also fused the batch of No. IX with 0.2 gram of selenium, with 1 gram selenium, and again with double and five times the amount. What he expected did not occur: he red coloration did not become intensified from an increase in the selenium content, and the rose color resulting from an addition of 0.1 gram selenium could not be distinguished from that from 0.2 gram selenium—in fact, both glasses were colored even more strongly than when 0.5 gram selenium was used.

No. X.—In this experiment lime was substituted by barium oxide, but otherwise the glass was the same. The batch was: 100 grams quartz, 35 grams potash, 33 grams barium carbonate, and 0.2 gram selenium. The first test had hardly been fused before it showed a rose tint. Two hours after the gas oven was started, the glass was thoroughly fused, but the rose color was brown tinted. Four hours later, tests showed that the product was somewhat brighter.

No. XI.—A more acid zinc glass than No. VII was obtained by substituting zinc oxide for barium oxide. The batch consisted of 100 grams quartz, 35 grams potash, 14 grams zinc oxide, and 0.2 gram selenium. Tests showed that at the beginning of the fusion there was a very weak rose tint, but the melt later became absolutely colorless; the addition of arsenic did not cause the least coloration.

No. XII.—Composition: 100 grams quartz, 35 grams potash, 39 grams minium, and 0.2 gram selenium. After 4 hours fusion, the tests showed a yellow glass, but later brownish yellow, and finally a glass colored a little more intensely.

The next three experiments were again with potassium—lime glasses, but boric acid, phosphoric acid, or stannic oxide was in part substituted. Replacement of part of the silicic by boric acid in the acid potash glasses diminished the red color; and phosphoric acid and stannic oxide acted in a similar manner and to a greater extent. Replacement of the lime by fluorspar gave only a colorless glass, owing, no doubt, to the volatilization of the selenium as fluoride during the fusion.

Kraze promises to investigate the existence of selenides in colored selenium glasses.

HEAVY OIL ENGINES.

The following is an abstract of an address by Capt. H. R. Sankey before the Royal Society of Arts, April 29, 1912:—

Some twenty years ago there was only one form of oil engine, of which the Hornsby-Akroyd and Priestman could be taken as types. These engines required external heat at starting for the evaporation of their fuel and worked on paraffin. In 1890, Daimler invented the petrol-engine, which worked with petrol of a specific gravity of about 0.68 and which required no external heat for the evaporation of its fuel. Seven years later Diesel introduced his engine, which worked with heavy oil and required no external heat, as the fuel was mechanically "pulverized" instead of being evaporated.

At the present time, two classes of oil-engines are in use, *viz.*: light-oil engines, which use fuel capable of forming explosive mixtures at ordinary temperatures and possessing a density of 0.68–0.72; and heavy-oil engines, which use fuel requiring high temperatures or mechanical "pulverization" for the formation of explosive mixtures, and possessing a specific gravity of 0.8–0.9. Of the heavy-oil class, the Diesel engine, which has received much space lately in the technical press, is the most important type. In it the compression occurs entirely on a charge of air, into which the fuel is afterwards injected, so that there is no danger of pre-ignition, and compression pressures up to 450–500 lbs. per sq. in. can be used. It is, in fact, in its high compression that the great efficiency of the Diesel engine lays. In the semi-Diesel type of engine, in which, after compression of air, the fuel is injected into a hot bulb, there is no danger of pre-ignition, but compressions up to about 200 lbs. per sq. in. are usually found to be sufficient to ensure ignition.

In the Diesel engine admission occurs at constant pressure and exhaust at constant volume, as compared with the gas-engine and petrol-engine, in which admission takes place at constant volume. This difference gives the Diesel engine an advantage, since there is a greater difference between the upper portions of the actual and theoretical diagrams in the two cases. The economy of the Diesel engine is also largely accounted for by the high compressions, up to from 450–500 lbs. per sq. in., which can be used. The temperature reached in the cylinder of a Diesel engine is usually about 1200° F. With a 2-stroke cycle gas-engine there is danger that some of the new working charge may be blown out of the exhaust by the scavenging air, but in a Diesel engine this can not happen, so that the Diesel may be regarded as essentially a 2-stroke engine.

According to *Industrial Engineering*, 11, 401, the thermal or indicated efficiency of the Diesel engine of to-day reaches 48 per cent., while the effective or brake efficiency reaches, in some cases, 35 per cent. of the heat value of the fuel. This engine converts the heat of the natural fuel into work in the cylinder itself, without any previous transforming process.

Allner (*J. Gasbel.*, 54, 321) reported that tests on a 100 h. p. Diesel motor showed vertical-oven tar was a very satisfactory fuel for this type of engine; later (*Progressive Age*, 29, 481) it was pointed out that tar fuel was the least expensive for Diesel engines and that with slight changes in the engine, no difficulty was experienced in using it; and Allner has more recently pointed out (*J. Gasbel.*, 54, 1025) that the present practice in using tar is to assist ignition by spurting into the cylinder about 5 per cent. of gas oil just ahead of the tar. Recently, however, it has been found possible to operate on tar oil and avoid the use of even this small amount of gas oil, and quite lately it has been ascertained that a 40 h. p. Diesel engine may be operated by the use of raw tar itself, using both vertical oven tar and certain kinds of retort oven tar, and wholly avoiding any use of ignition oil.

THE CLASSIFICATION OF SOAPS.

With the object of classifying different soaps on a commercial scale, the Commission appointed by the Italian Union of Soap Makers has proposed to divide them in the order of their requirements. Gianoli reports as follows concerning the recommendations of the Commission [*Chem. Trade J.*, 50, 465 (1912)]:

1. PURE SOAPS OF THE FINEST QUALITY.

(a) *Boiled Soaps*.—Hard, soft, floating, white and dyed, scented or unscented; not liable to change color or to become rancid; completely soluble in water and in alcohol; and constituted by a combination of soda and fatty acids when this is insoluble in sodium chloride solutions at 15° Bé., *i. e.*, free from oxy-fatty acids, and in which the total percentage of hydrated fatty acids, non-siccative, is not less than 60 per cent.

Free from unsaponified glycerides, hydrocarbons, wax, alkaline and metallic soaps; not more than 0.3 per cent. free sodium hydroxide; not more than 1.5 per cent. total mineral matter; not more than 2 per cent. foreign organic matter (coloring matter, perfume, or fatty acids of low molecular weight).

(b) *Resin Soaps*.—Boiled with not more than 15 per cent. of colophony, and otherwise corresponding to the requirements assigned to the preceding.

(c) *Mottled and Marbled Soaps*, in which the proportion of hydrated fatty acids is not less than 55 per cent., and the total free alkalis, carbonates, sulphates, and alkaline silicates do not exceed 3.5 per cent.

2. CURRENT SOAPS OF INFERIOR QUALITY.

Hard or soft, plain or marbled, containing, or not containing, alkaline mineral detergents, organic or mineral fillings in quantities greater than 3.5 per cent. when the soaps contain 33 per cent. humidity—namely, soaps containing carbonates and alkaline silicates, talc, kaolin, asbestine, fossil flour, or sugar, starch, fecula, hydrocarbons, etc. Soaps manufactured cold or hot with fatty acid or glycerides of any nature, with or without resin.

3. DRY SOAPS.

Soaps which do not give more than 20 per cent. of water when exposed for 3 hours to a temperature of 105–110° C. after being pulverized with 10 times their weight of powdered glass.

The soap classifications hitherto published have been generally based on the methods of manufacture. The above classification seemed to the Italian Commission to more nearly meet the requirements of the analyst and consumer. What the latter desires to know is the peculiar character of the soap he is buying, and not how it is made. Consequently, to satisfy the trade, the limits within which the composition may vary must be specified.

THE SPONTANEOUS COMBUSTION OF CHARCOAL.

In 1911, there were 64 reported fires in the transportation of charcoal in the United States, and of these 63 were evidently caused by spontaneous combustion. During 1911, experiments on the spontaneous heating and ignition of hardwood charcoal were started at Straight, Pa., and at Westline, Pa., by the Bureau for the Safe Transportation of Explosives and other Dangerous Articles. The charcoal, after varying treatment as to cooling and air exposure, was loaded into box cars, and the temperature of the interior of these cars was observed at intervals to detect any increase in temperature. From the incomplete series of experiments performed, it was reported (Bureau of Explosives, *Report No. 5*, February, 1912, p. 47) that "no conclusions can be drawn as to the relative efficiency of various periods of cooling and airing. In no case was there any ignition or an increase of temperature approaching ignition. In every case but one there was a noticeable rise of temperature, which can be ascribed only to the action of air on the cold charcoal, and not to any residual sparks or fire." The figures obtained so far have not shown that wetting the charcoal increases the heating effects, although it is the general belief that heating more frequently occurs in damp weather. "To attain absolute security from fires of spontaneous origin it is necessary to store the charcoal in the open till such time as it attains its equilibrium with regard to absorption of air"—an impracticable procedure, so "the logical alternative is to supplement the best present practice of cooling, airing and storing in open cars for 24 hours prior to shipment by a safe method of ventilation of cars during shipment."

The experiments on the spontaneous combustion of charcoal recently published by the National Physical Laboratory (*Report for 1910*, 85; 1911, 86) were conducted in an electrically heated oven, in which 1 cu. ft. of the charcoal was exposed to a uniform temperature (constant within 1° C.), measured by

means of thermocouples. The charcoal was surrounded by an air space about 3 inches wide, and the oven could be closed airtight or a current of air of any desired velocity passed through it. Experiments with flake charcoal showed that with air currents ranging from 5-62 cu. ft. per minute for 1 cu. ft. of charcoal, spontaneous combustion occurred at temperatures of from 96-110° C., while at lower temperatures no signs of spontaneous heating could be observed. Additional experiments showed that in a current of air containing 5 per cent. sulphur dioxide, spontaneous combustion of the charcoal took place after some hours; therefore, there is risk of danger in using sulphur dioxide for disinfecting rooms, etc., where charcoal is present in the walls. It is reported that decayed wood appears to be much less inflammable than charcoal.

ARTIFICIAL RUBBER FROM SEAWEED.

A product, now being marketed under the name "Seagumite," said to be non-inflammable, damp-proof, and unaffected by heat or cold, and to be expected to provide a substitute for rubber and leather, is the subject of a patent recently issued to J. S. Campbell, of London (English Patent 5395, 1911). His invention relates to improvements in the production of a substance having the characteristics of rubber and capable of vulcanization. It had previously been proposed to treat marine plants, lixiviated by acidulated water, with alkalis such as ammonia; and it is said that the material thus produced has, after impregnation with siccative oil or dissolved india-rubber, been found suitable for use in the whale-bone industry. The Campbell process consists in boiling washed and crushed seaweed in steam-jacketed pans with ammonia for about 45 hours, 1 gallon of ammonia (specific gravity, 0.88) being used for 5 cwts. of seaweed; drying in an agitating apparatus, to which heat is applied, and during agitation adding 1 gallon of a mineral or vegetable oil, as rosin oil; adding next a vulcanizing substance, such as sulphur, and subsequently mixing the whole mass with 25 per cent. by weight of a glutinous or resilient binder, as pontianac gum, jelutong, gutta-percha, or reclaimed rubber waste. The whole is then heated for 1 hour and finally dried in a vacuum pan or press. Prior to removing and drying, a preservative, as wood or bark extract, may be added to the amount of 0.85 per cent. by weight of the seaweed used.

The Campbell process seems to be primarily dependent upon the formation of ammonium alginate. Algin in its soluble form is recognized as having probable value as an agglutinant, and a substance resembling gutta-percha may be prepared from the alkaline alginates and shellac.

"TEMPERED COPPER" TOOLS.

According to *The Engineering and Mining Journal*, 93, No. 20, 986, the copper-cutting instruments of the Tarascans, found in the Balsas River ruins in Guerrero, are so hard that they would turn the edge of a modern knife, and it has been claimed that these people, along with the Aztecs and Toltecs, possessed the secret of tempering copper. On the other hand, copper knives and axes, found at Atcopotzalco, are so soft that they can be cut with an ordinary pocket knife. Analysis showed that in all three localities the copper implements were of the same composition as the copper ores found therein. The blades from Guerrero, which are hard and apparently tempered, were made from the natural ore carrying nickel and cobalt, thus rendering the smelted alloy steel-like in hardness. Thus, the natural product gave an alloy of great hardness when heated and sharpened, while the other ores of practically pure copper, when smelted, resulted in implements which were soft and

inferior in cutting value. The sharp cutting implements were therefore the result of Nature's handiwork, and it is indeed very questionable whether these people possessed the secret of tempering.

THE PURIFICATION OF AIR BY OZONE.

Nature, 89, 304, states that the system of ozone production and distributing plant installed for air purification and ventilation on the Central London Railway is a plenum one, and consists of Sirocco fans placed at each of the underground stations, except that at Shepherd's Bush. The total air supplied to the tubes is about 80,000,000 cu. ft. per day. Each fan draws its air through a filter screen, and works in conjunction with an ozone-generating plant. The latter consists of mica sheets with metallic gauze on each side, stacked side by side, and energized by alternating current at about 5,000 volts, in such connection that a silent discharge passes between the various plates, so that air passing between them is ozonized. The ozone generator is supplied with a small transformer, which in turn is supplied with 380 volts alternating current from a small rotary converter. The converter is connected on its direct-current side to the 550-volt lighting circuit of the railway.

THE USE OF COKE-OVEN GAS.

Cooper (*J. Gas Ltg.*, 118, 107) states that in Germany the towns of Waldenburg, Altwasser, Salzbrunn, Essen, Dortmund, and Mülheim have been supplied for some time with gas from the neighboring coke-oven plants. The entire supply of gas for Mülheim-on-the-Ruhr and for Barmen is obtained from two coke-oven plants. The installation consists of 50 Koppers' horizontal regenerator ovens, each of which is capable of taking a charge of 8-10 tons of coal; the period of carbonization is 24 hours and only the richer portion of the gas (that evolved from the second to the twelfth hour, representing 50 per cent. of the yield) is used for distribution. During this time one oven will produce 70,600 cu. ft. of gas possessing a calorific value well over 600 B. t. u. per cu. ft. and costing \$0.17 per 1,000 cu. ft. The gas is purified from hydrogen sulphide by the town authorities and distributed.

THE PRESERVATION OF WOOD WITH "BELLIT."

In order to increase the preservative effect of sodium fluoride on wood, it is now being mixed with nitro-phenols. According to Nowotny (*Oesterr. Chem. Ztg.*, 15, 100; cf. *Idem*, 13, 81), one of these mixtures, "Bellit," consists of 90 parts of 90-95 per cent. sodium fluoride and 10 parts of dinitrophenol-aniline. The latter compound is used because it does not, like free dinitrophenol, act upon the iron vessels in which the timber is impregnated; it is also active as an antiseptic. The selective phenomena observed when treating timber with mixtures of zinc fluoride and hydrochloric acid are reproduced in the "Bellit" treatment.

CHROME-NICKEL BRONZE.

Chrome-nickel bronze is now being manufactured by a Philadelphia company, the product being known as "Chromax Bronze." The proportions of metal in the alloy are said to be as follows: Copper, 66.66 per cent.; zinc, 12.13 per cent.; nickel, 15.15 per cent.; chromium, 3.03 per cent.; and aluminum, 3.03 per cent. The tensile strength of the alloy is said to be 79,000 lbs. per sq. in.; the color is white, and it takes a fine, silvery polish; the fracture is fine and dense, particularly after being remelted; and the alloy, owing to its high melting point, has a denser structure and greater compressive strength than manganese bronze. It can be rolled into sheets and wire.

NOTES AND CORRESPONDENCE

NOTES ON THE COMPOSITION AND ANALYSIS OF DESICCATED MILK AND CREAM.

By R. S. FLEMING.

The analysis of desiccated milk presents several difficulties which do not appear in the analysis of fresh liquid milk, and serious errors have been made through assuming that methods which apply to the one would necessarily apply to the other. Especially is this the case in the estimation of butter fat.

Before making the analysis the sample should be thoroughly mixed and then placed in a tightly stoppered bottle to prevent the absorption of moisture, most milk powders being quite hygroscopic.

Moisture is estimated by drying in a wide shallow weighing bottle one or two grams of milk powder to constant weight, preferably in a vacuum oven at 95° to 100° C. Five hours is generally sufficient. Do not dry longer than this without weighing. A slight increase in weight takes place after long drying, probably from oxidation of some of the constituents. In the absence of a vacuum oven an ordinary water or steam oven having a temperature of 99° to 100° would give fair results, but it takes considerably longer, about 10 hours, and even then the results are likely to be a trifle low.

Milk sugar can be best determined gravimetrically as follows: Weigh out in a small beaker 2½ grams of the milk powder or such a quantity that there is not over 0.3 per cent. of sugar in the purified solution. Add a little warm water at about 50° C. and stir up the mixture to a smooth paste, then add more warm water and wash into a 500 cc. flask. Shake up with the warm water until thoroughly dissolved. Small particles of the milk powder are liable to remain undissolved if care is not taken. Cool and make up the volume to about 400 cc. Add 10 cc. to Fehling's copper sulphate solution and proceed as in A. O. A. C. methods, *Bull.* 107, Bureau of Chemistry, pages 119 and 148. Preferably deposit the reduced copper electrolytically from sulphuric acid solution.

Cane sugar, if present, can be estimated readily by a modification of the Stokes and Bodner method, by which the cane sugar is inverted by means of citric acid, the citric acid having no inverting action on the milk sugar. In a 250 cc. Erlenmeyer flask, place 50 cc. of the sugar solution prepared as for milk sugar determination by precipitating proteins, etc., with copper sulphate and carefully neutralizing. Add 0.5 gram of citric acid. Boil with reflux condenser for 35 minutes. Neutralize and determine the reducing power of the solution in same way as for milk sugar, adding the boiling Fehling solution directly to the flask containing the sugar solution. From the weight of copper found, subtract the amount found in previous determination for the milk sugar, multiply by the factor 0.5395 as given by Allen, Volume 1, page 284. This gives the amount of cane sugar.

Casein is rather difficult to determine from the fact that it precipitates in very fine particles that clog the filter. The following has been found by the writer to be the most satisfactory of several methods tried: To 50 cc. of a 10 per cent. solution of the milk powder at 40° C. add 2 cc. of a warm saturated solution of potassium alum. Allow to settle. Filter on a large filter paper (15 cm.). If the filtrate is not clear, filter on another smaller paper. Transfer precipitate to filter. Wash and place filter papers and contents in a Kjeldahl flask. Determine nitrogen by any of the Kjeldahl modifications. If the Gunning method is used, add a little anhydrous copper sulphate to hasten the reaction. Three hours' digestion by this method is generally sufficient. Use the factor 6.38.

Albumin is approximately determined by subtracting the

casein from the total protein. The latter may be determined by digesting one gram of milk powder and proceeding in the regular way. It is to be noted that in milks which have been highly heated the albumin is partially or wholly coagulated. In that case the suspended albumin will precipitate with the casein, making the percentage of the latter higher than it should be.

Ash is best determined by incinerating one or two grams in a platinum dish at a low red heat. For the first half hour use a very low flame.

Butter fat may be determined by any of the following methods:

First. Extraction with pure ethyl ether of a specific gravity of 0.720 (anhydrous ether + 0.5 per cent. by volume of water) as described by McLellan, *Analyst*, 1908, page 353. It is unnecessary, however, to soak over night and re-extract. Sixteen hours' continuous extraction in a Soxhlet or a direct extraction apparatus is sufficient. Schleicher & Schuell's double thick extraction cartridges are excellent for retaining the fine particles of milk powder.

Second. The Werner-Schmidt method. This method is most conveniently applied as follows: Weigh out one gram of milk powder. Place on a well annealed glass stoppered tube of at least 80 cc. capacity. Add 5 cc. of water. Shake until homogeneous, then add 7.5 cc. of concentrated hydrochloric acid (sp. gr. 1.19). Shake until dissolved. Remove the stopper. Place in boiling water bath for five minutes, shaking gently to keep the mixture agitated. Remove and cool. Then add pure ethyl ether. Shake vigorously; allow to settle for ten minutes. Remove ethereal layer to a weighed flask by means of a wash bottle connection. Repeat the extraction three times. Evaporate off the ether and dry in the water oven. Cool and weigh. Should the fat be contaminated, as it will be at times, dissolve out the fat with petroleum ether, leaving the impurities adhering to the flask. Dry and re-weigh. Subtract the impurities.

Third. A new method worked out by Redmond in this laboratory and described in the accompanying paper, "A New Method for the Determination of Fat in Desiccated Milk," has been found to give splendid results.

Fourth. The Rose-Gottlieb method has been found to give satisfactory results, but is somewhat tedious.

The following methods have been found to be unsatisfactory as they give low results: Adams, Babcock, extraction with anhydrous ether or chloroform.

The composition of milk powder varies within wide limits. Very recently cream powder has been put on the market which has almost as high a butter fat content as butter itself. Small amounts of cane sugar are frequently added. Modified milk for infants has much less casein, more albumin and more milk sugar than normal milk. The accompanying table gives the analyses of a number of different milk and cream powders:

No.	Butter fat.	Casein.	Albu- min.	Milk sugar.	Cane sugar.	Ash.	Mois- ture.	Total.
1	29.12	24.06	1.86	37.52		5.72	1.48	99.76
2	1.81	32.31	5.85	49.32		8.21	2.53	100.03
3	15.26	27.18	4.84	43.92		6.46	2.03	99.69
4	0.6	2.3	10.20	77.2		9.10	1.40	100.80
5	11.25	11.30	7.57	60.10		7.66	1.37	99.25
6	53.08		16.89	26.04		3.78	0.81	100.60
7	67.64		12.21	15.92		2.67	0.76	99.20
8	21.00		18.90	23.82	29.98	3.93	2.94	100.57
9				47.16	2.25			
10				49.71	1.54			

No. 1, made from whole milk.

No. 2, made from skimmed milk.

No. 3, made from half skimmed and half whole.

No. 4, made from whey, the casein having been largely removed.

No. 5, made from whole milk modified with whey. When dissolved with the proper proportion of water it has approximately the composition of human milk.

No. 6, made from light cream and No. 7 from heavier cream.

Nos. 1-7, made from known milks.

No. 8, evidently from whole milk with the addition of cane sugar.

No. 9 and No. 10, evidently from skimmed milk with the addition of small amounts of cane sugar.

Nos. 8-10 made from unknown milks.

LABORATORY, MERRELL-SOULE CO.,
SYRACUSE, N. Y., Feb. 17, 1912.

A MODIFICATION OF THE BABCOCK TEST AS APPLIED TO THE ESTIMATION OF FAT IN DESICCATED MILK.

By N. GREGORY REDMOND.

As the Babcock method is the one most generally used by dairymen and manufacturers using milk products, either it or some equally unsuitable method is often applied to determine the fat in desiccated milk. Van Slyke¹ appreciates the fact that the ordinary Babcock method, when used with milk powder, gives results which are too low.

It occurred to the writer that it would be an advantage if the Babcock test could be so modified that it would give accurate results. This modification was finally worked out, and has been successfully used for several months. To test the accuracy of the method, the fat was determined on a sample of desiccated milk by several different methods. One of those used was the Werner-Schmidt method. That this method is trustworthy has been shown by H. D. Richmond² and also by an abstract in *The Analyst* of a recent paper by A. Burr³ on the "Composition of Dried Milk Powder." The results which are shown in the table prove that the direct extraction of the milk powder with anhydrous ether gives results which are too low. In each case where a direct extraction was made, the powder was first dried at 90° C. to 100° C. for at least five hours. In using the Werner-Schmidt method the fat was redissolved in petroleum ether and an allowance made for any impurities. This was also done with the direct extractions when the fat appeared to be impure.

In the ordinary Babcock test, the powder was weighed and transferred to the test bottle, then dissolved in warm water, cooled, and concentrated sulphuric acid added. This prevents any error which might occur from inaccurate sampling by measuring an aliquot part of a 10 per cent. or 20 per cent. solution. The general experience of this laboratory has been that this method is about 3 per cent. low.

The accuracy of the new method is shown by the fact that the average of ten determinations by the various methods (excluding the direct extraction with ether distilled over sodium and the ordinary Babcock method) is 28.49 per cent. fat, and the average of four determinations by the new method is 28.62 per cent. fat.

A determination in duplicate by the new method can easily be made in less than one hour. Some of its advantages are cheapness, simplicity, speed and accuracy.

The following is a description of the method:

Weigh 2.5 grams of milk powder and transfer it to an ordinary Babcock milk bottle, graduated to 10 per cent. A glass funnel (about 2" in diameter and with the stem cut off to 1/2") is inserted in the neck of the bottle and is of great help in transferring the powder. Add 31 cc. of dilute sulphuric acid (395 cc. concentrated H₂SO₄ diluted to 1 liter) and place the bottle upright in a dish of gently boiling water. Shake frequently and keep in the boiling water until all the powder is dissolved and the solution is dark brown in color. This usually takes from 7 to 10 minutes. After removing the bottle from the

water add 12 cc. concentrated H₂SO₄ (sp. gr. 1.82-1.83) and mix thoroughly, taking care to keep the solution out of the neck of the bottle. Agitate with a rotary motion. Place the bottle in a centrifuge and whirl for 4 or 5 minutes. Add hot water until the solution reaches the lower end of the neck, whirl again for 1 minute, then add hot water until the fat rises. Whirl again for 1 minute. In order to secure accurate results, the fat column must be read at a temperature not above 140° F. nor below 130° F; by setting the bottle in water, the desired temperature may be reached. Readings should be made to 0.05 on the bottle. The reading multiplied by 7.2 gives the percentage of fat.

$$2.5 \text{ grams} : 18 \text{ grams} = \text{Reading} : X.$$

$$\text{If reading} = 4.00, \text{ then } 2.5 : 18 = 4.00 : X.$$

$$\text{Or } X = 4.00 \times \frac{18}{2.5} = 4.00 \times 7.2 \text{ or } X = 28.80 \text{ per cent.}$$

A COMPARISON OF DIFFERENT METHODS OF DETERMINING FAT IN MILK POWDER.

	Fat. Per cent.	Aver- ages.
Squibb's ether—16 hours' direct extraction.....	28.30 } 28.45 }	28.37
Ether containing 5 cc. H ₂ O per liter, 16 hours' direct extraction.....	28.50 } 28.55 }	
Ether containing 5 cc. H ₂ O per liter, 18 hours' direct extraction.....	28.50 } 28.60 }	28.55
Ether containing 5 cc. H ₂ O per liter, Werner-Schmidt method.....	28.50 } 28.56 }	
Anhydrous ether (distilled over sodium), Werner-Schmidt method.....	28.39 } 28.54 }	28.46
Average of ten determinations above.....		
By the proposed new method.....	28.44 } 28.44 } 28.80 }	28.62
Anhydrous ether (distilled over sodium), 16 hours' direct extraction.....	13.55 } 13.40 }	
Babcock method.....	25.20 } 25.20 }	

Babcock bottles vary in volume. It is more convenient to use bottles which hold at least 45 cc. of water when filled to the lower end of the neck. The bottle should be thoroughly cleaned, rinsed with alcohol and dried (to prevent powder sticking in the neck) before using. This insures clear and accurate readings. Commercial sulphuric acid has been used in making the dilute H₂SO₄ solution and good results were obtained. It is better, however, to use c. p. acid and thus avoid contamination of the fat column by impurities in the acid.

LABORATORY, MERRELL-SOULE CO.,
SYRACUSE, N. Y., Feb. 17, 1912.

ALUNDUM NOT CONSTANT IN WEIGHT.

By E. B. FORBES.

The invention of porous earthenware laboratory utensils immediately satisfied a large number of urgent and long-standing requirements. As is inevitable under such circumstances this new ware has been put to some uses which it is not adapted to serve, and a correct appreciation of its very great value in the laboratory requires that we search out and recognize its limitations.

In an effort to shorten and improve upon the usual method for crude fiber determination, we followed the Morgan P. Sweeney modification except that instead of straining through an unstandardized cloth we conducted our filtration, washing and ignition all without transfer, in an alundum extraction capsule. It appeared to be a beautiful method, and through the substitution of an efficient, standardized filter for the rag strainer it seemed to remove from this very unscientific determination one of the principal grounds for our objections; but things were not as they seemed. Alundum is not constant in weight through treatment with water and heat.

¹ "Modern Methods of Testing Milk and Milk Products," 1906, Ed., p. 86.

² *The Analyst*, 31, No. 364, pp. 218-224.

³ *Ibid.*, 36, No. 423, p. 279.

TABLE I.—EFFECTS OF HEAT AND WATER ON WEIGHT OF ALUNDUM.

Capsule No.	Wt. after washing with water and drying 2 hrs. at 100°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after washing with water and drying 3 hrs. at 100°. Grams.	Wt. after washing with water and drying 2 hrs. more at 100°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after 2nd ignition compared with wt. after 1st ignition. Mg.
1	11.3179	11.3136	-4.3	11.3180	11.3180	11.3146	-3.4	+1.0
2	13.1128	13.1098	-3.0	13.1130	13.1130	13.1108	-2.2	+1.0
3	13.0326	13.0292	-3.4	13.0326	12.0326	13.0310	-1.6	+1.8
4	11.5042	11.5014	-2.8	11.5044	11.5044	11.5032	-1.2	+1.8

Table I sets forth results of a test with four alundum extraction capsules. They were washed with water, dried at 100° for 2 hours, weighed, burned in a muffle and weighed again. In all weighings the capsules were contained in glass weighing bottles where they had been placed while as hot as they could be without breaking the glass. The weighing bottles were dried with the capsules in the oven and were kept in desiccators over sulphuric acid.

The weight after firing showed that all of the capsules had lost in weight, the amounts varying from 2.8-4.3 mg. Perhaps they were not dry. We then washed with water and lengthened the drying to 3 hours at 100°, weighed, dried 2 hours more at 100° and weighed again. There was no change in weight between dryings, but when fired all lost in weight from 1.2-3.4 mg.; and what is more, the capsules did not return to the weight obtained after the first firing but during this second test gained 1.0-1.8 mg.

TABLE II.—EFFECTS OF HEAT AND WATER ON WEIGHT OF ALUNDUM.

Capsule No.	Wt. after washing with water and drying 3 hrs. at 110°. Grams.	Wt. after drying 3 hrs. at 120°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after washing with water and drying 3 1/2 hrs. at 160°. Grams.	Wt. after ignition in muffle. Grams.	Change in wt. during ignition. Mg.	Wt. after 2nd ignition compared with wt. after 1st ignition. Mg.
1	11.3160	11.3160	11.3138	-2.2	11.3164	11.3136	-2.8	-0.2
2	13.1128	13.1128	13.1102	-2.6	13.1116	13.1096	-2.0	-0.6
3	13.0326	13.0326	13.0309	-1.7	13.0340	13.0306	-3.4	-0.3
4	11.5044	11.5044	11.5024	-1.8	11.5036	11.4996	-4.0	-3.0
5	10.2566	10.2566	10.2544	-2.2	10.2566	10.2530	-3.6	-1.4
6	13.4062	13.4062	13.4040	-2.2	13.4066	13.4028	-3.8	-1.2
7	11.7162	11.7162	11.7146	-1.6	11.7166	11.7142	-2.4	-0.4
8	10.8086	10.8086	10.8070	-1.6	10.8092	10.8060	-3.2	-1.0

We then added four more capsules to the test (Table II), washed with water, dried for 3 hours at 110°, weighed, dried for three more hours at 120°, weighed, fired and weighed again. Between dryings the weights were absolutely constant, but on firing we got a loss of 1.6-2.6 mg.

Next we washed in water, dried for 3 1/2 hours at 160°, weighed, ignited and weighed. This time there was as before

TABLE III.—EFFECTS OF HEAT ON WEIGHT OF ALUNDUM.

Capsule No.	Wt. after last previous ignition. Grams.	Ignited and weighed. Grams.	Change in wt. during ignition. Mg.	Ignited and weighed again. Grams.	Change in wt. during ignition. Mg.	Ignited and weighed again. Grams.	Change in wt. during ignition. Mg.
1	11.3136	11.3142	+0.6	11.3174	+3.2	11.3172	-0.2
2	13.1096	13.1110	+1.4	13.1144	+3.4	13.1140	-0.4
3	13.0306	13.0312	+0.6	13.0354	+4.2	13.0350	-0.4
4	11.4996	11.5008	+1.2	11.5046	+3.8	11.5038	-0.8
5	10.2530	10.2538	+0.8	10.2564	+2.6	10.2566	+0.2
6	13.4028	13.4043	+1.5	13.4082	+3.9	13.4078	-0.4
7	11.7142	11.7144	+0.2	11.7180	+3.6	11.7178	-0.2
8	10.8060	10.8064	+0.4	10.8101	+3.7	10.8095	-0.6

a loss in each case from 2.0-4.0 mg. and this last weight as compared with the one after the previous ignition showed in each case an appreciable loss.

One point had become clear. Water combines chemically with some constituent of the alundum capsule, a combination which is not broken up at 160° but which is destroyed at a temperature considerably below 1000°.

To throw more light on the apparent change in the weight of the capsule aside from that caused by the hydrating and dehydrating process above referred to, we subjected the same eight capsules to three consecutive firings and weighings without treatment with water. The weights are set down in Table III. In the first firing the capsules gained 0.2-1.5 mg., in the second from 2.6-4.2 mg. more, and in the third firing one capsule gained 0.2 mg. while the rest lost 0.2-0.8 mg.

Thus aside from the change in weight due to the taking up and loss of water there seems to have been operative a second factor resulting in a gain in weight which partially compensated for the losses occasioned as above mentioned, this gain not reaching its limit, under conditions existing in the muffle, until the second firing after the tests reported in Tables I and II. The reddish yellow color of the alundum became much lighter during these tests, perhaps due to change in the condition of the 0.5 per cent. of iron contained therein.

OHIO AGRICULTURAL EXPERIMENT STATION,
February 19, 1912.

THE CENTENARY OF THE INTRODUCTION OF GAS.

The Centenary of the Introduction of Gas was celebrated in Philadelphia on Thursday and Friday, April 18th and 19th, according to the program published in the April issue of THIS JOURNAL, p. 309.

The addresses are now appearing in full in the *American Gas Light Journal* and in the *Proceedings of the American Gas Institute*. A limited edition is also being printed in book form; 180 pages, illustrated. Price, \$2.00. Copies should be ordered at once of the American Gas Institute, 29 West 39th St., New York City.

Brief abstracts of the five addresses follow:

By-Products in Gas Manufacture. By CHARLES E. MUNROE, Professor of Chemistry at George Washington University.

Professor Munroe's address gave an excellent review of the scope and influence of the gas industry since it took up not only the real by-products of gas manufacture, but the subsidiary products which are often those of allied industries.

Among the subsidiary products were mentioned dyes, explosives, flavoring materials, perfumes, synthetic drugs, sweetening principles and photographic developers—all obtained from the by-product, coal-tar, while water-gas, tar yields light oils of the benzole series, creosoting oils, naphthalene oils, road compounds and pitches.

The U. S. Bureau of Mines has taken up the study of the entirely unknown constitution of coals in connection with the work they are doing toward the more complete and economic development of our fuel resources.

The by-products of the coal gas industry are coke, gas, carbon, tar, ammoniacal liquor and spent purifying material, either lime or oxide: in the water gas industry, tar and purifying material with a meager amount of ammoniacal liquor: in the oil gas industry, lampblack, tar and spent purifying material for the new Low process, and "hydrocarbons" for the cracked and compressed oil gases. In the acetylene gas industry calcium hydroxide is practically the only product incidental to the reaction other than the acetylene.

The importance of the many varieties of nitrogen and ammoniacal products to the fertilizer industry as well as to the nation were presented with care, as well as the methods for their

preparation, special attention being given to the processes for cyanide recovery.

Finally the speaker's scheme of producing gas at the coal mine and shipping it by pipe line was discussed, and it was noted that Sir Wm. Ramsay had recently given this suggestion his endorsement.

The Commercial and Financial Aspects of the Gas Industry. By GEORGE B. CORTELYOU, President of the Consolidated Gas Company of New York.

A portion of this address was devoted to a historical account of the development of the gas industry together with a discussion of the objections raised to the introduction of gas.

The ever-increasing output of gas, notwithstanding the competition from electricity, kerosene lamps, etc., has been accompanied by a steadily diminishing price of gas. Sales of gas in large cities grow almost twice as fast as the population. In view of this fact, the speaker predicted a steady growth of the gas business, if properly operated, with constant provision for invention and improvement. The importance of scientific salesmanship, combined with efficient and prompt service, was strongly emphasized.

The speaker discussed the relations of employees to the company and the public; franchises, municipal and private ownership; competition *vs.* monopolistic control of Public Utilities; and Commission Regulation.

The Technic of Gas Manufacture. By ALFRED E. FORSTALL, Secretary Trustees Gas Educational Fund of the American Gas Institute.

Being unable to find a description of manufacturing apparatus specifically stated to have been used in the first works of the Chartered Gas Light & Coke Company, the speaker told of the apparatus described by Accum in 1815. This was followed by a detailed account of the modern coal gas plant, the various improvements being noted in order.

The fact that more than two-thirds of the total amount of illuminating gas made and sold in this country is carburetted water gas, called for a description of its methods of manufacture. Brief mention was made of the California process, the use of wood gas and of "Mond gas."

Especial attention was called to the many factors which enter into the control of gaseous products and by-products due to the complex nature of the raw materials, final products and the reactions that take place in the process of manufacture.

Gas as an Illuminant. By VAN RENSSELAER LANSINGH, President of the Illuminating Engineering Society, New York.

After a discussion of lighting by torches, candles, oil lamps and kerosene lamps, the speaker took up gas lighting, beginning with Murdock's burner which was merely a small iron tube open at the end. This was succeeded by the bats-wing, the fish tail, the Argand and the regenerative burners.

The invention of mantle burners by Auer von Welsbach in 1885 made modern gas lighting possible.

Flat flame burners are now used only in special instances and no reliance can be put in the consumption rating of these burner tips on the American market.

Much poor gas service can be traced to failure to select mantle burners adapted to the existing quality of gas and pressure conditions. With ordinary shades, flat flame burners give spherical distribution of light, upright incandescents give two-thirds of their light above, and inverted burners two-thirds below horizontal. High pressure increases the candle power of mantle burners as much as two and one-half times and is used chiefly in street lamps. With increased candle power, diffusion becomes more and more necessary so that bare mantle burners are rare.

Methods of gas ignition were merely noted.

The speaker recommended greater range in size of units, reliable methods of commercially rating lamps and standardization of mantles, lamps, and fittings.

The Use of Gas for Heat and Power; The Testing of Gas. By MR. E. B. ROSA, Chief Physicist, Bureau of Standards, Washington, D. C.

With more than 1300 gas companies in the country, with a combined capital of one billion dollars and annual sales of two hundred million dollars, the gas industry is indeed an important one.

Mr. Rosa discussed the use of coal, acetylene, natural and producer gases, and the historical development of the use of gas for cooking, water heating, room heating and industrial purposes. This was followed by a brief resumé of the work that has been done on the various types of gas engines.

Thanks were extended on the part of the Bureau of Standards to the officers and technical staffs of the various gas companies and to the members of public service commissions, gas inspectors and consulting engineers for the fairness and broad-minded spirit they have shown in discussing the questions connected with the work now being done by the Bureau towards the standardization of the testing of gas.

The work accomplished already was discussed and special stress was laid on the necessity for using the *net heat* for measurement of the heating value of a gas. The effect of atmospheric conditions on the gross heat was shown and it was suggested that a committee of the American Gas Institute cooperate with the Bureau in studying the question "*Shall the actual net heat be substituted for the gross?*" Mr. Rosa believes that since instruments and methods of measurement are more accurate than ever before, uniform standards of gas quality should be adopted, taking into account varying density as well as accurate measurements of volume and quality. The next publication of the Bureau will take up these questions of testing methods, and the cordial cooperation of the gas interests is earnestly solicited.

AMERICAN ELECTROCHEMICAL SOCIETY RESEARCH FUND.

In order to further the objects of our Society as given by our Constitution, it has seemed wise to try the experiment of assisting purely scientific research work in electrochemistry where this is done under conditions which would make the application of a few hundred dollars annually of effective and efficient assistance.

For this purpose, \$250 is made available for this year, to be given in whole or in part to help members of the Society who need such assistance to carry on some predetermined work.

The Committee does not wish to burden the scheme with unnecessary rules or requirements, and proposes to carefully consider requests for this assistance on the merits of the case as it may be presented. If the further developments of the scheme warrant the issuing of limitations on the distribution of the fund, such will be published.

The Committee's aim will be to give assistance to those who are apparently equipped to do effective work along those purely scientific lines which are not usually explored by commercial or industrial organizations. In other words, we wish to advance the science of electrochemistry.

The research work thus assisted must be published in the Transactions of the Society.

Applications may be sent to the Chairman of the Committee and should be received before August first.

W. R. WHITNEY, *Chairman*,

W. H. WALKER,

F. A. J. FITZGERALD.

MAINE SECTION OF THE AMERICAN CHEMICAL SOCIETY.

The recently authorized Maine Section of the American Chemical Society held its initial meeting in Fernald Hall on the University of Maine Campus on May 16, 1912. The meeting was attended by about thirty enthusiastic members of the

Section and at the afternoon meeting, at which papers were presented, there were present a number of student chemists of the University of Maine. Papers were presented by Mr. A. B. Larchar, of Oldtown, on "Some Practical Observations on the Electrolysis of Brine;" by R. H. McKee on "An Oil from the Red Spruce;" and by L. M. Burghart on "Some New Forms of Chemical Apparatus."

After discussion the meeting temporarily adjourned to give opportunity for the preparation of a lunch which was served in the laboratory. After lunch a short business meeting was called to order by R. H. McKee and a committee nominated the following officers who were elected to serve until organization has been perfected and by-laws adopted: *President of the Section*, A. B. Larchar, Oldtown; *Councilor*, R. H. McKee, Orono; *Secretary and Treasurer*, H. H. Hanson, Orono. The officers named were elected as an executive committee to arrange for the next meeting and to present at that meeting by-laws to govern the Section. H. HANSON, *Secretary*.

ORGANIZATION OF COMMITTEES FOR STUDY OF INDUSTRIAL DISEASES.

The membership of the Committee on Industrial Diseases of the New York Association for Labor Legislation is made up of the following:

PROF. HENRY R. SEAGER, *President of the American Association for Labor Legislation, Chairman.*

PROF. SAMUEL McCUNE LINDSAY, *President New York Association for Labor Legislation, Ex Officio.*

DR. CHARLES L. DANA, *Chairman Committee Public Hygiene, Academy of Medicine, Ex Officio.*

DR. JOHN B. ANDREWS, *Secretary American Association Labor Legislation.*

CHAS. BASKERVILLE, *Professor of Chemistry, College of the City of New York.*

DR. WARREN COLEMAN, *New York Academy Medicine.*

MR. MILES M. DAWSON, *Actuary.*

MR. LEONARD W. HATCH, *Statistician Department Labor, State of New York.*

MR. FREDERICK L. HOFFMAN, *Statistician Prudential Life Insurance Co.*

DR. JOHN H. HUDDLESTON, *New York Academy Medicine.*

DR. JAMES ALEX. MILLER, *New York Academy Medicine.*

DR. W. GILMAN THOMPSON, *New York Academy Medicine.*

DR. LINSLEY R. WILLIAMS, *New York Academy Medicine.*

PROF. C. E.-A. WINSLOW, *College of the City of New York.*

MR. PAUL KENNADAY, *Secretary New York Association Labor Legislation.*

The Committee on Occupational Diseases in Chemical Trades, New York Section of the American Chemical Society, is as follows:

DR. GEO. P. ADAMSON, *Baker & Adamson Chemical Co., Easton, Pa.*

MR. W. H. BASSETT, *American Brass Co., Waterbury, Conn.*

MR. WM. F. DOERFLINGER, *Mutual Chemical Co. of America, 55 John St., New York City.*

DR. A. C. LANGMUIR, *Chairman New York Section, 9 Van Brunt St., Brooklyn, N. Y.*

DR. GEO. D. ROSENGARTEN, *Powers, Weightman & Rosengarten, Philadelphia, Pa.*

DR. A. H. SABIN, *National Lead Co., 129 York St., Brooklyn, N. Y.*

MR. E. C. UHLIG, *Secretary, Brooklyn Union Gas Co., 5th & Hoyt Sts., Brooklyn, N. Y.*

ORGANIZATION OF RUBBER SECTION.

Editor of the Journal of Industrial and Engineering Chemistry:

At a meeting of the Rubber Section of the American Chemical Society held on June 5th, the following committees were appointed:

General Rubber Consideration Committee: D. A. Cutler, *Chairman*; H. van der Linde, W. E. Piper, G. T. Cottle, A. D. Hopkins, D. Spence, Dorris Whipple, C. R. Boggs, H. Fay, W. C. Geer.

Analytical Committee: Dorris Whipple, *Chairman*; J. W. Schade, P. H. Walker, J. B. Tuttle, G. T. Cottle, Geo. Oenslager, W. A. Duca.

Committee on Specifications: C. R. Boggs, *Chairman*; G. H. Savage, H. Fay, W. C. Geer, H. B. Rodman, D. A. Cutler.

It was also decided to have the General Rubber Consideration Committee ask all the members of the Section to submit the best known method for analyzing rubber goods; the Committee is then to select the best method, submitting same to the American Chemical Society asking the Society to publish this as being the best authority known to it at the present time. The Analytical Committee will, in the meantime and in the future, attempt, by research and such other methods as it may select, to revise this adopted method from time to time, as may seem best for the interests of the Rubber Section, the object being that any chemist in the country who may have occasion to analyze rubber goods may have an authorized standard method of procedure.

When this has been accomplished there should not be such a variance in the results reported from different chemists who analyze vulcanized rubber products. We hope to have this accomplished so that it may be announced at the coming International Conference in September.

D. A. CUTLER, *Chairman.*

PAINT AND VARNISH IN THE U. S. NAVY.

Editor of the Journal of Industrial and Engineering Chemistry:

I notice in your issue of May, 1912, a communication from Professor Sabin, in which he refers to the steps taken recently by the Naval authorities looking toward the use of so-called "newer paint materials."

Professor Sabin seems to be under the impression that the Navy Department expects to find these materials not so efficient as those previously used, and that they are even willing that such should be the case.

As I have been identified, to some extent, with literature on this subject, and a good deal of prominence has been given to a paper which I presented to the Naval Institute in December last, I feel that I should attempt to correct the impression given by Professor Sabin in his letter.

Although one of the arguments advanced in favor of the use of cheaper paint materials was to the general effect that even if they were not quite so lasting, there would be still ample reason for their use in view of the frequent repainting that is necessary from other considerations, the use, however, of materials that are less effective than those heretofore used actually has not been accepted and all of the changes that have been made by the Navy Department have been made only after extensive experiments showed that there would be no loss in efficiency. The changes to date have been the use to some extent of lower priced and more effective paints in place of red lead as a priming coat, the use of hydrocarbon spirits in place of turpentine, the use of blanc fixe in slate colored outside paint for battleships and cruisers, and the tentative use of fish oil in place of a portion of the linseed oil. These changes were not made, however, until, as noted above, the naval authorities were convinced that there would be no loss of efficiency in durability of the paints or in protective effect.

HENRY WILLIAMS.

NAVY YARD, NEW YORK.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF CARBON IN IRON AND STEEL. A NOTE OF PROTEST.

The Editor of the Journal of Industrial and Engineering Chemistry:

In the May number of THIS JOURNAL, there is, under the title "A Colorimetric Method of Determining Carbon in Iron and

Steel," what purports to be a "novel" method of determining carbon by a modification of the Eggertz process; as this "new" method has probably been practiced ever since the Eggertz process was introduced, I think it is time a protest was entered against such self-evident modifications being published as original. I do not know to whom this particular method of dilution is originally due, but it has been used by nearly all steel works chemists in this country for the past 17 or 18 years to my personal knowledge.

A modification of the Eggertz process which I do not know to be so commonly used, as it might well be, refers to the determination of carbon in very soft steel, etc., and when the carbon is below 0.10%, is carried out by weighing a portion of a standard steel, say 0.1 gram, and adding 0.1 gram of the sample to it; this is dissolved alongside a 0.2 gram portion of the same (or other) standard and the two compared, when a simple calculation will give the result for the steel.

Any one who is associated with the comparison of low carbon steels, *i. e.*, steel with carbon under about 0.10 per cent., will be acquainted with the difficulty of comparison on account of the greenish tint; the above process is designed to overcome this difficulty and I can confidently recommend its trial.

While on the subject of carbon determination, I might mention that I have successfully used a similar process in connection with the determination of carbon by direct combustion in oxygen of the more refractory ferro alloys: by placing a known quantity of a standard steel in the combustion boat and sprinkling the weighed portion of the alloy over this, when the heat generated by the combustion of the steel standard has been sufficient to insure complete combustion of the alloy.

I am not claiming originality for these modifications which are in this country looked upon merely as "shop kinks."

E. ESCOTT WOOD.

LABORATORY OF THE BRYMBO STEEL WORKS,
WREXHAM, WALES.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF CARBON IN IRON AND STEEL—A NOTE.

Editor of the Journal of Industrial and Engineering Chemistry:

In the May issue of THIS JOURNAL for the current year there appeared an article entitled "A Colorimetric Method for the Determination of Carbon in Iron and Steel." This method is claimed to be similar to the one proposed by Eggertz. This statement was very surprising to me because I had studied Eggertz' method under him in the Royal Mining School at Stockholm, Sweden, and later, in my own laboratory, I made about five thousand determinations using his method. When reading Mr. Kohout's method, I found same identical with Prof. Eggertz' method. At present I can only refer to a foot-note in Blair, "Analyses of Iron and Steel" on page 170, 5th edition, and page 175, concerning the dilution of the standard.

Yours very truly,

C. G. HELLMAN.

165 GRAND STREET,
JERSEY CITY, N. J.

VALUATION OF FLUORSAPAR—A CORRECTION.

In my article in this paper, Vol. 4, No. 3, March, 1912, I quoted incorrectly Mr. F. Julius Fohs' statement published in *Bulletin 9* of the Kentucky Geological Survey, *viz.*, "silicates occurring associated with Kentucky fluorspar." The word "Kentucky" should be omitted: it disturbs the meaning of the

following discussion, changing the same to a depreciative criticism of Mr. Fohs' statement, which I did not intend to do. Mr. Fohs states that the silicates mentioned in my article occur occasionally associated with fluorspar, but not with Kentucky fluorspar.

ERNST BIDTEL.

GENERAL BAKELITE COMPANY STARTS INFRINGEMENT SUITS.

General Bakelite Company has brought suits for infringements of its Bakelite patents against the Condensite Company of America and several users of "Condensite;" among them the Dickinson Manufacturing Co. of Springfield, Mass., The Duranoid Mfg. Co. of Newark, N. J., and Hardman & Wright of Belleville, N. J.

In relation to this, it is of interest to note that the fundamental Bakelite patents have been allowed in Germany and have been sustained by the German Patent Office, notwithstanding the fact of several public contestations.

THE END OF THE COÖPERATIVE GLASS FACTORIES IN ITALY.

In the "Fachgenosse", 28, No. 58 (an organ of the German glass unions), appears an article noting the failure of the coöperative glass factories of Italy in their struggle with the trust (cf. *C. A.*, 5, 166).

These rival glass factories were started by the labor unions in 1903 with the small capital of \$5,750. They proceeded to compete with the trusts for the control of the market, hoping at least to compel recognition of their union and improve conditions for the men. During the last nine years these factories have been increased to seven in number at the time of the bankruptcy. Business conditions in the Italian glass industry throughout the last year particularly have been very unfavorable. In 1910 occurred a shortage in the grape crop result in a lessened demand for bottles, and the Turko-Italian war proved to be the last straw in the situation for the coöperative factories. They were scattered over the northern part of Italy, with the exception of one factory in the vicinity of Naples, and with their scanty capital and lack of close coöperation were unable to cope with the hard times and consequent losses.

J. B. PATCH.

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY. ANNOUNCEMENT BY SECTION I, ANALYTICAL CHEMISTRY.

The President of Section I, Analytical Chemistry of the approaching Congress of Applied Chemistry, desires to call the attention of chemists to an official notification received by him, that two important propositions will be advocated at the Congress.

It will be moved by the Verein deutscher Chemiker: To adopt for practical purposes an atomic weight table only once in five years and on a given date to introduce this generally and recognize it as binding in mutual dealings.

The Sectional Group, "Analytical Chemistry," of the Verein deutscher Chemiker will make the following suggestion: To request the Sub-committee on Uniform Sampling of the International Committee on Analyses to take up the sampling of ores.

For fuller details, consult *Chemiker Zeitung*, June 6, page 635, and *Zeitschrift für angewandte Chemie*, June 7, page 1171.

BOOK REVIEWS

Corrosion of Iron and Steel. By J. NEWTON FRIEND, PH.D. Longmans, Green & Co., 1911. pp. 300; 62 figures. Price, \$1.80 net.

With the exception of an occasional failure due to so-called fatigue, the life of a structure made from iron or steel is in general determined by the rate at which it corrodes, or as we say rusts. A voluminous literature of the past exists, while that of the present is constantly being swollen by contributions from the many investigators now in the field. We therefore welcome heartily a book such as the one here considered which so carefully digests the work already reported and collates in such a clear, unbiased way that portion of the literature which seems to be worthy of consideration. The subject is one of immense practical importance, and no engineer or metallurgist can afford to be ignorant of either the purely scientific aspects of the matter, or of those observations which have proved a genuine help in the solution of an apparently simple, but really highly complex problem.

After a brief historical introduction the author discusses what might be called the mechanism of rusting and gives a clear statement of the different theories which have been advanced to explain rusting and the experiments on which such theories are based. He falls into an obvious error, however, when in attempting to distinguish between the so-called acid theory and the electrolytic theory of corrosion, he states that the latter "stands or falls with the solubility or otherwise of iron in perfectly pure water." Elaborate experiments are described which are intended to prove that iron in water in the entire absence of carbonic acid or other electrolyte is not dissolved. What these experiments prove and all that they prove is that under certain conditions below a definite temperature, iron does not dissolve rapidly enough in pure water to be easily noticed. The rate of the reaction increases so rapidly with rise of temperature that it might be expected that if the temperature were raised without changing in any way the other conditions, rusting should become evident; Mr. Fleming in an article in this number of the Journal seems to have proved this to be a fact. But is this all not "using a sledge hammer to kill a flea?" Suppose it were true that at ordinary temperatures iron did not rust in perfectly pure water; this fact in no way invalidates the electrolytic theory. When iron dissolves in water with carbonic acid or without it, energy is set free and can take the form of electrical energy in the same way as that set free by the reaction taking place in a Daniell cell; and the phenomenon is just as truly electrolytic in one case as in the other.

The studied attempt of the author to avoid all the concepts introduced by the electrolytic theory renders the treatment of many important phenomena less clear than it would otherwise be. How else can one explain the accelerating action of metallic platinum or forge scale on the rusting of iron? How explain the protection of iron by zinc, or the fact that the area of iron protected by zinc is a function of the conductivity of the water surrounding the two, and a hundred other facts? To call such phenomena "galvanic action" is simply admitting the facts while refusing to utilize the conclusions which such facts warrant and to use the benefits which may accrue from broader generalizations based upon such facts and conclusions. The book gains nothing by this careful exclusion of the electrolytic theory, while it loses much.

In the chapter devoted to the rusting of iron as influenced by natural forces and conditions the author shows his broad grasp of the literature, and presents the subject in a well balanced discussion of the influence of dissolved oxygen, in water the rate

of movement of the water, the action of light, biological activity, etc. To the action of acids, alkalies, aqueous solution of simple salts, and solution of two or more electrolytes on iron there is devoted a chapter respectively. The passive state of iron is the subject of an interesting chapter which brings this interesting subject well up-to-date, as is also true of the section on the influence of the chemical composition of iron on its corrosion. In considering the relative rate of corrosion of iron and steel the author suggests a "Corrosion Factor" and points out that an American firm has made this possible by placing on the market a "pure iron," that is, a metal containing 99.954 per cent. iron. These figures are taken from an analysis given on page 114 as furnished by the American Rolling Mill Co. of Middletown, Ohio, for its product: much to the author's surprise he later found by analyzing the sample himself, that it contained 0.172 per cent. copper.

Throughout the volume, attention is called to the gaps in our present knowledge and its study should prove a source of fruitful suggestion for those looking for subjects for investigation.

The book constitutes a distinct and valuable contribution to the literature on the subject of corrosion, and will prove of interest to the general reader as well as of great service to those particularly interested in the field.

WM. H. WALKER.

Technologic Papers of the Bureau of Standards, No. 3: Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Damp-Proofing and Waterproofing Compounds and Materials. By RUDOLPH J. WIG and P. H. BATES. 127 pages, 53 figures; 8vo. Washington: Government Printing Office, 1912.

The investigations reported in this brochure cover some previously unstudied phases of the important subjects of Portland cement mortars and concretes. The account of the work is divided into two parts: Part I comprises the results of a series of tests on 11 different mortars and 23 concretes to ascertain their permeability at various ages, for various consistencies and thickness of test piece, and the absorption on 12 mortars at various ages and for various consistencies, while Part II embodies the results of a series of comparative tests of 40 compounds and several void-filling materials recommended for use or advertised as "damp-proofing" or "waterproofing" mediums, purchased privately in the open market.

Valuable as are the data contained in Part I, the series of tests made on various "damp-proofing" and "waterproofing" compounds and materials should be of more interest to the engineer, architect and contractor—to all those engaged in construction work who have been misled by such statements as, "This compound waterproofs the heart of concrete construction," or "To make the whole mass of the masonry waterproof... add to the cement a compound which is water repellent and breaks up the continuity of the capillaries." It is demonstrated by Wig and Bates, in a quite convincing manner, that Portland cement mortar and concrete can be made practically watertight or impermeable to any hydrostatic head up to 40 feet without the use of any of the so-called "integral" waterproofing materials (19 were tested). Furthermore—but in this case the authors urge cautious interpretation—"The damp-proofing tests as conducted would indicate that Portland cement mortars can be made not only impermeable but damp-proof as well... without the use of any damp-proofing or waterproofing compound."

There are about fifty waterproofing compounds (coatings and "integrals") on the American market. The addition of "integral" compounds will not, according to Wig and Bates, compensate for lean mixtures, poor materials nor for poor workman-

ship; but at least some of the coating compounds have a use, for "As a precaution, under certain conditions, it is undoubtedly desirable to use bituminous or similar coatings, even on new work, as a protection where cracks may occur." However, even in such cases the authors assert that "where cracks can be prevented no coating whatever is required to make the structure impermeable."

W. A. HAMOR.

A Dictionary of Applied Chemistry. Second edition, by SIR EDWARD THORPE and other eminent contributors. To be issued in five volumes. Revised and enlarged. Volume I, 758 pages. Price of complete set when issued \$50.00. Price per volume, \$13.50. Longmans, Green & Co., London and New York, 1912.

The first edition of this well known work appeared twenty-two years ago. In the meantime, great advances have been made in the science of chemistry and its applications, new industries have been developed and established processes have undergone great changes. The appearance of this second completely revised and enlarged edition is therefore a matter of importance to the chemical profession.

The editorial board has been enlarged under the able guidance of Sir Edward Thorpe and now includes forty-five eminent experts selected from England, Germany, Switzerland and America. It would be difficult to find a more representative set of men than those chosen to treat the subjects presented in this volume.

All articles of the first edition have been carefully revised or rewritten and a large amount of new subject matter has been introduced. References to original papers have been more carefully preserved and brought up-to-date. From the standpoint of bibliography alone, the work is of inestimable value and a careful comparison of individual articles shows a consistent and judicious editorial policy.

Volume I covers in its 758 pages, the words A to Che compared with 715 pages in the first edition from A to Dy.

New chapters have been introduced on Abrasives, Acetins, Adhesives, Adrenaline, Amines, Anaesthetics, Argon, Asparagine, Boiler Incrustation, Casein, and a particularly good chapter on Chemical Affinity. These, together with the extension of other subjects which have increased in importance since the first edition, make a book of great reference value to the chemist and chemical engineer.

The general workmanship on the volume is excellent. The paper and binding are well adapted to withstand the hard service of the reference library and laboratory and the chemical profession will receive the timely revision and reissue of this well known work with gratitude to both editors and publishers.

M. C. WHITAKER.

Allen's Commercial Organic Analysis. Fourth Edition, Vol. VI. Edited by W. A. DAVIS and S. S. SADTLER. Philadelphia: P. Blakiston's Son & Co., 1912. Cloth, Octavo viii + 726 pages. Price, \$5.00 net

The appearance of this volume, devoted chiefly to the alkaloids and corresponding to Vol. III, Part II, of the previous edition, is especially welcome because of the lack of comprehensive modern literature on the analytical chemistry of the alkaloids. Although 20 years have elapsed since the last edition of this part of Mr. Allen's work, and the material has been entirely rewritten and reset, the scope and general arrangement are but little changed.

As in the other volumes of the fourth edition, the work of revision has been divided among a number of contributors—in this case ten English and four American. The division is as follows: Amines and Ammonium Bases, by W. A. Davis, 49

pages; Aniline and its Allies, by S. S. Sadtler, 60 pages; Naphthylamines, Pyridine, Quinoline and Acridine Bases, by W. H. Glover, 55 pages; Vegetable Alkaloids, by T. A. Henry, 44 pages; Volatile Bases of Vegetable Origin, by F. O. Taylor, 25 pages; Nicotine and Tobacco, by R. W. Tonkin, 18 pages; Aconite Alkaloids, by F. H. Carr, 36 pages; Atropine and its Allies, by F. H. Carr, 28 pages; Cocaine, by S. P. Sadtler, 33 pages; Opium Alkaloids, by F. O. Taylor, 86 pages; Strychnous Alkaloids, by C. E. Vanderkeed, 38 pages; Cinchona Alkaloids, by O. Chick, 72 pages; Berberine and its Associates, by E. Horton, 28 pages; Caffeine, Tea and Coffee, by J. J. Fox and P. J. Sageman, 76 pages; Cocoa and Chocolate, by R. Whympfer, 37 pages. Those alkaloids which in the previous edition were included in Part III of Volume III are left for Volume VII of the present edition. Since the work is being entirely reset it seems unfortunate that the descriptions of all the alkaloids should not be brought into one volume.

The division of the subject matter among such a number of contributors has its advantages, as for example in permitting the introduction of a chapter on Cocoa and Chocolate by such a specialist as Mr. Whympfer, but it seems also to have resulted in some over-specialization within the volume with a corresponding loss to the more general features. One fails to find in the present volume a satisfactory development of those 33 pages in which 20 years ago Mr. Allen so clearly summarized the general analytical reactions and methods of isolation and purification of the alkaloids as a group.

The separate sections have been extensively rewritten and much new matter included, the volume as a whole being about one-fifth larger than its predecessor. In most sections the descriptive matter is more prominent than the strictly analytical, and the volume will doubtless be used as much for a reference text as for a laboratory guide.

H. C. SHERMAN.

The Chemistry of Breadmaking. By JAMES GRANT, M.Sc. TECH., F.I.C., F.C.S. Longmans, Green & Co., 1912. 224 pages, 47 illustrations. Price, \$1.25.

This small volume was written to assist the beginner as an introduction to the chemistry of breadmaking. With this purpose in view the author does not attempt to cover the same ground as other more special treatises.

The first 5 chapters of the book take up in a very elementary way the applications of chemistry and physics to the problems of the bakery. Succeeding chapters discuss the composition of cereals and of their milling products, the functions of yeasts and other ferments, breadmaking processes, bakehouse hygiene, fuels and ovens, and the analysis of cereal foods.

As an introductory handbook for students the present volume is in every way much better suited than the more exhaustive work of Jago (*THIS JOURNAL*, 4, 313) which is preëminently a book for the specialist and one in which the beginner may have difficulty in finding his way.

The design of Prof. Grant to put forward an introductory volume for beginners which would fill a gap in the literature and text books upon breadmaking is a laudable one and has been very well carried out.

C. A. BROWNE.

The Laboratory Apparatus Blue Book, published by the Scientific Materials Co., of Pittsburgh. Sent free of charge to chief chemists, metallurgists and professors.

This book describes and illustrates the apparatus manufactured or imported and sold direct to laboratories by the authors.

A complete list of all the modern and approved laboratory material is given, and arranged alphabetically. The descriptions are clear and a large number, perhaps 2000, different illustrations are used. This catalogue contains a great deal of new and improved apparatus, which will no doubt be of interest to up-to-date chemists.

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- Analysis; Notes on the Electrical Method of Morse and Gray for the Simultaneous Determination of Carbon, Hydrogen and Sulfur in Organic Compounds.** By E. EMMET REID. *American Chemical Journal*, Vol. 47, 1912, No. 5, pp. 416-429.
- Castings; New Processes for Chilling Gray Iron—.** By THOMAS D. WEST. *The Foundry*, Vol. 40, 1912, No. 238, pp. 244-251.
- Cell; Tentative Report of American Electrochemical Society Committee on Dry— Tests.** By C. F. BURGESS, et al. *Metallurgical and Chemical Engineering*, Vol. 10, 1912, No. 6, pp. 361-366.
- Coal; a New Apparatus for the Coking Test of—.** By B. LESSING. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 10, pp. 465-468.
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- Condensing; Reduction in Temperature of— Water Reservoirs.** By W. B. RUGGLES. *Industrial World*, Vol. 46, 1912, No. 23, pp. 666-667.
- Corrosion of Iron, Steel and Alloys.** By J. NEWTON FRIEND, et al. *Industrial World*, Vol. 46, 1912, No. 22, pp. 641-646.
- Corrosion in Nickel, Chromium, and Nickel Chromium Steels.** By J. NEWTON FRIEND, J. LLOYD BENTLEY AND WALTER WEST. *Industrial World*, Vol. 46, 1912, No. 23, pp. 670-672.
- Dyes and Patents in the German Patent Office.** By WEIDLICH. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 22, pp. 1096-1102.
- Explosions; Coal Dust— and their Prevention.** By J. HARGER. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 9, pp. 413-416.
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- Lubrication in Coal Mining Practice.** By L. A. CHRISTIAN. *Industrial World*, Vol. 46, 1912, No. 24, pp. 702-704.
- Ozone; Atmospheric—.** By HARRY N. HOLMES. *American Chemical Journal*, Vol. 47, 1912, No. 6, pp. 497-508.
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- Pyrometers; The Installation and Use of— in Steel Mills.** By C. S. GORDON. *Metallurgical and Chemical Engineering*, Vol. 10, 1912, No. 6, pp. 331-334.
- Refrigeration; Mechanical— as Applied to the Brewing Industry.** By LEUIG CHEW. *Journal of the Institute of Brewing*, Vol. 18, 1912, No. 4, pp. 274-312.
- Sewage; The Influence of Waste Liquor from Sulfate of Ammonia Plants on the Purification of—.** By G. J. FOWLER, E. ARDEN AND W. T. LOCKETT. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 10, pp. 471-477.
- Sewage; Notes on the Digestion of— Sludge.** By CHARLES SAVILLE. *Engineering Record*, Vol. 65, 1912, No. 21, pp. 576-577.
- Steel; The Electric Furnace as a Possible means of Producing an Improved Quality of—.** By WILLIAM R. WALKER. *Metallurgical and Chemical Engineering*, Vol. 10, 1912, No. 6, pp. 371-373.
- Sugar; Examination of Pellet's Method of Making the Acid Direct Reading in the Double Polarization Method.** By JAMES P. OGILVIE. *International Sugar Journal*, Vol. 14, 1912, No. 161, pp. 264-269.
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- Thymol; A New Bromine Method for the Determination of—, Salicylates and Similar Compounds.** By ATHERTON SEIDELL. *American Chemical Journal*, Vol. 47, 1912, No. 6, pp. 508-526.
- Water; Determination of Free Carbon Dioxid in—.** By H. NOLL. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 20, pp. 998-1005.
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- Water Purification and the Prevention of Boiler Scale.** By K. BRAUNGARD. *Chemiker Zeitung*, Vol. 36, 1912, No. 56, pp. 521-523.
- Zinc; Production of— in the Blast Furnace with the Aid of Water Gas.** By OSKAR NAGEL. *Chemiker Zeitung*, Vol. 36, 1912, No. 67, pp. 621-622.

RECENT INVENTIONS

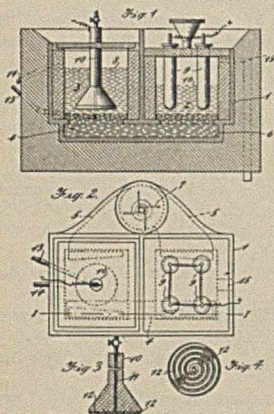
Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

METHOD OF PRODUCING NITROGEN COMPOUNDS.

U. S. Patent No. 1,018,802, to Charles E. Acker, of Ossining, New York, Assignor to the Nitrogen Company of New York.

The patentee has discovered that a direct current of electricity from an alkali-metal alloy, *e. g.*, sodium-lead alloy, through molten alkali cyanid to a carbon cathode liberates the alkali metal in the pure state at the cathode; but if ammonia, hydrocarbon amines or their decomposition products, singly or mixed, or other suitable nitrogenous reagent be brought into contact with the surface of this cathode, while the current is passing, such reagent will instantly combine with the liberated alkali metal and carbon of the cathode, to form more alkali cyanid which immediately mixes with the mass of molten cyanid already present.

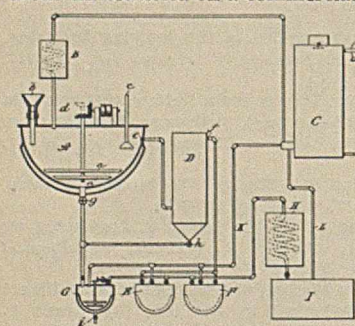
The hydrogen-carbon-nitrogen compound must have carbonaceous and nitrogenous constituents capable of combining to form a radical comprising carbon and nitrogen when the compound is reacted upon by the nascent metal.



METHOD OF MAKING ANHYDROUS TIN CHLORID.

U. S. Patent No. 1,018,805, to Gervais Baillio, of Niagara Falls, New York, Assignor to Castner Electrolytic Alkali Company.

A continuous process for converting metallic tin into anhydrous tin bichlorid on a commercial scale.



In manufacturing anhydrous tin bichlorid in the dry way, *i. e.*, by passing dry chlorin gas over metallic tin, sufficient heat is developed to melt the tin, and part of the tin forms stannic oxid, causing a loss of tin.

The patentee avoids any oxidation of the tin by submerging it in a quantity of anhydrous

liquid, so that the tin is completely covered; chlorin gas is then applied. This operation must be carried out in a water-jacketed vessel fitted with steam connections, as temperature control is necessary. While the tin used may be perfectly pure, it is not necessarily so, as very satisfactory results have been obtained from a compound containing about 90 per cent. tin, the remaining 10 per cent. being composed of lead, iron and other impurities.

Carbon tetrachlorid or any suitable anhydrous liquid may be employed as the substance in which the tin is submerged, but the patentee recommends the use of anhydrous tin bichlorid for this purpose. When the chlorin is admitted to the tin bichlorid, or other anhydrous liquid, it attacks the tin contained therein and forms additional tin bichlorid. The latter is perfectly free from moisture (notwithstanding the fact that moist chlorin gas may be used) and may be drawn off from time to time, without interfering with the continuity of the process.

THE MANUFACTURE OF SODIUM CYANIDE.

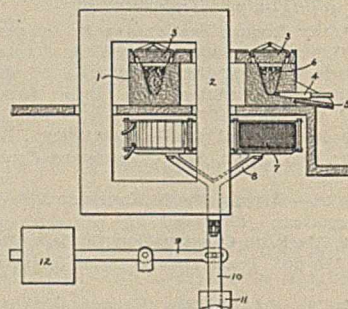
U. S. Patent No. 1,019,002, to Chas. E. Acker, of Ossining, New York.

This process consists in passing a current of electricity through an electrolyte of sodium and barium chlorides, using molten lead for the cathode; circulating the resulting alloy of sodium, barium and lead through the apparatus by means of a centrifugal pump; introducing a large amount of finely-divided charcoal in a reaction chamber, then lowering a plunger until slightly submerged; introducing at this stage fuel oil under pressure through this plunger and nitrogen through another pipe. The fuel oil is decomposed into hydrogen, which escapes, and carbon, which, with some of the carbon of the charcoal, forms barium carbide; the nitrogen combines with the barium carbide to form barium cyanide. The latter compound is then decomposed by the sodium, regenerating the barium and forming sodium cyanide which rises to the top of the bath, and can be drawn off.

INDUCTION FURNACE.

U. S. Patent No. 1,020,688, to Richard Fleming, of Lynn, Massachusetts, Assignor to General Electric Company.

This invention relates to electric furnaces of the induction type, in which the mass of metallic ore to be fused forms the closed secondary circuit of a transformer, the primary circuit



consisting of a suitable coiled conductor in inductive relation to a magnetic core common to both circuits.

Heretofore it has been customary to incorporate the primary winding in the structure of the furnace, concentric with the core which passes also centrally through the circular crucible in which the ore to be smelted is placed.

As all parts are stationary, the apparatus calls for additional devices for regulating the current and adjusting it to the load; because with different quantities or qualities of ore, different quantities of current must be used.

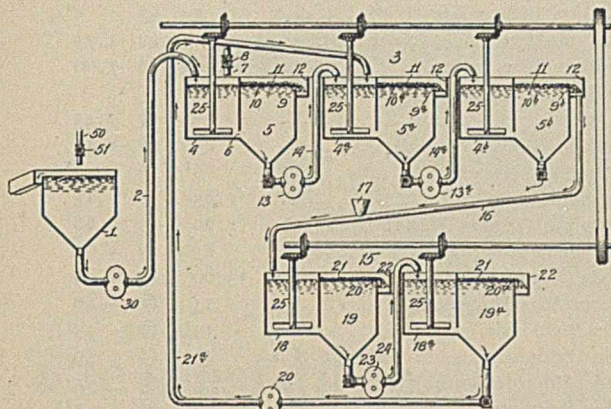
The object of this invention is to render the furnace self-regulating so that it will automatically adjust itself to any variation in load. This is accomplished by making the primary coil separate from the furnace as shown; and mounting it adjacent thereto in such a manner that it can move under the mutual repulsion which exists between it and the secondary circuit. A counterweight 12 tends to force the movable coil toward the crucible in order that the repulsion may be opposed until the current exceeds the desired strength.

ART OF CONCENTRATION OF MINERAL SUBSTANCES.

U. S. Patent No. 1,022,085, to James M. Hyde, of Basin, Mont.

This is a process of separating by flotation the valuable part of the mineral substance of ore pulps from the valueless or less valuable gangue minerals, by first preferentially coating the valuable part by means of a fat or oil whereby it exhibits markedly different surface tension phenomena from the remainder of the ore. The mixture is then agitated, permitting the valuable parts of the ore to float in the form of a froth which is separated from the balance of the ore by overflowing it together with

some water to insure overflow of the entire froth mass. The separated froth is subjected to a cleansing operation which consists in reagitating the concentrated material to free impurities entrapped therewith and permit the concentrates to



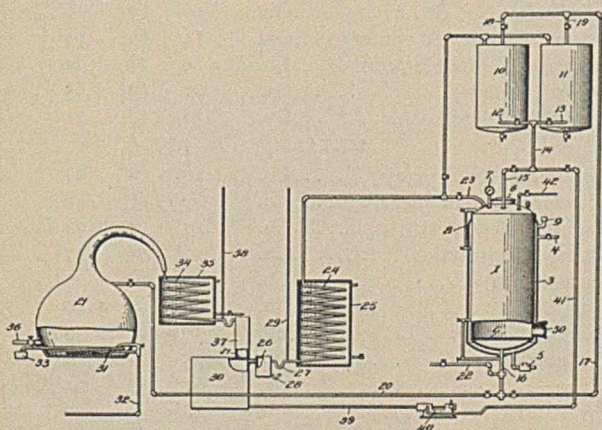
again form a froth. This froth is overflowed without any free flowing water and the settled impurities and the part of the froth not carried into the overflow is returned to the part of the pulp which is undergoing the separation treatment.

METHOD OF RECOVERING RESIN FROM WASTE PRODUCTS.

U. S. Patent No. 1,022,194, to Frank L. Huggins, of Wilmington, N. C., Assignor of one-half to John P. Moore, Jr., of Wilmington, N. C.

This process as carried out continuously is as follows:

The material is placed in the digester 1 and a solvent, such as gasoline, is admitted from a solvent tank 11 to submerge the charge which is then heated. Steam is then admitted to the upper part of the digester to expel the solvent through pipes 16 and 17 back to the tank 11. The residue in the digester 1



is then removed and a fresh supply of material placed in the digester and subjected to the action of the previously used solvent. This solvent is again forced back into the tank 11 and a supply of fresh solvent from tank 10 admitted. This after a heating operation is forced back into tank 10. Steam is then passed through the residue which is then ready for removal. The solvent is distilled from time to time in the still 21 to separate the resin.

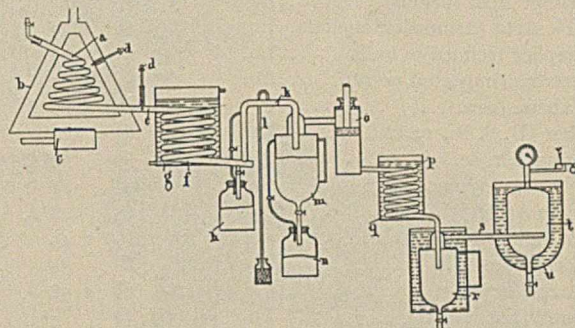
MANUFACTURE OF ISOPRENE.

U. S. Patent No. 1,022,338, to Oswald Silberrad, of Buckhurst Hill, England.

This is a process for the depolymerization of turpentine oil for the production of isoprene.

The invention consists in subjecting turpentine oil vapor to the action of heat having the pressure in the apparatus considerably below atmospheric pressure.

The apparatus, in which the process is carried out, consists of a heating coil, *a*, inside a heating chamber, *b*, heated by the products of combustion from a number of gas burners, *c*, using electric pyrometers, *d, d*, to determine the temperature. From

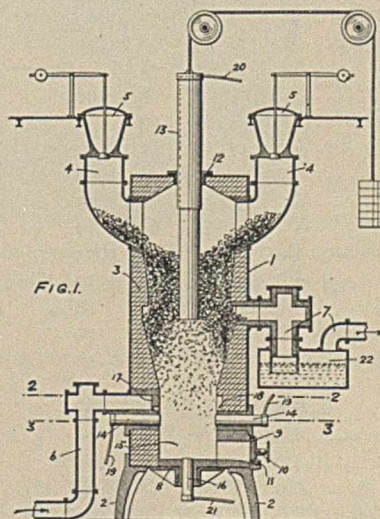


the heating coil, a pipe, *e*, leads to a water-cooling coil, *f*, situated in a water chamber. The hydrocarbons condensed in the coil *f* pass into a vessel, *h*, and the uncondensed vapors pass through a pipe, *k*, provided with a mercury gage, *l*, into another condensing chamber, *m*, from which further hydrocarbons are collected in the vessel *n*. The vacuum is produced by means of the vacuum and compressing pump *o*, and the vapors passing the pump pass through a cooling coil, *p*, immersed in brine. Isoprene is condensed in the coil *p*, and is collected in the chamber *r*. From the chamber *r*, the uncondensed vapor passes by the pipe *s* to the chamber *t*, immersed in brine. A blow-off valve, *v*, is provided from the top of this last condensing chamber.

PROCESS OF TREATING NATURAL GAS.

U. S. Patent No. 1,023,783, to Isaac N. Knapp, of Ardmore, Pa., Assignor to The United Gas Improvement Company of Philadelphia, Pa.

The purpose of the process is to make acetylene from natural gas. Natural gas containing approximately 92 per cent. to 97 per cent. of methane or marsh gas, CH₄, is passed through a bed of coke or coal from which air is excluded and which is maintained at a heat higher than that of ordinary or atmospheric combustion. The marsh gas is converted into acetylene, C₂H₂, the reaction being represented by the equation CH₄ + 3C = 2C₂H₂.



MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JUNE.

ORGANIC CHEMICALS.

Acetanilid.....Lb.	20 1/2 @	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.	10 3/4 @	11 1/2
Benzoic Acid.....Lb.	23 1/2 @	28
Carbon Tetrachloride (drums).....Lb.	nominal	
Carbon Bisulphide.....Lb.	nominal	
Chloroform.....Lb.	20 @	30
Carbolic Acid (drums).....Lb.	15 @	16
Citric Acid (domestic), crystals.....Lb.	38 1/2 @	39
Camphor (refined in bulk).....Lb.	44 @	—
Dextrine (imported potato).....Lb.	6 @	7
Dextrine (corn).....C.	3.05 @	3.26
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	19 @	21
Oxalic Acid.....Lb.	8 1/8 @	8 1/2
Pyrogallic Acid (bulk).....Lb.	1.35 @	1.45
Salicylic Acid.....Lb.	32 @	34
Starch (corn).....C.	2.28 @	2.58
Starch (potato).....Lb.	5 1/4 @	5 3/4
Tannic Acid (commercial).....Lb.	35 @	35 1/2
Tartaric Acid, crystals.....Lb.	30 1/2 @	31

INORGANIC CHEMICALS.

Acetate of Lime (gray).....C.	2.50 @	2.60
Acetate of Lead (brown, broken).....Lb.	7 3/4 @	8
Alum (lump).....C.	1.75 @	2.00
Ammonium Carbonate, domestic.....Lb.	8 1/4 @	8 1/2
Ammonium Chloride, gray.....Lb.	6 1/8 @	6 1/4
Aluminum Sulphate.....C.	90 @	1.75
Aqua Ammonia (drums) 16°.....Lb.	2 1/4 @	2 1/2
Arsenic, white.....Lb.	4 1/2 @	5
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chloride.....C.	1.40 @	1.55
Barium Nitrate.....Lb.	4 3/4 @	5
Borax, crystals (bags).....Lb.	3 1/2 @	4
Boric Acid, crystals (powd.).....Lb.	7 @	7 1/2
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.25 @	2.00
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	5 1/2 @	5 3/4
Calcium Chloride.....C.	65 @	90
Chalk (light precipitated).....Lb.	4 1/2 @	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.	8 3/8 @	8 1/2
Lithium Carbonate.....Lb.	65 @	70
Magnesite (raw).....Ton	7.50 @	8.50
Nitric Acid, 36°.....Lb.	3 7/8 @	4 1/4
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.	9 1/4 @	9 7/8
Potassium Cyanide (bulk) 98-99 per cent.....Lb.	19 1/2 @	21
Potassium Iodide (bulk).....Lb.	2.45 @	2.50
Potassium Chlorate, crystals.....Lb.	8 1/4 @	9 1/2
Potassium Nitrate (crude).....Lb.	4 3/4 @	5
Potassium Bichromate, 50°.....Lb.	6 7/8 @	7
Quicksilver.....Flask	40.50 @	42.00
Salt Cake (glass-makers').....C.	55 @	65

Silver Nitrate.....Oz.	38 1/4 @	39
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 1/4 @	5
Sodium Chlorate.....Lb.	8 1/4 @	9 1/2
Sodium Bicarbonate (English).....Lb.	2 3/4 @	3
Sodium Bichromate.....Lb.	5 @	5 1/4
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.	6 7/8 @	7 5/8
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.	13 1/4 @	13 1/2
Tin Oxide.....Lb.	46 @	50
Zinc Chloride (granulated).....Lb.	4 1/4 @	4 1/2
Zinc Sulphate.....Lb.	2 1/4 @	2 1/2

OILS, WAXES, ETC.

Beeswax (pure white).....Lb.	40 @	44
Black Mineral Oil, 29 gravity.....Gal.	12 @	12 1/2
Castor Oil (No. 3).....Lb.	9 1/2 @	10 1/2
Ceresin (yellow).....Lb.	9 @	15
Corn Oil.....C.	6 1/4 @	6.30
Cottonseed Oil (crude), f. o. b. mill.....Gal.	43 @	47
Cylinder Oil (light, filtered).....Gal.	19 1/2 @	20
Japan Wax.....Lb.	9 1/2 @	10
Lard Oil (prime winter).....Gal.	85 @	90
Linseed Oil (double-boiled).....Gal.	79 @	82
Paraffine Oil (high viscosity).....Gal.	25 1/2 @	26
Paraffine (crude 120 & 122 m. p.).....Lb.	3 @	3 3/8
Rosin Oil (first run).....Gal.	38 @	40
Spindle Oil, No. 1.....Gal.	16 @	16 1/2
Sperm Oil (bleached winter) 38°.....Gal.	74 @	76
Stearic Acid (double-pressed).....Lb.	9 @	10
Tallow (acidless).....Gal.	62 @	65
Tar Oil (distilled).....Gal.	30 @	31

METALS.

Aluminum (No. 1 ingots).....Lb.	20 @	21
Antimony (Hallet's).....Lb.	7 3/4 @	8
Bismuth (New York).....Lb.	2.10 @	2.15
Copper (electrolytic).....Lb.	17 5/8 @	17 3/4
Copper (lake).....Lb.	17 3/4 @	17 7/8
Lead, N. Y.....Lb.	— @	4.40
Nickel.....Lb.	50 @	55
Platinum (refined).....Oz.	46.35 @	47.00
Silver.....Oz.	61 3/8 @	61 1/2
Tin.....Lb.	48 1/2 @	49
Zinc.....Lb.	— @	7

FERTILIZER MATERIALS.

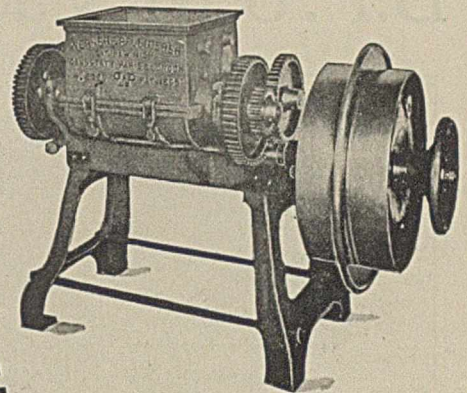
Ammonium Sulphate.....C.	3.35 @	3.40
Fish Scrap, domestic, dried.....Unit	2.45 @	& 10
Blood, dried.....Unit	2.72 1/2 @	2.75
Tankage, high grade.....Unit	2.60 @	& 10
Bone, 4 1/2 & 50, ground, raw.....Ton	27.00 @	—
Potassium, "muriate," basis 80 per cent.....Ton	38.55 @	—
Phosphate, acid, 16 per cent.....Ton	7.25 @	7.50
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	0.13 1/4 @	0.13 1/2
Castor meal.....Unit	nominal	
Mowrah meal.....Ton	8.50 @	9.00



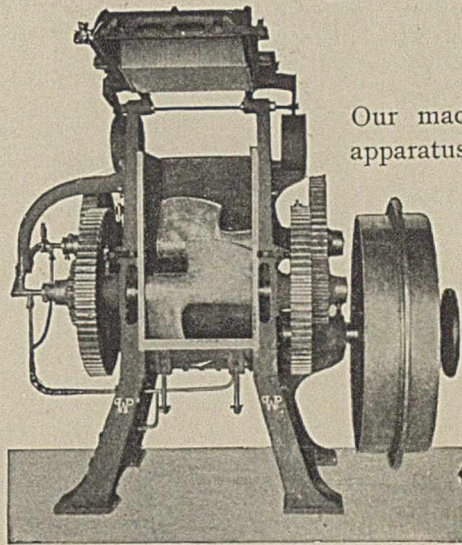
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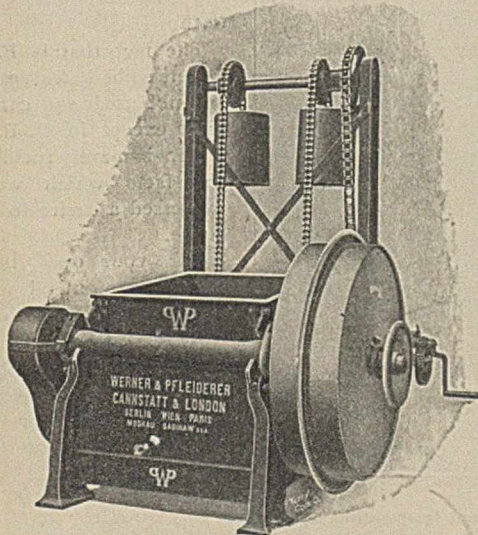


There are over 15,000 machines at work in all parts of the world and for all purposes—chemical and pharmaceutical products, colors, paints,

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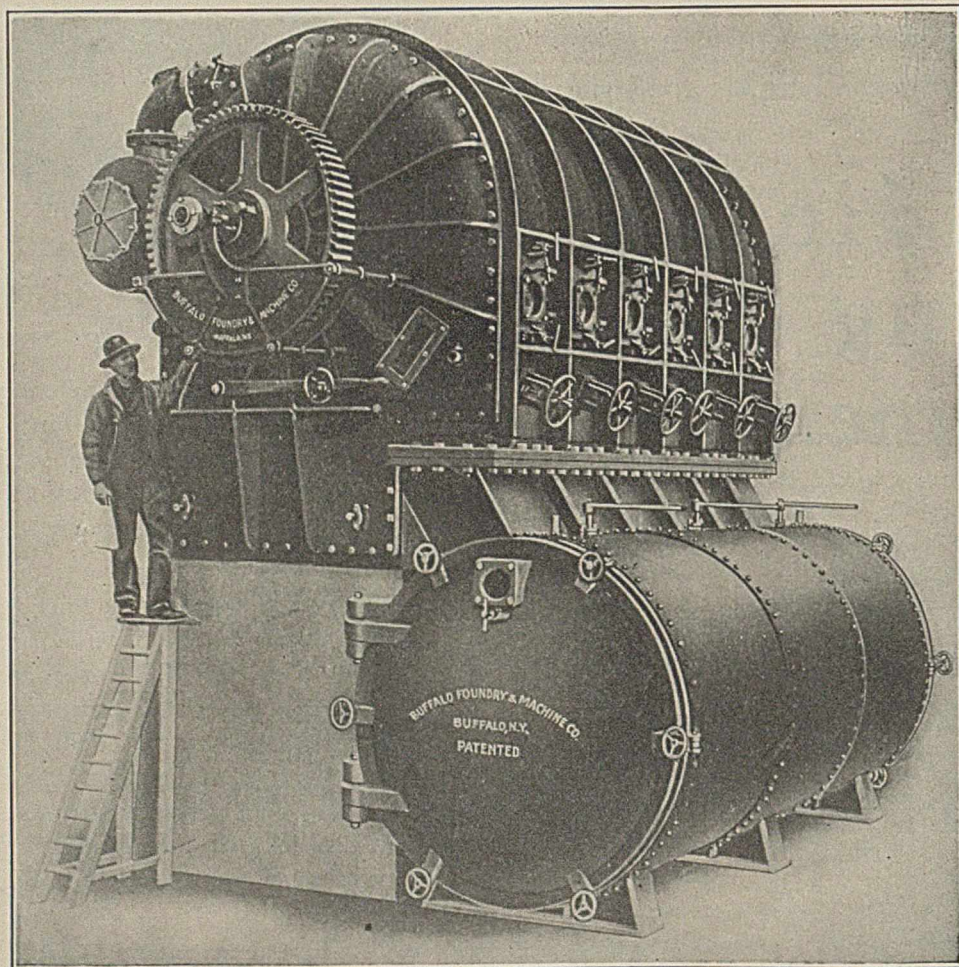


Vacuum Drying Apparatus

The Highest Attainment in Vacuum Dryer Construction

Please read the above line again. It is not merely a slogan or a catch-phrase. It is really an accurate designation of what has been accomplished in the design and manufacture of

B.F. & M. Vacuum Rotary Drum Dryers



Stripping the discussion of all that might be said on the subject, consider the one fact that we are ready to prove, in any reasonable way you can suggest, that B. F. & M. VACUUM ROTARY DRUM DRYERS will work *more* successfully on your material in *your own* plant, will require *less* attention, *less* labor, *less* power, *less* steam and produce *more* output and *more* uniform product than you can secure by any *other* means.

Details of construction interest you only as they affect the considerations we have outlined.

The fact that B. F. & M. Dryers embody features which are not used and cannot be used except in B. F. & M. Dryers is merely incidental to the facts which we have expressed a desire to demonstrate.

For your own interests, which are identical with our own, would it not be distinctly worth while for us to get together and bring the vital facts into the limelight so that you will see for yourself exactly what is best for your own interests?

Vacuum Rotary Drum Dryer for producing continuously dry materials direct from liquid solutions.

We build all types of Vacuum Dryers equally efficient for any material or capacity.

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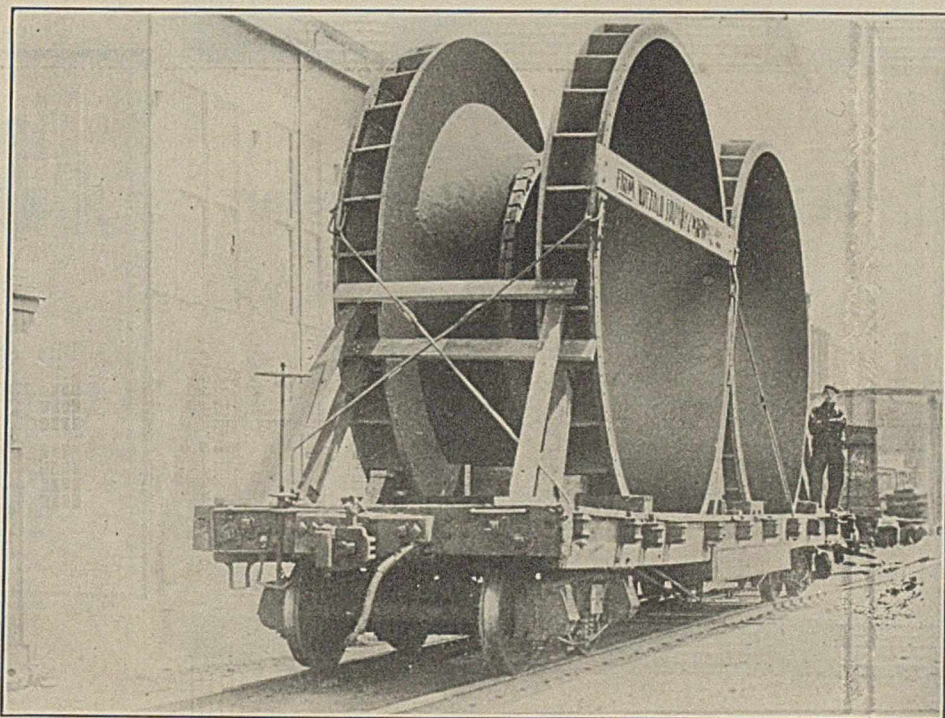
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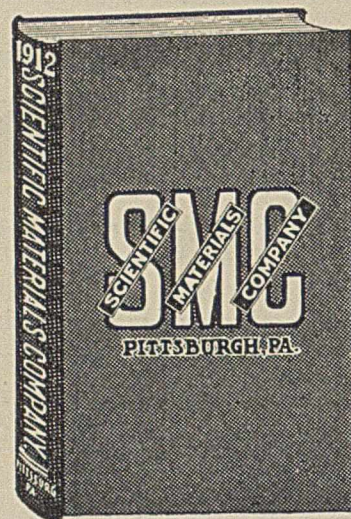
Our studies and long experience in supplying chemical and caustic castings have given us valuable data, not only as to the metal itself, but also as to methods of gating and pouring, kind and condition of sands forming facing of moulds, shrinkage strains, heat treatment after pouring, temperatures at which to remove castings from moulds, and so on.

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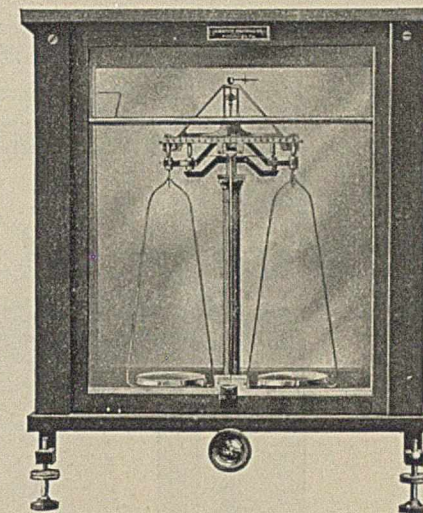
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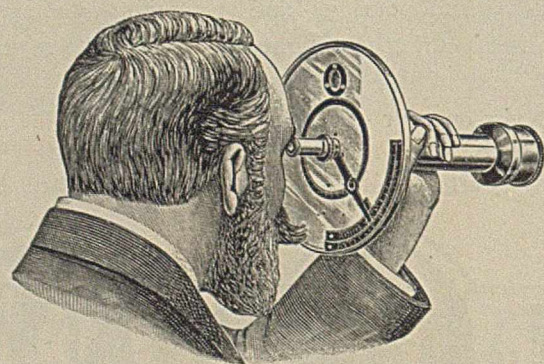
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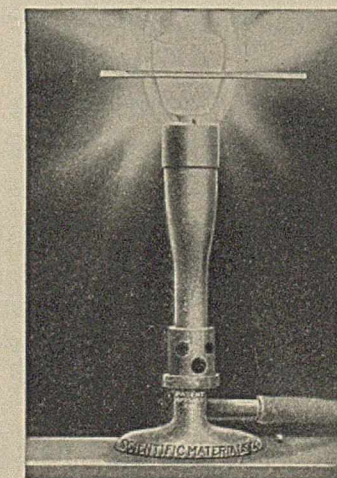
Meker Burners

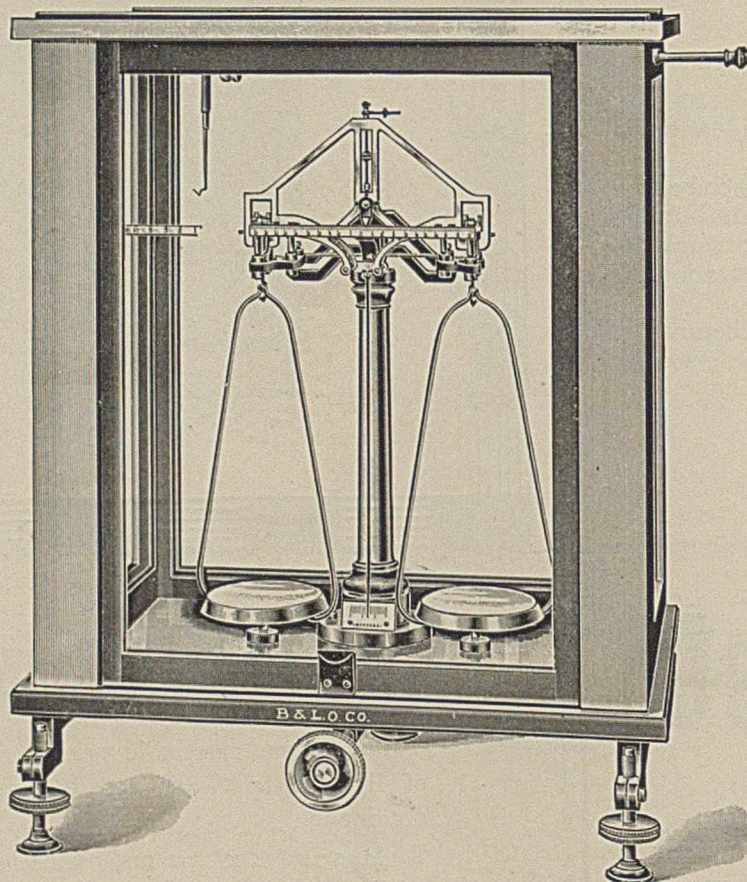
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The uniform flame saves breakage of apparatus being heated.

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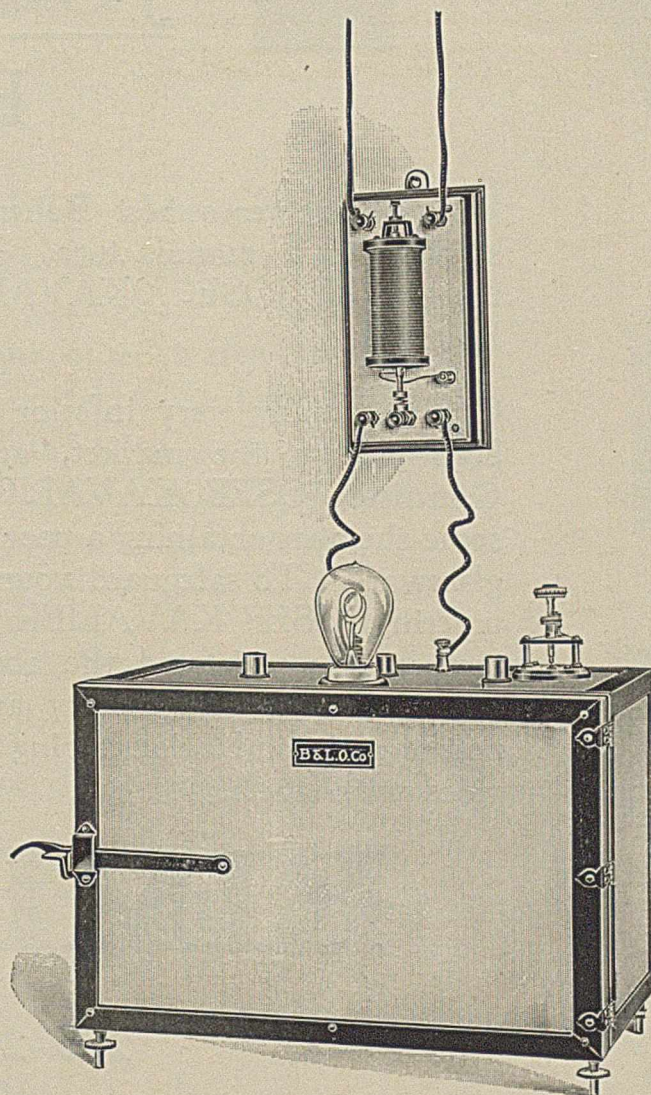
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Mechanical Rider Displacement which cannot be injured by friction and which allows perpendicular release and replacement of the rider. This rider displacement is movable along the whole length of the case of the balance, so that the rider weights, which are suspended on a support ready for use, can be easily reached.

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Outside measurements, 400 x 225 x 250 mm.

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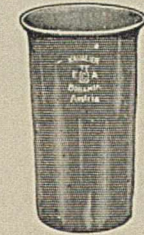
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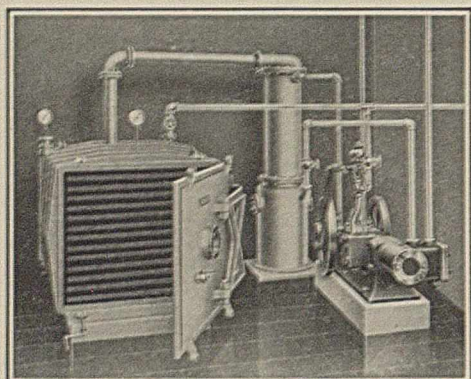
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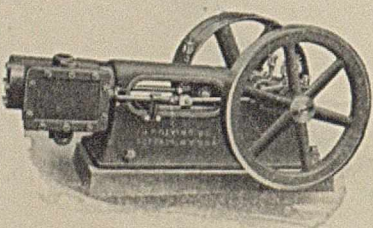
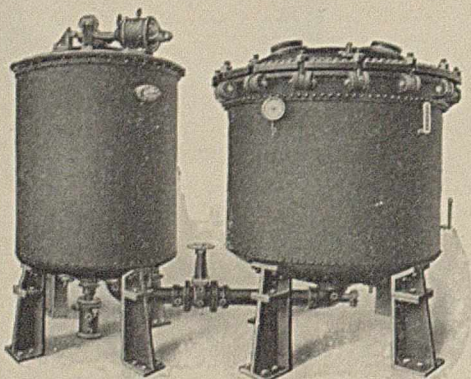
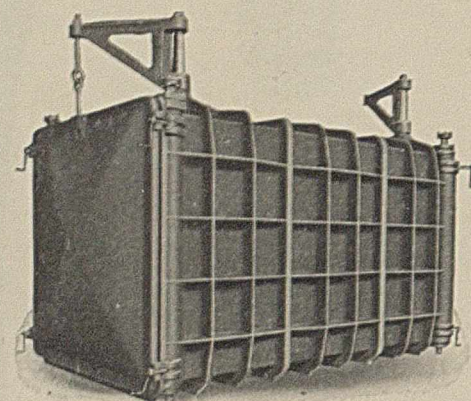
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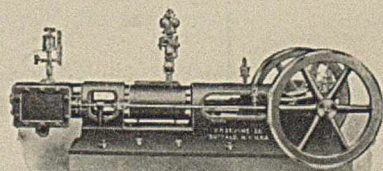
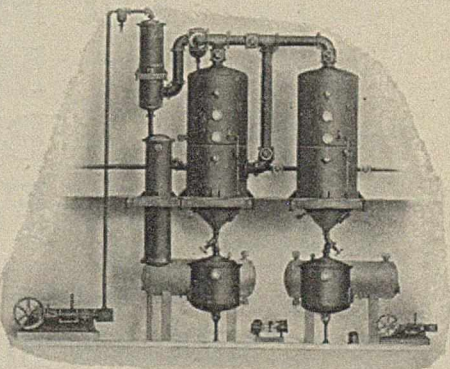
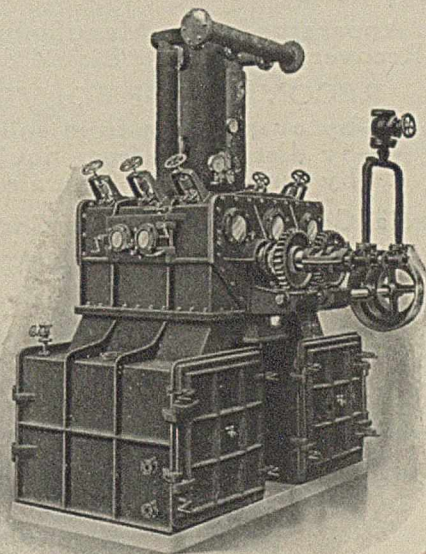
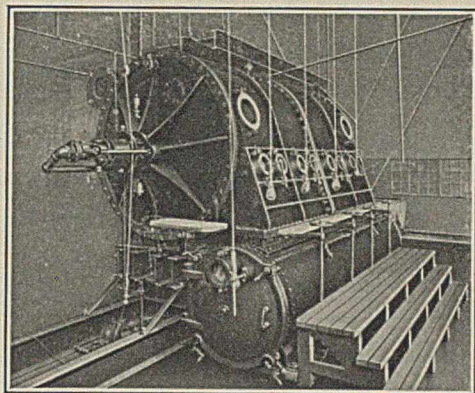
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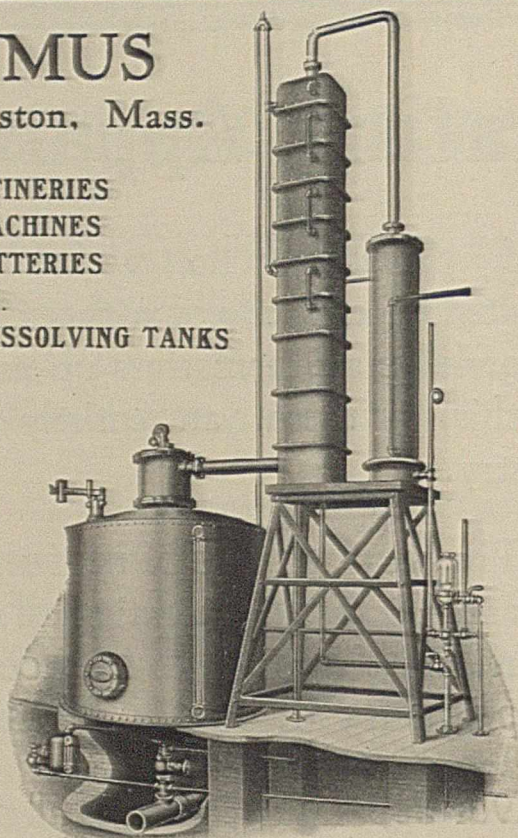
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