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EDITORIALS.

THE ENDOWMENT FUND.

I use the word "the" as though the visions of Chairman Hyde, indicated by the insert in the June number, were already realized. Like Crockett's coon, the aiming of a gun when a good man's behind it, is almost the same as having hit the mark already.

In the minds of all good members of the Society, there is a more or less well-defined spirit of altruism. The willingness to help is prevalent. This common feeling is certainly developing with rapidity in our country-at-large. In spite of the criticism of a few apparently short-sighted people and of conservatives who ask, "What has posterity done for us, that we should plan and spend for it?" we find all sorts of efforts being expended for the general, as distinct from the individual good. The term "conservation of natural resources" is rapidly becoming an activity. It is a moving force which acts not as the exceptional idea of a single able enthusiast, but as an advance for which our time is ripe. A few seem to fear what they call paternalism, but this name less perfectly fits the case than fraternalism, against which fewer could scoff. Our very laws are many of them founded upon the same fraternalism. Our factory laws, the pure food law, etc., stand for the wish that every one should be assisted in his life, liberty, and pursuit. A federal department devoted to the instruction of mining engineers and miners in the safer execution of their work is not alone a monument to the peculiar foresight and ability of a single man, however much he may have developed the idea. He was not separated from his environment. The work was largely a growth of the times. It is an indicator like the wind-indicating straw. How far the principle may develop, not even the most visionary can imagine. So long as it calls for more life, more effort, more hope, it seems reasonable. When, if ever, it merely reduces for the individual the call for his efforts, instead of substituting needs calling for greater total efficiency in living, then the years of the lean kine will arrive. Paternalism might do this. And this leads to the subject of our Endowment.

An endowment controlled by the American Chemical Society could do a great deal of good. According to the Constitution of the Society, we stand for "the advancement of chemistry and the promotion of chemical research." This is really quite distinct from the advancement of certain chemists and their promotion. An artificial help to the latter might cripple some of them, but any amount of help to the science will only enable the chemists to more efficiently help themselves and the rest of mankind.

Many men who are connected with manufacturing find themselves in contact with new materials, with physical, chemical and electrical phenomena, with which they, and possibly others, are not familiar. The necessary work of discovery is undertaken after the available knowledge is utilized. This individual research, which discloses necessary and always some unnecessary facts, often remains solely the property of the discoverer. It usually has an intrinsic value because of this fact. The more knowledge we have available, the better, and this applies to the industries and to the individual chemist. It is along this line that I believe in the power and utility of an endowment. It is that our stock of general knowledge may be increased.

Consider examples a moment. A couple of men working for a prize discovered and disclosed the law that permits all of us to know and always remember the approximate specific heats of elements and even solid compounds. Thousands of men have made good use of this law. Countless time has been saved to investigators in this way. Imagine the increase in the rapidity of an advance if we knew the laws governing the hardness, the ductility, the tensile strength, the expansion coefficient, etc., etc., of metal mixtures, especially if these were simply related to some other known properties.

A number of chemists have advanced a little way along the road of agricultural chemistry. It is public knowledge that plants need potash, nitrogen, phosphorus, etc., but the crops of the farmer who places more reliance on the common chemical knowledge than on the old barnyard manure can scarcely be considered hardy. Certainly this condition will improve, but the speed would be greater if facts were collected faster.

There are a great many laws, principles and facts in chemistry the discovery of which seem particularly fitting to our teaching laboratories. The discoveries of the fundamentals of our industries usually originate there. It is there, too, that financial help is most needed. When discoveries assist solely a single industry, it seems fair to expect the industry to bear the cost, but all chemists and manufacturers may share in the product of general chemical research such as the universities of the world are producing. In general, one would apparently not be far wrong who said, let us raise an endowment fund to help young chemists to advance themselves and their science by carrying out research work for publication under the guidance of our good teachers. W. R. WHITNEY.

PURE DRUGS AND MEDICINES.

The protection of the public is amply provided for through our national codex, the United States Pharmacopoeia, which defines the standards of purity and quality of most medicines and chemicals used in compounding prescriptions. This U. S. Pharmacopoeia is the standard accepted by our National Food and Drug Law. It is also the standard adhered to by all conscientious pharmacists and manufacturing chemists.

Upon the request of the "New York World," the writer undertook the analysis of about 230 prescriptions compounded in various pharmacies located in New York City. The prescriptions in question were of the average type calling for chemicals, galenical preparations, tinctures and fluid extracts. About half of those compounded were materially below the official standards or such standards as were demanded by the physician who wrote the prescriptions. Due allowance was made for deviations in approximate weighing and compounding. The following summary will illustrate the deviations above or below the standards in a number of instances.

Solutions of sodium iodid, 15 to 16 per cent. short and 14 to 21 per cent. in excess. Solutions of potassium iodid, 12 to 70 per cent. short. Solutions of three alkali bromids, 8 to 22 per cent. short. Solutions of strontium bromid, 20 per cent. short to 298 per cent. in excess. Solutions of rubidium iodid, 9 to 36 per cent. short. One party dispensed plain hydrant water in place of the salt.

Guaiacol.—All samples were below the U. S. Pharmacopoeia standard, varying from —45 to 60 per cent. of true guaiacol.

Iodine Ointment.—Of 14 prescriptions, five were passed as being within reasonable limits. The shortage in iodine varied from 20 to 92 per cent. while that of potassium iodid varied from 14 to 79 per cent. Several specimens were *colored* brown to cover their deficiency in iodine.

Fluid Extract of Ipecac.—These varied from 24 to 43 per cent. below the standard in alkaloidal content. One sample dispensed was not ipecac.

Fluid Extract of Coca.—While these were fairly good, one party dispensed a fluid not coca extract.

Tincture of Ipecac.—From 16 to 42 per cent. short in alkaloidal content.

Tincture of Opium.—Four samples showed a deficiency, below the standard, varying from —56 to —67 per cent. Another lot, of five, varied from 8 to 15 per cent. below.

Spirits of Camphor.—Two samples out of five were 30 and 37 per cent. short in camphor content.

Solution of Ethyl Nitrite.—The five prescriptions were below the official standard, namely, —10, —25, —37, —44 and —92 per cent. Since manufacturers supply ethyl nitrite in concentrated alcoholic solution, contained in small sealed tubes ready for dilution, there is no excuse for this deficiency. Eight ounces of the sweet spirits of niter were called for.

Fluid Extracts of Pilocarpus.—Belladonna (leaves and root) and Gelsemium were practically all far below normal standards.

Physiological assays of such active drugs as digitalis and strophanthus demonstrated a very wide variation in their relative potency. This demonstrates the necessity of the adoption of physiologic standards.

The retail pharmacist cannot be criticized for the discrepancies occurring among some of the preparations dispensed for he depends upon the wholesaler for his supplies. He should, however, be more discriminating as to the origin of these goods before dispensing for the sick. A careful review of our findings is given in order to point out the various causes of the deficiencies.

1st. Carelessness in Weighing.—This means careless weighing of the medicinal ingredients that enter either into prescriptions or in making up pharmaceutical preparations. Some pharmacists depend too much on their ability to *guess* accurately in weighing or measuring, not taking the time to do this as they are taught. There are druggists who measure by eye what they judge to be the accurate volume of a fluid. The majority of samples examined showed gross carelessness in weighing out the medicinal constituents of prescriptions.

2d. Carelessness in Measuring.—This means carelessness in measuring the volume of the fluid in making up prescriptions or pharmaceutical mixtures. We ascribe most of the shortages found to faulty measuring, in that the dispenser simply guessed at the capacity of the bottle used instead of using a graduated measuring vessel. Vials vary considerably in their volume capacity, so then if the dispenser should accurately weigh the medicine and then dissolve it in a fluid without measuring this correctly, naturally the objects of exact dosage will be defeated.

3d. Intentional Short Weighing in compounding prescriptions or making up preparations where expensive ingredients are to be used. For example, potassium iodide, 8.9 grams, instead of 30 grams as ordered in solution. Rubidium iodide, 0.96 gram, in place of 1.5 grams in solution. Ammonium iodide, 3.8 grams, instead of 5 grams. Tinctures of opium, 0.4 and 0.5 gram morphine in 100 cc., instead of 1.2 to 1.25 grams as the Pharmacopoeia demands. Ointments of iodine containing 25 to 40 per cent. less iodine than the standards demand, etc., etc.

4th. Deliberate Fraud.—Cases of this kind are rare among pharmacists, and when they occur, should be severely punished. Such practices are not countenanced anywhere. For example, the dispensing of water for a valuable medicinal agent as rubidium iodide; the substitution of an inert preparation instead of an active one, as in the case of fluid extract of coca or ipecac; the sale of tablets adulterated with a foreign chemical instead of the one prescribed; the use of colored lard in making up iodine ointment in order to cover the deficiency in iodine.

5th. Addition of Foreign Chemicals to Improve Appearances.—There is no excuse for adding "hypo" to solutions of potassium iodide when prescribed by a physician, nor any other preservative without his knowledge. Solutions of this chemical keep very well. Also inexcusable is the substitution of petrolatum (vaseline) in place of benzoinated lard in pharmacopoeial preparations where this ointment vehicle is specifically ordered. There are definite medical grounds for using the one (lard) or the other (petrolatum). If changes are made by the dispenser, the physician should be so informed.

6th. Market Supply.—Practically all of the drugs and chemicals obtained through reputable wholesalers are fully up to the rigid requirements of the U. S. Pharmacopoeia. Unfortunately, however, there are many unscrupulous dealers and peddlers of low-grade and rejected drugs, who impose on easy-going although well-meaning, druggists struggling for an existence. Let it be distinctly understood that at no time does a pharmacist experience any difficulty in obtaining drugs of the highest quality. It is only when seeking 'cheap stuff that he is imposed upon.

7th. Deterioration.—Some chemicals undergo rapid deterioration in spite of all efforts to the contrary. In such cases the manufacturer provides means of supplying the article in small packages or partially prepared so that the prescription may be made of fresh new material. We refer more particularly to sweet spirit of niter. This will not keep its strength up to the standards set for any length of time, hence, must be made fresh when called for. Since our manufacturers provide especially for the quick dispensing of full strength spirit of niter, there can be no excuse for dispensing preparations containing only 0.3, 2.2 and 2.5 per cent. when the standard requires that at least 4 per cent. should be present.

8th. Adulteration.—This represents one of the worst phases of the evil, since the motives are purely for gain, while deception and fraud are perpetrated upon the sick and injured, a crime of the worst type. *This practice is confined to circles outside of our dispensing druggists.* It occurs among the crude and powdered botanic drugs and more especially in the important medicinal organic chemicals which are extensively used in modern medicine. Many of the more popular of this class of remedies are peddled about by wandering dealers and firms of many aliases, who, when necessary, cross the border, or are now located there. These men do a prosperous business in selling these imitations and "just-as-good" products.

9th. Substitution.—This practice consists in substituting a drug of similar therapeutic action in place of one prescribed, either because it may be cheaper or because the pharmacist may be out of the desired article, or through carelessness. Several instances of this kind occurred: some were the substitution of an entirely different drug for that prescribed by the physician. Other cases were of a harmless nature, but still open to censure on grounds of carelessness. We refer to the substitution of the fluid extract of the "leaf" for that of the "root." There is a difference in the degree of activity (therapeutic) of the preparations of the leaves and roots of various drugs as well as a decided difference in color.

The New York College of Pharmacy, as well as other colleges of pharmacy and their graduates, who make up a very large proportion of our best dispensing pharmacists, maintain the highest standards of service and use every endeavor to protect the practice of pharmacy along correct and scientific lines. Our first national law regulating the importation of drugs and chemicals, enacted in June, 1848, was the result of action taken by the New York College of Pharmacy, seconded by medical and other pharmaceutical colleges.

This action also resulted in the organization of the American Pharmaceutical Association, whose aims have been solely to promote the practice of pharmacy along scientific and ethical lines. This war on substitution and sophistication of medicines has been constantly waged with varying results, chiefly owing to faulty legislative action or difficulties in enforcing the laws already enacted. As the matter now stands, the market is abundantly supplied with the purest of drugs and chemicals supplied by manufacturing firms whose names are guaranties for the very best that skill and science can produce. If our druggists will buy only from such houses and employ competent, conscientious assistants, they will render such service as the public has a right to expect.

VIRGIL COBLENTZ.

ORIGINAL PAPERS.

THE ELECTRICAL PRECIPITATION OF SUSPENDED PARTICLES.

By F. G. COTTRELL.

Received May 22, 1911.

The removal of suspended particles, from gases, by the aid of electric discharges is by no means a new idea. As early as 1824 we find it suggested by Hohlfeld[1] as a means of suppressing ordinary smoke, and again a quarter of a century later by Guitard.[2] These suggestions, which do not seem to have stimulated any practical study of the question, were soon entirely forgotten and only brought to light again by Sir Oliver Lodge[3] many years after he himself had independently rediscovered the same phenomena and brought them to public attention[4] in a lecture before the Liverpool Section of the Society of Chemical Industry Nov. 3, 1886. The first recorded attempt to apply these principles commercially appears to have been made at the Dee Bank Lead Works. The general principle of electrical precipitation of suspended matter was at this time patented by Alfred O. Walker of the above firm in several countries,[5] but these patents have long since expired. The apparatus was installed in 1885 by the works manager, W. M. Hutchings, with the coöperation of Prof. Lodge and briefly described by the former[6] just before its completion as consisting of a system of metallic points situated in the flue from the lead furnaces and excited from two Wimshurst influence machines with glass plates 5 ft. in diameter, each machine being driven by a one-horse power steam engine.

The apparatus undoubtedly did not in practice fulfil expectations as we find nothing further of it in the literature. The most apparent weakness of the project lay perhaps in the reliance on the Wimshurst machine, which had then just been brought out and from which a great deal more was anticipated[7] than has been justified by experience, at least as far as commercial applications are concerned.

Since that time an occasional patent[1] or article[2] has served to keep the subject in the public eye and in 1903 Lodge himself took out a patent[3] covering the use of the then new mercury arc for rectifying high potential alternating currents for this purpose.

Up to the present time none of these patents seem to have been carried into successful commercial operation on the large scale in the chemical or metallurgical industries.

Some four years ago while studying various methods for the removal of acid mists in the contact sulfuric acid process, the author had occasion to repeat the early experiments of Lodge and became convinced of the possibility of developing them into commercial realities. The work described in the present paper may fairly be considered as simply the reduction to engineering practice as regards equipment and construction of the fundamental processes long since laid open to us by the splendid pioneer work of Lodge, a feat vastly easier to-day than at the time of Lodge and Walker's orginal attempt.

The precipitation of suspended matter whether in gases or liquids may be accelerated by electricity in the form of either direct or alternating current, but the mode of action and the type of problem to which each is best applicable differ in certain important respects.

Where an alternating electromotive force is applied to a suspension the action consists for the most part in an agglomeration of the suspended particles into larger aggregates out in the body of the suspending medium and a consequently more rapid settling of these aggregates under the influence of gravity.

Thus if powerful Hertzian waves are sent out into foggy air the alternating fields set up in space cause an agglomeration of the particles of liquid into larger drops which then settle much more rapidly. Considerable work aimed at the application of this phenomena to the dispelling of fog on land and sea has recently been done in France and England but very little as to definite results seems as yet to have been published. The field appears, however, one of considerable promise. Another application of alternating current along these lines is found in a process now in use in the California oil fields for separating emulsified water from crude oil. This process grew out of the work here described and was developed some

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[1] "Das Niederschlagen des Ranchs durch Electricität Hohlfeld," *Kastner Archiv. Naturl.*, **2**, 205–6 (1824).

[2] C. F. Guitard, *Mechanics Magazine*, Nov., 1850.

[3] Historical Note on "Dust Electrification and Heat," O. J. Lodge, *Nature*, **71**, 582 (1905).

[4] "The Electrical Deposition of Dust and Smoke with Special Reference to the Collection of Metallic Fumes and to a Possible Purification of the Atmosphere," *J. Soc. Chem. Ind.*, **5**, 572–6 (1886), with appended bibliography.

[5] Great Britain, 11,120, Aug. 9, 1884; Belgium, 68,927, May 19, 1885; Spain, 7,211, July 10, 1885; Germany, 32,861, Feb. 27, 1885; Italy, 18,007, Mar. 31, 1885; United States, 342,548, May 25, 1886.

[6] *Berg.- und Hüttenmännisch. Zeitung*, **44**, 253–4 (1885).

[7] A. O. Walker, *Engineering* (Lond.), **39**, 627–8 (1885). G. Tissandier, *London Electrician*, **17**, 33 (1886).

[1] Lorrain, British Pats., 6495 and 6567 (1886); Thwait, U. S. Pat., 617,618, Jan. 10 (1899); Hardie, U. S. Pat., 768,450, Aug. 23 (1904).

[2] J. Wright, *Elect. Rev.* (Lond.), **47**, 811, Nov. 23 (1900); see also *Jour. Roy. Sanitary Institute*, **27**, 42.

[3] Brit. Pat., 24,305 (1903); U. S. Pat., 803,180, Oct. 31 (1905).

two years ago by Mr. Buckner Speed and the author to meet certain peculiar conditions existing in these fields, but as it is to be described more at length in a subsequent article the details will be here omitted.[1]

Alternating current may thus be used to advantage where the masses of gas or liquid to be treated are fairly quiescent and a simple agglomeration of the suspended particles into larger aggregates is sufficient to effect separation by gravity or otherwise.

In the case of the large volumes of rapidly moving gases in smelter flues the agglomerating and settling process is, however, too slow even when the flues are expanded into as large dust chambers as are commercially feasible. It is in such cases that direct current methods have been particularly important.

If we bring a needle point connected to one side of a high potential direct current line opposite to a flat plate connected to the other side of the line we find that the air space between becomes highly charged with electricity of the same sign as the needle point irrespective of whether this is positive or negative, and any insulated body brought into this space instantly receives a charge of the same sign. If this body is free to move, as in the case of a floating particle, it will be attracted to the plate of opposite charge and will move at a rate proportional to its charge and the potential gradient between the point and plate.

Even if there are no visible suspended particles the gas molecules themselves undergo this same process, as is evidenced by a strong wind from the point to the plate even in perfectly transparent gases. The old familiar experiment of blowing out a candle flame by presenting it to such a charged point is simply another illustration of the same phenomena.

As above indicated the first step toward practicability was of necessity a commercially feasible source of high tension direct current. The obstacles to building ordinary direct current generators for high voltages lie chiefly in difficulties of insulation, and if this is avoided as to individual machines by working a large number in series the multiplication of adjustments and moving parts intrudes itself. On the other hand, high potential alternating current technique has in late years been worked out most thoroughly, and commercial apparatus up to 100,000 volts is available in the market. The mercury arc rectifier has been made practical for series arc lighting service up to some 5000 volts direct current, but although higher voltage units were at one time attempted by the electrical companies they were later withdrawn from the market as unsuited to practical operating conditions. For high voltages they seem like the static machines to work well under the careful management and light duty of the laboratory but to fail in practice. This is particularly so in the application to metallurgical and chemical work where the electrodes in the flues have to be placed close together and worked near the potential of disruptive discharge, the occasional occurrence of which later places much more severe requirements upon generating apparatus than in the case of the series arc lighting, to which the rectifier seems particularly well adopted.

This restriction does not necessarily apply to the conditions under which fog and smoke would be treated in the open air. It is to these latter cases that Lodge's efforts in late years seem to have been the more particularly directed, and here the mercury rectifier in connection with high potential transformers may find a useful field.

The procedure actually used in the installations described below consists in transforming the alternating current from an ordinary lighting or power circuit up to some 20,000 or 30,000 volts and then commutating this high potential current into an intermittent direct current by means of a special rotary contact maker driven by a synchronous motor. This direct current is applied to a system of electrodes in the flue carrying the gases to be treated.

The electrodes are of two types corresponding to the plate and point in the experiment above cited. The construction of electrodes corresponding to the plate presents no special problem as any smooth conducting surface will answer the purpose. With the pointed or discharge electrodes it is quite otherwise and the working out of practical forms for these has proved the key to much of the success thus far obtained.

In laboratory experiments when the discharge from a single point or a few such is being studied fine sewing needles or even wire bristles answer very well, but when it is attempted to greatly multiply such discharge points in order to uniformly treat a large mass of rapidly moving gas at moderate temperatures great difficulty is met in obtaining a powerful and, at the same time, effective distribution of current.

It may be of interest to note that the clue to the solution of this difficulty came from an almost accidental observation. Working one evening in the twilight when the efficiency of the different points could be roughly judged by the pale luminous discharge from them, it was noticed that under the particular conditions employed at the time, this glow only became appreciable when the points had approached the plates almost to within the distance for disruptive discharge, while at the same time a piece of cotton-covered magnet wire which carried the current from the transformer and commutator to the discharge electrodes, although widely separated from any conductor of opposite polarity, showed a beautiful uniform purple glow along its whole length. The explanation lay in the fact that every loose fiber of the cotton insulation, although a relatively poor conductor compared to a metallic point, was still sufficiently conductive from its natural hygroscopic moisture to act as a discharge point for this high potential current and its fineness and sharpness, of course, far exceeded that of the sharpest needle or thinnest metallic wire. Acting on this suggestion it was found that a piece of this cotton-covered wire when used as a discharge electrode at ordinary temperature proved far more effective in precipitating the sulphuric acid mists, which were then the object of study, than any system of metallic

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[1] See also "Dehydration of Crude Petroleum, a New Electrical Process," Arthur T. Beazley, *The Oil Age*, **3**, 2–4, Apr. 21, 1911.

points which it had been possible to construct. Perhaps the greatest advantage thus gained lay in the less accurate spacing demanded between the electrodes of opposite polarity in order to secure a reasonably uniform discharge.

In practice of course a more durable material than cotton was demanded for the hot acid gases to be treated and this has been found in asbestos or mica, the fine filaments of the one and the scales of the other supplying the discharge points or edges of the excessive fineness required. These materials are twisted up with wires or otherwise fastened to suitable metallic supports to form the discharge electrodes in such wise that the current has to pass only a short distance by surface leakage over them, the slight deposit of moisture or acid fume naturally settling on them serving to effect the conduction. If the condition of the gases does not supply sufficiently such coating then a special treatment of the material before being placed in the flue is resorted to.

The construction and arrangement of the electrodes as also of the chamber containing them naturally varies very widely with the conditions to be fulfilled under the varied applications to which the process may be put. Some of the more general features of this work are described in the patents[1] already issued in this and foreign countries, while further details and modifications are covered in other patents not yet issued from the Patent Office. The accompanying photographs give perhaps a better idea of the gradual development of the work than any detailed description which would be possible in the space here at command.

Fig. 1 is the apparatus used for the orginal laboratory experiments in the spring of 1906. Sulphuric acid mist was generated by bubbling the gas from the little contact sulphuric acid plant, seen on the table, through water in the U-tube beneath the inverted glass bell jar, whose inner walls were quickly wetted sufficiently with acid to act as the collecting electrode, a wire being inserted along side of the stopper through which the U-tube connected with the bell jar and served to connect the jar walls to the induction coil on the left, the latter acting as the step-up transformer. This coil received alternating current at 110 v. from the lighting circuit and gave about 3700 volts at its secondary. The other high potential terminal of the induction coil was connected to the discharge electrode within the bell jar through a make and break operated by the synchronous motor. This latter was improvised by substituting a plain iron cross for the squirrel cage armature in an ordinary fan motor operated from the same 110 v. line as the induction coil, and brought into step by the induction motor on the right. A momentary contact with the discharge electrode was thus established once each complete cycle at the peak of the voltage wave, and served to charge this electrode to the maximum voltage of the line, always with the same polarity. In order to help maintain the charge on the electrode in the interval between these contacts the Leyden jar seen in the picture was connected in parallel with the electrodes. The wire leading to the jar walls or collecting electrode was usually grounded for convenience and safety, as in fact has been done throughout all the practical installations. This leaves but one high potential conductor to deal with in each precipitation chamber and greatly increases the safety of operation.

Fig. 2 is a closer view of the precipitation chamber through which the acid fume is being blown at the rate of about 20 liters per minute, the electric current being shut off of the apparatus. Fig. 3 shows the effect of turning on the electric current with the same gas steam still flowing.

The discharge electrode in this case consisted of a cylinder of wire screen wrapped with a few turns of asbestos sewing twine and suspended by a wire passing through a glass tube as shown. The suspended particles of acid were driven away from the asbestos filaments and deposted on the walls of the bell jar, finally running down into the U-tube below.

The next undertaking was to duplicate these experiments on a scale some two-hundred-fold larger. This was carried out during the same summer at the Hercules Works of the E. I. du Pont de Nemours Powder Company at Pinole on San Francisco Bay, where the contact gases from one of their Mannheim contact sulphuric acid units were kindly placed at our disposal. These gases at the point selected contained about 4 per cent. by volume of dry gaseous sulphur trioxide, and in order to convert this into sulphuric acid mist they were brought in contact with water. Under these conditions very little of the sulphur trioxide is absorbed by the liquid water, but the latter evaporating into the gas combines with the sulphur trioxide to form the far less volatile sulphuric acid which immediately separates as a dense white cloud of suspended particles so fine as to represent one of the most difficult of all materials to remove by filtration.

Figs. 4 and 5 are photographs taken about a minute apart with the same current of fume-laden gases passing into the precipitation chamber, but with the electric current respectively off and on. The apparatus was the same in general plan as the small laboratory unit described above, except that instead of a single cylinder of wire screen for the discharge electrode, two concentric cylinders were used, while intermediate in diameter between these two and resting on the lead pan bottom of the apparatus was a third cylinder, also of iron wire screen, but without asbestos winding, which together with the outer leaded glass cylinder constituted the collecting electrodes. The precipitated acid drained off from this precipitation chamber into the carboy on the right. The space between successive cylinders of opposite polarity was as nearly as possible an inch and a quarter. Current was supplied from three 1-kw. 110 v. to 2,200 v. transformers connected in series on their 2200 v. side to give 6600 v. The fume was delivered as before to the bottom of the precipitation chamber at its center and had to pass through the three-wire cylinders and

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[1] U. S. Pats., 866,843, 895,729 and 945,717. The second of these also practically reprinted by *Eng. Min. J.*, **86**, 375–7 (1908).

up between the outer of these and the glass container, thus being subjected to three electric fields in succession. In this apparatus the power consumption was about one-fifth of a kilowatt, and between one hundred and two hundred cubic feet of gas per minute could readily be treated. This apparatus was of course merely for experimental and demonstration purposes but a still larger unit built for permanent operation and to handle all of the gas from a Mannheim unit has since been installed at this plant and put into steady commercial operation.

These experiments at Pinole attracted the attention of the Selby Smelting and Lead Company whose smelter located at Vallejo Junction a few miles farther up the Bay was at that time the object of injunction proceedings brought by the farmers of the surrounding country. At the time the suits originated three separate stacks at the Smelter contributed to the alleged nuisance. The first, and admittedly the most serious offender, handled the gases from the lead blast furnaces and discharged several tons of lead fume daily into the air. Shortly before the commencement of our work at the plant this had been obviated by the installation of the bag house[1] shown in Fig. 6. After correcting this evil there still remained, however, a stack discharging the gases from the roasters, which besides the invisible sulphur dioxide furnished dense white clouds consisting chiefly of sulphuric acid, arsenic and lead salts, and to which the bag house was inapplicable on account of the corrosive action of these gases upon the bags. Lastly there was the stack of the refinery carrying the mists escaping from the pots of boiling sulphuric acid used to dissolve the silver out of the gold and silver alloy coming from the cupels.

The blast furnace and the roaster stacks each carried something over 50,000 cu. ft. of gas per minute while the refinery stack represented scarcely a tenth of this volume. As a first step we accordingly commenced operations on this latter, and after several months' experimenting, as to the best form of construction, adopted a system of vertical lead plates 4 in. wide by 4 feet in length and spaced about 4 in. apart. Several rows of such plates were assembled in a 4 by 4 foot lead flue. Between each pair of plates hung a lead-covered iron rod carrying the asbestos or mica discharge material, the latter finally proving the more serviceable in this highly acid atmosphere. These rods or discharge electrodes were supported on a gridwork of buss bars extending over the heads of the plates and through apertures in the sides of the flue to insulators on the outside. Fig. 7 is a view looking down on the top of this flue with the cover removed from above the electrodes. Figs. 8 and 9 show the effect on the appearance of the stack when the electric circuit is respectively open and closed, the stack in the immediate left foreground being the one into which this flue discharges. The large stack in the middle background is from the roasters to be discussed below. Fig. 10 shows the corresponding stream of dilute sulphuric acid (about 40° Bé.) running out from the flue as precipitated. When the acid kettles are at a full boil it often amounts to over two gallons a minute.

The electric current is taken from the power circuit of the plant at 460 volts, 60 cycles, and transformed up to 17,000 volts thence through the synchronous contact maker or rectifier to the electrode system. At first a glass plate condenser was connected across the high potential line in parallel with the electrode system in order to assist in maintaining the potential of the electrodes between the intervals of contact but was found troublesome and unnecessary in practice and in this and other installations is now omitted.

The power consumption for this installation is about 2 kw. including the driving current for the synchronous motor. The switchboard transformer and rectifier are located in the engine room of the plant and require no more attention than a feed pump or a blower. The installation has now been in successful daily operation for over three years at a cost for labor attendance and repairs of less than $20 a month. In fact while the plant was making enough bluestone to utilize all the weak acid recovered, the saving on purchase of the latter paid for the entire cost of operating five times over.

The next undertaking was naturally an extension of the process to the treatment of the gases coming from the pyrites and matte roasters of the same plant. This presented a somewhat more difficult problem as the material to be removed consisted of a mixture of solid dust and fume with liquid sulphuric acid. From small scale experiments it was at first thought possible to precipitate the material in a reasonably dry form and shake it in this condition from the electrodes, thus permitting of brick and iron construction. Quite an extensive installation was carried through on this plan, a general view of which is seen in Fig. 11. It consisted of four parallel brick flues or chambers each 22 ft. long., 7 feet wide and 9 feet deep, and containing an electrode system of iron plates as grounded or collecting electrodes and wire and asbestos discharge electrodes somewhat similar in general arrangement to that in the refinery flue. In this case, however, the insulating supports of the discharge electrodes were carried above the flue as seen to right and left in the figure.

In practice, however, this type of equipment was found poorly adapted to the particular gas conditions here met with, as a very much higher proportion of free sulphuric acid was encountered than the preliminary tests had given reason to expect, the weight of this free acid often exceeding, in fact, that of all the solids in the gas put together. The gases were also highly charged with water vapor both from the wet ore and the steam atomizing oil burners in the roasters, and this tended further to dilute the acid and produce a muddy deposit. The iron and brick construction made removal of this deposit by washing impracticable so it was decided to further cool the gases and treat them in a lead flue similar to that used in the case of the refinery. However, the experience gained with the large brick flues in which a wide

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[1] For detailed description see *Eng. Min. J.*, **86**, 451–7 (1908).

variety of electrodes were tested out, made it possible to compress this new construction into far smaller compass than would otherwise have been thought possible.

The resulting construction is seen in Fig. 12. This is a sheet lead flue 6 × 6 feet cross section and 32 feet long, containing 38 rows of 16 lead plates each 6 feet long by 4 in. wide with the corresponding discharge electrodes between each pair. The effect of the treatment upon the appearance of the gases issuing from the stack is shown in Figs. 13 and 14 which, as before, represent respectively the electric current switched off and on being taken about three minutes apart. When Figs. 6 and 12 are compared and it is remembered that in this 32 feet of 6 × 6 ft. flue about the same volume of gases was being treated as in the bag house measuring about 98 × 125 × 55 feet, and further that actual tests showed that even the woolen bags used in this bag house are completely distroyed by these roaster gases in less than half an hour, a better idea may be gained of some of the possibilities which this process appears to open. The power consumption in this case was between 10 and 15 kw. The material precipitated upon the plates was a grayish mud easily washed off and drained out through the bottom of the flue to settlers. For this purpose it was necessary once in about every four to six hours to by-pass the gases, shut off the current from the flue, raise its covers as seen in Fig. 12 and close down the electrodes from above. One man could easily carry out this whole operation in from five to ten minutes. For continuous operation on such material it is, of course, necessary to subdivide the treatment into two or more units in order that while one is being cleaned the others may be in operation.

In order to insure that essentially all the free sulphuric acid and arsenic of these roaster gases should be condensed from true gases into suspended particles, which latter are all the apparatus purports to collect, and also to protect the lead construction from softening from the heat, it was found necessary to cool the gases down to less than 150° C. To accomplish this a system of water sprays was first used in the mouth of the lead flue just before the electrodes. This served the purpose very well as long as clean water which would not stop the sprays was available, and successful test runs of a week or more duration were made with this system, but as the circulating and cooling water of the entire plant is derived from the Sacramento River, which is often very muddy, the difficulties of keeping the sprays clean and open determined the management of the plant to resort to cooling by radiation through a lengthening of the flue before the precipitator. This construction and the refitting of the apparatus for continuous operation has not as yet been undertaken, and as the litigation with the farmers seems for the present at least to have centered more about the question of sulphur dioxide, it is likely that the completion of the work will be allowed to await the reaching of an understanding on this matter.

The next installation in order of size to be undertaken was at the Balaklala Smelter at Coram, Shasta County, California. The vast body of low-grade copper ore reaching for many miles across this county and commonly known as the Copper Crescent has recently been described in detail by L. C. Grafton[1] and characterized as the second largest copper deposit which can be considered as a single geological unit in the United States.

The first commercially successful smelter in this region was erected at Keswick in 1896 by the Mountain Copper Co., Ltd., under the management of Louis T. Wright and was of especial interest as one of the pioneers in pyritic smelting. Extensive heap roasting was also carried on at this plant with the result of wide-spread deforestation of the surrounding country and the final closing down of the plant in 1905 through injunction proceedings instituted by the U. S. Forestry Service. The company has since built a small smelter and acid phosphate works at Martinez on San Francisco Bay and now ships its ore to this point nearly 250 miles distant for treatment, but even this latter plant has at various times come in for its share of fume litigation.

In 1901 the Bully Hill Smelter at Delamar with a capacity of 250 tons a day was started. This was later purchased and is now owned by the General Electric Company, but since last July it has been closed as a result of complaints by the U. S. Forestry Service who insisted, at that time, that the plant either close or at least commence efforts on a practical scale looking toward controlling its fumes.

In 1905 the Mammoth Copper Mining Company, a subsidiary of the U. S. Smelting, Refining and Mining Company, blew in its present smelter at Kennett. This plant when running full has a capacity of some 1200 tons of ore per day.

The Balaklala, or First National Copper Company, is the most recent of the Shasta County smelters, having blown in its first furnace in 1908.

These smelters are all situated in the narrow precipitous cañon of the upper Sacramento River and its tributary, the Pitt. The region itself is too steep and rocky for agriculture but was once heavily wooded, although now swept bare of vegetation for miles. As far as the cañon itself is concerned probably all the damage possible has already been done unless reforestation were undertaken. This latter even would probably be slow and difficult work as since the loss of vegetation the steep hillsides have been washed bare of soil for miles around. At Redding, however, some 13 miles below Coram and 17 miles below Kennett, the cañon widens out into the fertile Sacramento valley and from this point southward for some 12 miles further lies the region from which for the past two years have come increasingly insistent complants against the smelters. These culminated a little over a year ago in agreements between the farmers and the smelters under which friendly suits were brought in the federal courts and injunctions issued by stipulation requiring the smelters to remove the suspended matter from their exit gases and dilute

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[1] U. S. Geological Survey, *Bull.* **430***b*.

the latter to such an extent that their sulphur dioxide content should not exceed seventy-five hundredths of one per cent. by volume as discharged from the stacks, with the further general and sweeping provision that they should do no damage.

To accomplish this the Mammoth Smelter installed a bag house which has been in very successful operation since last July. Fig. 15 is a view of this plant showing the bag house on the left in operation. It will be noted that the gases discharged from the five stacks (each 21 feet square) are to all intents and purposes free from suspended matter and consequently invisible. This represents a notable achievement, being the first time that the bag house, so efficient in lead smelters, has been successfully applied to copper blast furnace gases on the large scale.

It is made possible in this instance through neutralization of the sulphuric acid in the gases by the zinc oxide carried over in the fume from the very heavy zinc content of the ore smelted. The Company is also the owner of patents[1] on the introduction of finely divided metallic oxides into the gases for this purpose. In addition it was necessary to provide an extensive system of cooling pipes seen in front of the bag house in the picture. There are 39 of these pipes each 4 feet in diameter and averaging about 200 feet in length. They represent a very large part of the cost of the installation. It was expected that they would be sufficient to cool the entire gases of the plant to a safe temperature to protect the $30,000 worth of woolen bags with which the house is filled, but upon starting up it was found that only a little over half the full capacity of the plant could thus be treated with safety and operations were accordingly restricted to this. In the cold weather of winter a considerably larger tonnage can be handled with safety than during the hot summer. Notwithstanding this, however, the bag house is to be considered a decided success at least for the particular conditions met with at this plant and the management deserves great credit for the courage and skill with which it has carried through this new, and after all largely experimental, undertaking, representing as it does the expenditure of over a quarter of a million dollars.

In the case of the Balaklala Smelter, of which Fig. 16 is a general view, the use of a bag house was also considered and in fact a small experimental unit containing a few bags was run for some months in comparison with tests both by the electrical process here described and also a centrifugal apparatus in which the gases passed through a rapidly rotating cylindrical shell equipped with radial baffles to insure the gas being raised to full velocity. As a result of these tests the electrical process was adopted for the full-sized installation.

The smelter treats from 700 to 1000 tons of $2^{1}/_{2}$ to 3 per cent. ore carrying over 30 per cent. of sulphur with considerable but varying amounts of zinc. The greater proportion of this is handled in blast furnaces but the fines including everything under an inch and amounting to less than 10 per cent. of the whole go through MacDougal roasters and an oil-fired reverberatory. The plant has also two converter stands. The gases from all these departments pass into a common flue 18 × 20 feet in cross section, an interior view of which at the main by-pass damper is shown in Fig. 17. The volume of gases passing through this flue varies with operating conditions from a quarter to half a million cubic feet a minute which means in round numbers a mean linear velocity in the flue shown of 10 to 20 feet per second.

Before attempting to design the full-sized equipment for treating these gases a small precipitation chamber capable of treating about 1 per cent. of the total gases was erected and an extended set of experiments made with it. Fig. 18 shows this small unit with its exhaust fan and stack. In the original tests it was located nearer the base of the main stack, the figure showing it in its present state as modified for other experiments and tests.

Figs. 19 and 20 indicate the degree of success attained with this small unit in its original position having been taken a few minutes apart with the electric current respectively off and on, the same gas volume issuing in both instances from the stack which is 2 ft. in diameter.

With this miniature unit as a guide the equipment of the whole plant with similar apparatus was undertaken in March of last year. This was completed and first put into operation the end of the following September, since which time it has been in continuous operation, with the exception of the latter half of December when changes were decided upon during whose carrying out it became necessary under the terms of the court decree to shut down the plant for a couple of weeks.

As was naturally to be expected many difficulties were encountered, some of which have already been entirely overcome while others are giving way more gradually before the systematic study of operating conditions.

Fig. 21 is a plan of the nine electrical precipitation units or chambers in their relation to the flue system and stack. It should here be noted that the two large fans indicated in the drawing are not required for the operation of the precipitating system nor to overcome any added resistance due to its introduction, as this latter is very slight indeed. The fans were made necessary by that section of the court's decree requiring dilution of the sulphur dioxide to three-quarters of a per cent. or less. When the furnaces are running on a high sulphur charge this feature of the decree necessitates a considerable dilution of the gases with fresh air and corresponding diminution of stack draft. At these times the fans are operated, but during a considerable portion of the time the sulphur dioxide in the gases can be brought low enough without interference with the draft, and during these periods the fans are stopped entirely although the gases still pass through them.

At the rectifier building the current is received from the companies' three-phase power circuit at 2300 volts,

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[1] Clarence B. Sprague, U. S. Pats., 931,515, Aug. 17, 1909 and 984,498, Feb. 14, 1911. See also W. C. Ebaugh, This Journal, **1**, 686–9 (1909) and **2**, 372–3 (1910).

60 cycles, and after being transformed up to from 25,000 to 30,000 volts under the control of the operator through variable resistance and induction regulators is rectified into an intermittent direct current as already explained and distributed to the individual precipitating units.

Fig. 22 shows a cross section through one of these units or precipitating flues as first installed. The double vertical lines represent the collecting or grounded electrodes each 6 inches wide by 10 feet high made of No. 10 sheet iron. The dotted lines represent the discharge electrodes consisting of two iron wire strands between which is twisted the discharge material, for which both asbestos and mica preparations have been used in this plant. Each unit contains 24 rows of 24 electrodes of each type. The collecting electrodes are carried by bars connected directly to the frame of the chambers themselves while the discharge electrodes are spanned by springs between a system of buss bars carried on externally placed insulators as shown in the figure. To the auxiliary chambers surrounding these insulators a small regulated amount of air is admitted to prevent conductive dust or fume from working back and settling on the insulators.

The cam and shaker rod extending across the middle of the unit was originally designed for the purpose of vigorously shaking the electrodes as it was greatly feared that the removal of precipitate from the electrodes in units of this size might be one of our most serious problems. In actual operation it has been found however that the electrodes can easily be shaken by hand from the top entirely free from dust, the whole operation including cutting the unit in and out of the system and the removal and replacement of its covers requiring only about ten minutes, and this having to be repeated every six or eight hours, depending on the dust content of the gases. The precipitated dust and fume as it falls from the electrodes is carried by the conveyor in each unit to a common longitudinal conveyor which in turn discharges into cars carrying it away for treatment and recovery of its values.

Fig. 23 is the interior of the rectifier house or control station showing the general arrangement of the apparatus and wiring. Fig. 24 shows the precipitation units in course of construction, while Fig. 25 is a view over the tops of six out of the nine units after completion. Figs. 26 and 27 are photographs of the main stack taken a few minutes apart with the electric current respectively off and on.

Filtration tests show that this plant under favorable working conditions precipitates between 80 and 90 per cent. of the suspended matter in the gas, the average over the whole period of operation to date being somewhat less. Under present operating conditions at the smelter this represents some 6 to 8 tons of precipitate per 24 hours. Fig. 28 shows this steady stream of precipitated smoke as it flows night and day from the end of the conveyor coming from the units.

The gas treating plant as a whole including flues fans, motors and electrical apparatus cost up to the time it was first put in operation a little less than $110,000. Although many minor changes have since been made none of the larger or more expensive elements of construction have been greatly altered.

The total average power consumption for the precipitation plant at present is in the neighborhood of 120 kws. One man can readily control the whole operation in the rectifier house although as a matter of precaution for a new plant under the high tension here used two have usually been on duty. Two laborers and a foreman are employed on the precipitating units and dust-handling system, although this can probably be reduced somewhat by automatic shaking devices, since as yet the main efforts at improvement have been directed elsewhere.

The volume of gases to be treated varies considerably with the conditions at the furnaces but at present may fairly be taken as averaging between 200,000 and 300,000 cubic feet per minute, and entering the units at from 100° to 150° C.

One of the greatest difficulties met with in this particular installation has been the maintenance of conductivity in the fine fibers of the asbestos and mica of the discharge electrodes. At ordinary room temperatures these materials readily take on enough moisture from the air to afford sufficient surface leakage for all the discharge necessary, and the same is true at higher temperatures if the gases contain traces of sulphuric acid or other conductive matter, but in the particular gases here met with the high and variable amount of zinc oxide at times robs them of all conductive matter, thus reducing the conductivity of the fibers of the electrodes and seriously effecting their efficiency. The possible methods of overcoming this and giving the fibers a permanent conductivity of their own as well as other details of the more purely electro-technical matters underlying the whole process will be treated more at length elsewhere as the present article is intended more as an outline sketch of the history and practical development of the work thus far accomplished. Nor is this the place to speculate upon the final outcome of situation between the farmers and the two great smelting plants which have adopted the remedial measures above described, for this is in the end a question for the botanical and agricultural expert, as to whether or not, or to what extent actual damage is still being done, no matter whether this comes from suspended matter or from the sulphur dioxide, which neither the bag house nor the electrical precipitation make any claim to remove. The two smelting companies have done and are doing everything in their power to better the conditions while on the other side the farmers, through the executive committee of their protective association, have earnestly tried to carry out their part in a spirit of fairness to all concerned.

To those who know the circumstances of the many bitter conflicts between farmers and smelters all over this country, with the attendant expense and usual barrenness of results, the present developments in Shasta County present a very suggestive illustration of what may be accomplished in the technical development of our industries by spending the money on experiment and construction instead of all on litigation. Irrespective of the local issues involved the work done at both of these smelters during the past year has been a real and decided step forward in practical metallurgy. Both plants have already sufficiently demonstrated the applicability to large scale operation of the principles underlying them to ensure these principles finding a permanent place from now onward in the field of engineering, and each for the particular cases for which it is peculiarly adapted. Before us, of course, still looms the question of the sulphur dioxide and the solution for this on an equally large scale is unfortunately not yet clearly in sight.

Before leaving the subject I cannot but make grateful acknowledgment to those who have worked so earnestly and loyally shoulder to shoulder during the past year and to whose energy and ability such measure of success, as has been met with thus far, is entirely due. Especially do I wish to express appreciation of the courage, determination and ability of Mr. R. T. White, until recently general manager of the Balaklala Company, and now holding the corresponding post with the Braden Copper Company in Chili, in undertaking and carrying through this new developmental work with all its attendant risks under the most trying of circumstances. Fig. 29 is a snapshot of this staff at the works. From right to left on the back row they are: A. H. Trotter, chief engineer; H. R. Hollbrook, chemist; C. A. Van Amberg, master mechanic; R. B. Rathbun, chief electrician; R. House, chief operator precipitation plant; C. S. Hull, osillograph expert, General Electric Co.; and in the front row, from right to left: W. Eaton, engineer of tests; H. A. Burns, my own assistant and co-worker throughout all the work of the past four years; R. T. White, general manager; R. B. Green, smelter superintendent; and the author.

Of the other possible applications of the process, one of the most recent to be actively prosecuted is the collection of dust from Portland cement kiln gases. The chief stimulus to this development has again been the nuisance to the surrounding population and its attendant litigation. This has been especially acute in southern California where several cement plants are located in the heart of an exceedingly rich orange country. In the case of the Coulton plant with a capacity of 2500 barrels a day an injunction has already been issued by the court which, if sustained, will close the plant, unless they can control their dust which the court estimates at present at some 20 tons per day. This case differs from that of the smelters in that here there is no question of damage from gases but merely the deposition of a large tonnage of impalpable dust of lime and clay.

From the technical side a new condition is here met with in the high temperature of the gases to be treated, which are 450° C. and upwards as they leave the present stacks. The dust itself is furthermore entirely devoid of electrical conductivity, but notwithstanding this it is easily and completely precipitated by the electrodes when these are properly adapted to the new conditions.

Experiments on a scale of a few hundred cubic feet per minute have been carried on for the past few months under the direction of Mr. Walter A. Schmidt, at the Riverside Portland Cement Works, and these have recently been extended to treat a good portion of the gases coming from one kiln. Fig. 30 represents this installation at its present stage. It is the intention after determining the most advantageous conditions for construction and operation on this kiln to equip the remaining seven kilns accordingly at which time a more complete description of the application of the process will be presented.

Another extensive field in which it is hoped this process may find useful application is the cleaning of iron blast furnace gas for use in gas engines. Outside of the poisonous and combustible nature of these gases and the consequent necessity for keeping the whole apparatus gas-tight there would appear to be no new difficulties here to overcome and steps are being taken to thoroughly test the matter on a practical scale, this work at present being in direct charge of Mr. L. L. Johnson, of Indianapolis.

A question which naturally presents itself is whether this work has any bearing upon the coal smoke problem of large cities. In answer it may be said that for the great majority of cases at present the more logical line of attack would seem to lie in improved methods of combustion, to avoid making smoke in the first place, but in some special instances where such methods may happen to be particularly difficult of application and the suppression of smoke is especially desirable, electrical precipitation may eventually be found of use, for experiments show that it acts upon ordinary smoke in essentially the same manner as upon the fumes and dust above discussed.

NOTE RECEIVED JULY 7, 1911.

Since the manuscript of the above article was sent to the printer the case of the Balaklala Company *versus* the Shasta farmers has come up for formal hearing in the United States Circuit Court in San Francisco, before Judge Morrow, on June 19th.

The evidence presented from the farmers' side consisted of a considerable number of affidavits from individual residents of the District in question, stating that they believed damage was still being done. They naturally made little or no attempt to distinguish between damage from gases and that from suspended matter. Of much more interest in the present connection was the report from Messrs. Gould and Burd, the chemists employed by the Shasta County Farmers' Protective Association, to examine the operating conditions at the Smelter itself and determine to what extent the terms of the decree were being fulfilled.

Their tests extended over the period from March 10th to April 3d and credit the electrical apparatus with removing during that period an average of 72.8 per cent. of the total solids in the gases entering it. In nearly one-third of the individual determinations the removal of solids reported is over 85 per cent.

They report the average concentration of sulphur dioxide as 0.56 per cent. by volume, but state that several times during the month the concentration rose slightly above the 0.75 per cent. prescribed as maximum by the Court.

The outcome of the hearing was the entering of a judgment by agreement and stipulation between the contesting parties whereby the plant is allowed thirty-five days under existing conditions in which to run through the ore on hand, but is then required to close down completely until such time as it can live up to the letter of the original decree, *viz.*, remove *all* solids, never exceed 0.75 per cent. sulphur dioxide and do no damage.

During the time in which the plant still remains in operation experimentation and development is being carried on as vigorously as ever, but it is scarcely expected even under the most favorable conditions that a shut-down can be entirely avoided. During such shut-down, however, the progress of the work at other plants already undertaken thoroughly insures the uninterrupted development of the process in general.

PAPER-MAKERS' CLAYS.

By J. Stewart Remington, Douglas A. Bowack and Percy Davidson.

Received April 17, 1911.

The commerical value of a china clay for use as a loading material depends largely upon the whiteness of the body, and essentially its freedom from grit and sand. For example, should "fillers" be used which contain more gritty matter than is desirable in a china clay, the detrimental effects on the machinery will be quickly noticed, more especially when the wear and tear of the wires is taken into consideration.

The coloration of the clay, which is of the greatest importance, is due partly to organic matter and partly to the various minerals contained in the clay. The latter, especially the compounds containing iron, exercise a great influence on the color of the natural clay, and it is therefore imperative that the fullest use should be made of information gathered from a chemical analysis. The iron exists chiefly in the form of ferric oxide (hydrated), ferrous carbonate (siderite), ferric sulphide (pyrites) and occasionally as ferric silicates. Hence, although the actual figures found for iron on the analysis of any two samples may correspond, it is known that deposits vary so much in their physical and chemical properties that the percentage of iron is not a direct criterion of the value of a china clay for paper-making purposes.

It is not, therefore, sufficient that merely the amount of each constituent of clay be ascertained: information is required as to the various proportions of true kaolin, silt, sand and gritty particles present, and also the state of fineness of the sample. The foregoing is best obtained by mechanical analysis, the principle of which consists in carefully and systematically washing the clay in an apparatus specially devised for the purpose, whereby the lighter "true-clay" substance is readily washed away from the larger and heavier constituents. Moreover, if desirable, the residual matter may be microscopically examined in order to ascertain the exact nature of the different minerals in the clay.

To obtain evidence as to the nature of the various clay deposits in England it is necessary to compare the composition, color and fineness of the best known brands, and with this object in view the following summaries have been prepared from a selection of analyses and reports, made by the authors to the interests of paper manufacturers concerned:

Table and Results of the Practical Investigations.

Analyses: Chemical Constituents.

No. of clay.	Silica. SiO_2.	Alumina. Al_2O_3.	Ferric oxide. Fe_2O_3.	Lime. CaO.	Magnesia MgO.	Total water.	Alkalies. K_2O.	Total.		Order of merit.	Residue, per cent., Standard grit test.	Nos. fineness, etc. Order of merit in:	Suitable uses for:
1	46.21	39.82	0.38	0.45	0.10	12.81	0.23	100.00	B	A	0.09	100	Coating papers
2	46.32	39.76	0.40	0.41	0.11	12.69	0.31	100.00		B	0.07	100	Coating papers
3	47.60	38.26	0.55	0.42	0.20	12.40	0.57	100.00		C	0.32	95	High-grade papers
4	47.74	37.66	0.58	0.61	0.22	12.60	0.59	100.00		D	2.96	75	News
5	45.74	36.84	1.86	0.60	0.11	11.06	3.79	100.00	F	B	0.24	85	High-grade papers and coating papers
6	46.46	37.40	2.00	0.86	0.21	11.81	1.26	100.00		A	2.22	70	News
7	48.16	38.45	2.06	0.50	0.14	10.59	0.10	100.00		D	3.90	65	Cheaper loadings and news
8	46.20	36.23	1.57	0.76	0.11	11.00	4.13	100.00		C	4.10	65	Cheaper loadings and news
9	46.60	37.48	1.26	0.64	0.22	12.74	1.06	100.00	A	C	1.19	90	High-grade papers
10	46.28	38.38	1.03	0.72	0.15	12.87	0.66	100.00		B	1.30	90	High-grade papers
11	46.38	39.00	0.79	0.58	0.11	12.70	0.44	100.00		C	1.00	90	High-grade papers
12	47.26	37.84	1.08	0.54	0.29	12.07	0.82	100.00		D	2.35	75	News
13	46.12	38.80	1.08	0.82	0.15	12.62	0.41	100.00	E	D	1.15	90	High-grade papers
14	46.90	38.53	1.01	0.76	0.11	12.49	0.20	100.00		C	0.61	90	High-grade papers and coating papers
15	46.86	39.24	0.75	0.61	0.15	12.24	0.15	100.00		A	0.77	90	High-grade papers and coating papers
16	46.62	38.98	0.81	0.69	0.10	12.30	0.50	100.00		B	0.98	90	High-grade papers
17	45.92	38.43	0.71	1.18	0.21	12.77	0.78	100.00	D	A	2.28	75	Ordinary white printings
18	44.82	38.69	1.30	0.94	0.20	12.79	1.26	100.00		B	2.10	75	Ordinary white printings
19	46.74	37.87	0.89	0.50	0.24	12.44	1.36	100.00	C	B	0.93	90	High-grade papers
20	46.76	38.06	0.86	0.82	0.20	12.01	1.29	100.00		A	1.12	90	High-grade papers

The results of the investigation of this representative list of clays point to the conclusion that these products are of first-rate commercial value, and com-

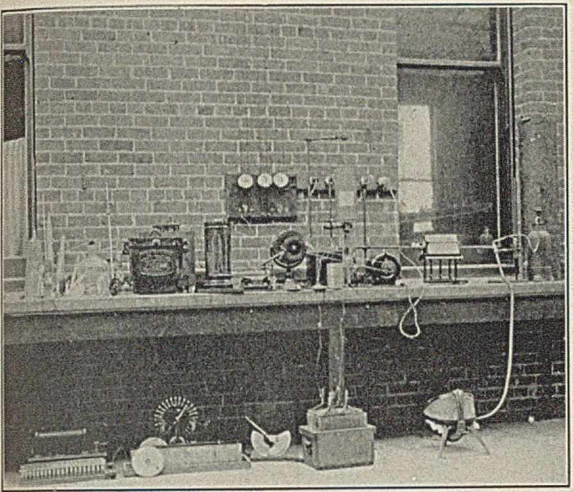


Fig. 1.

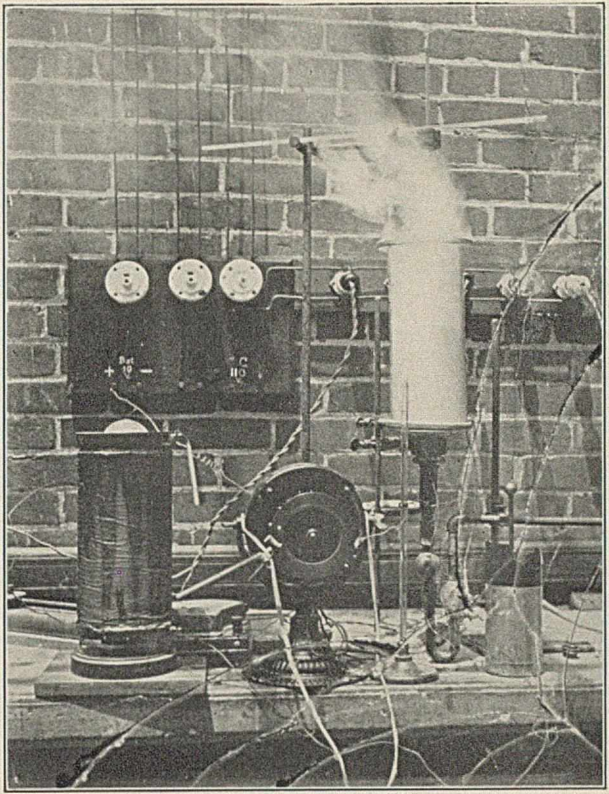


Fig. 2.

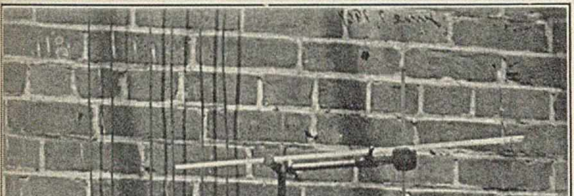


Fig. 3.

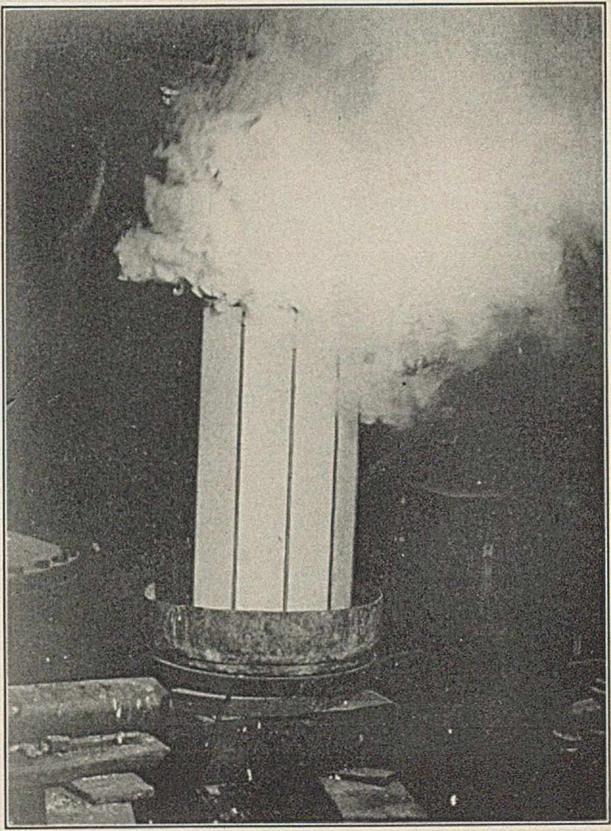


Fig. 4.

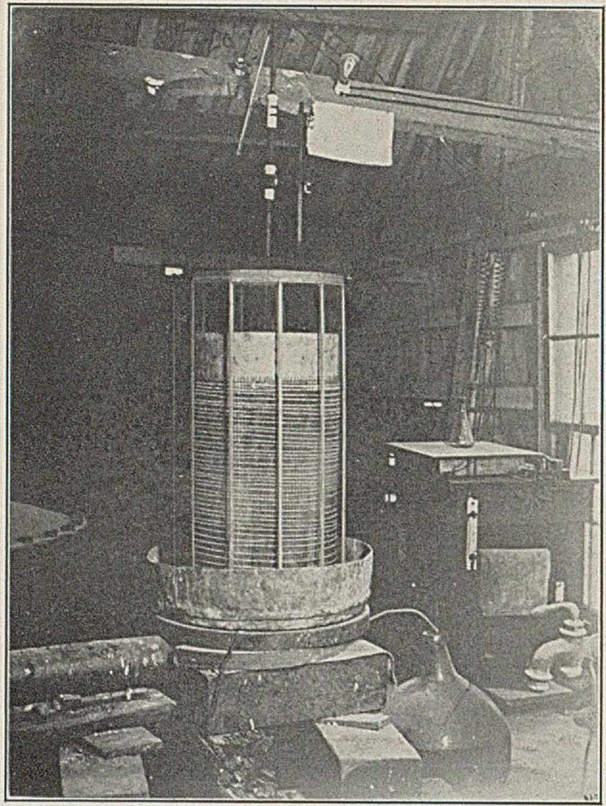
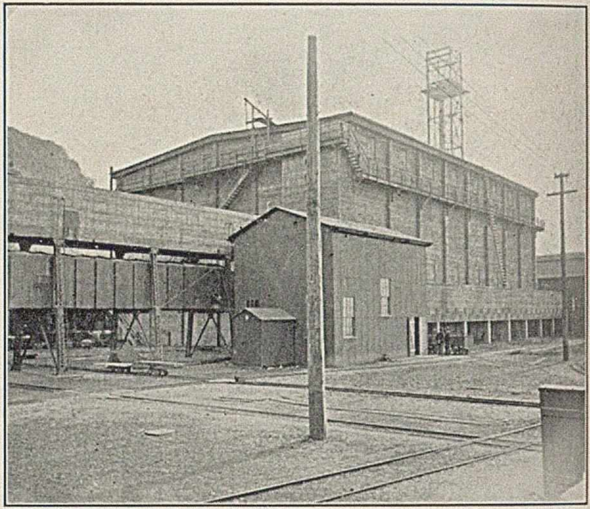


Fig. 5.



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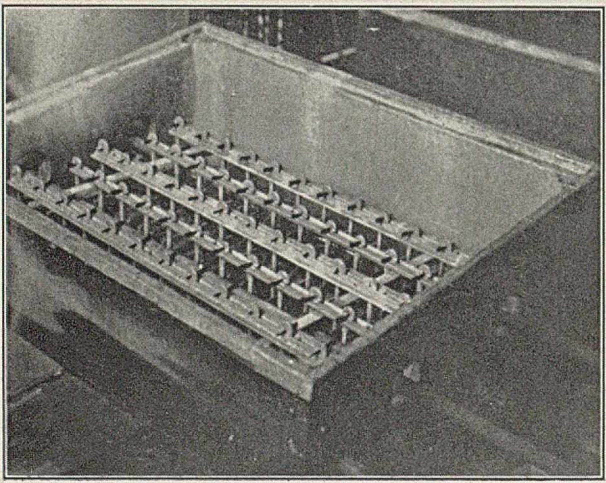

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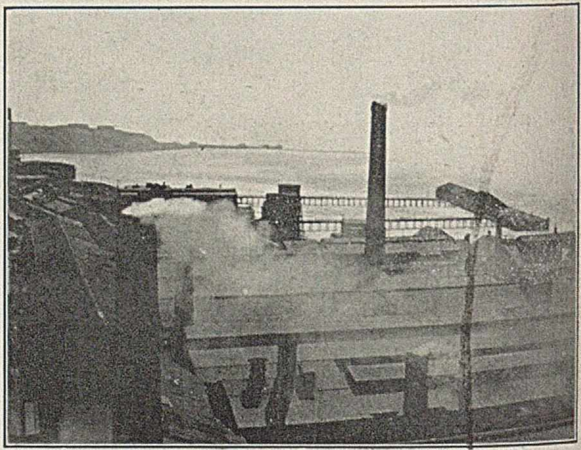

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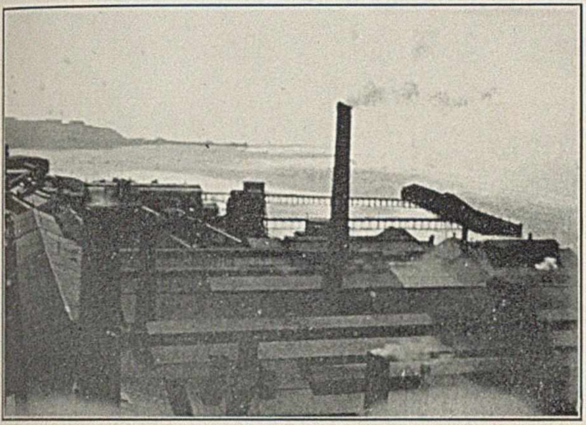

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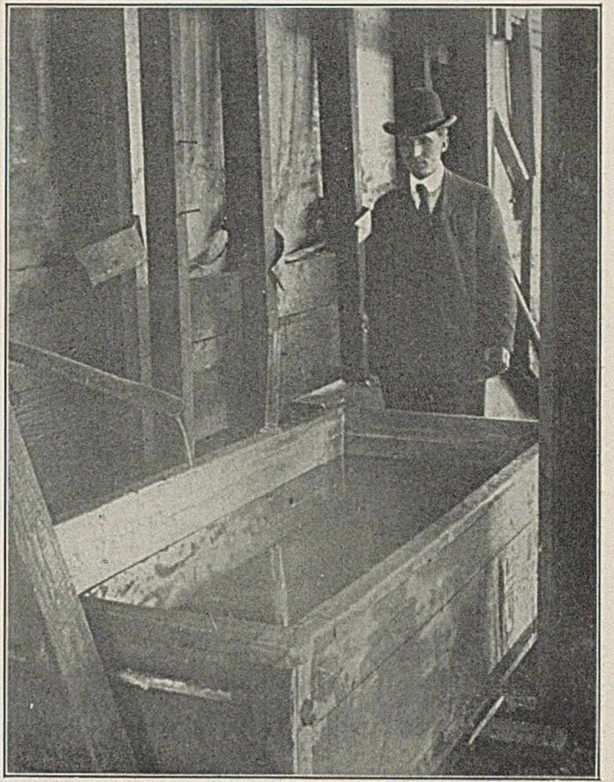

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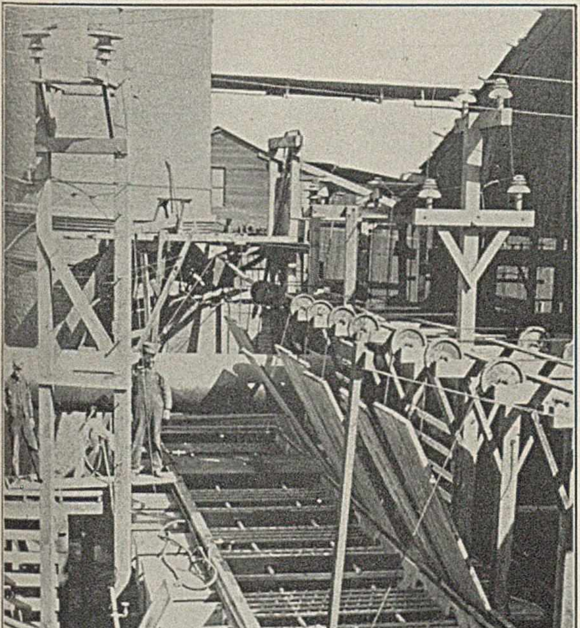

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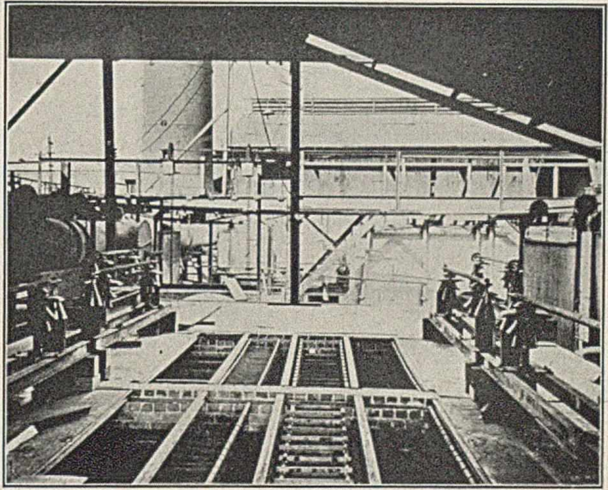

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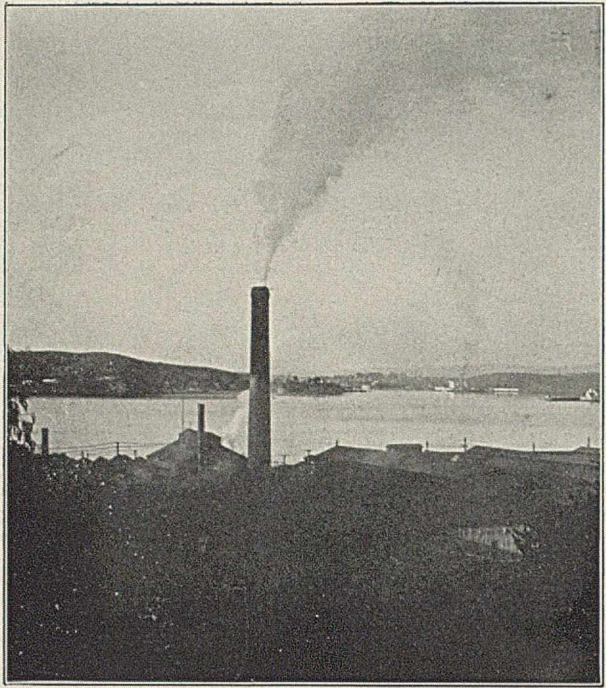

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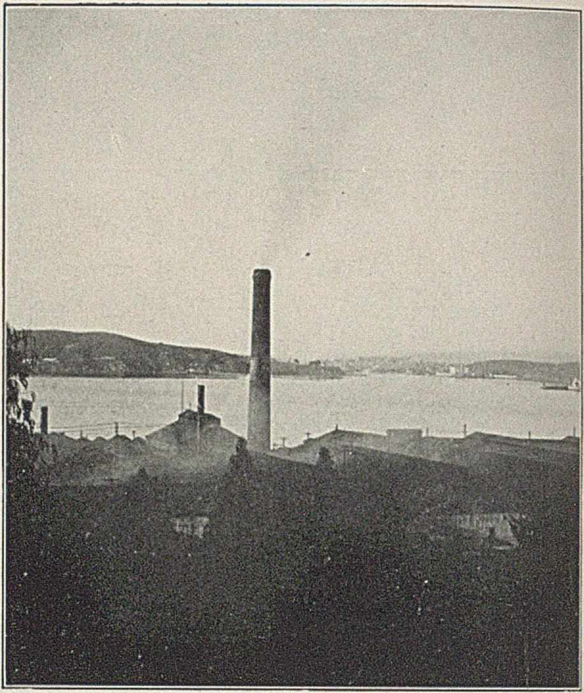

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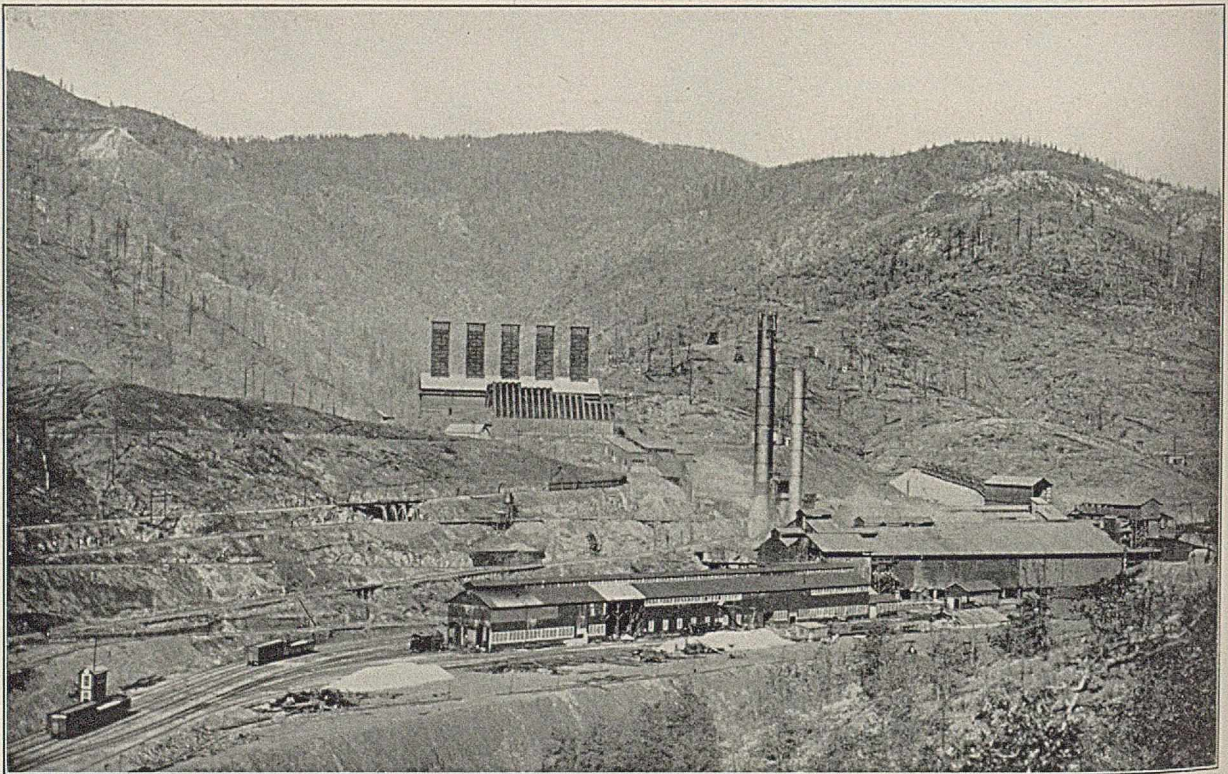

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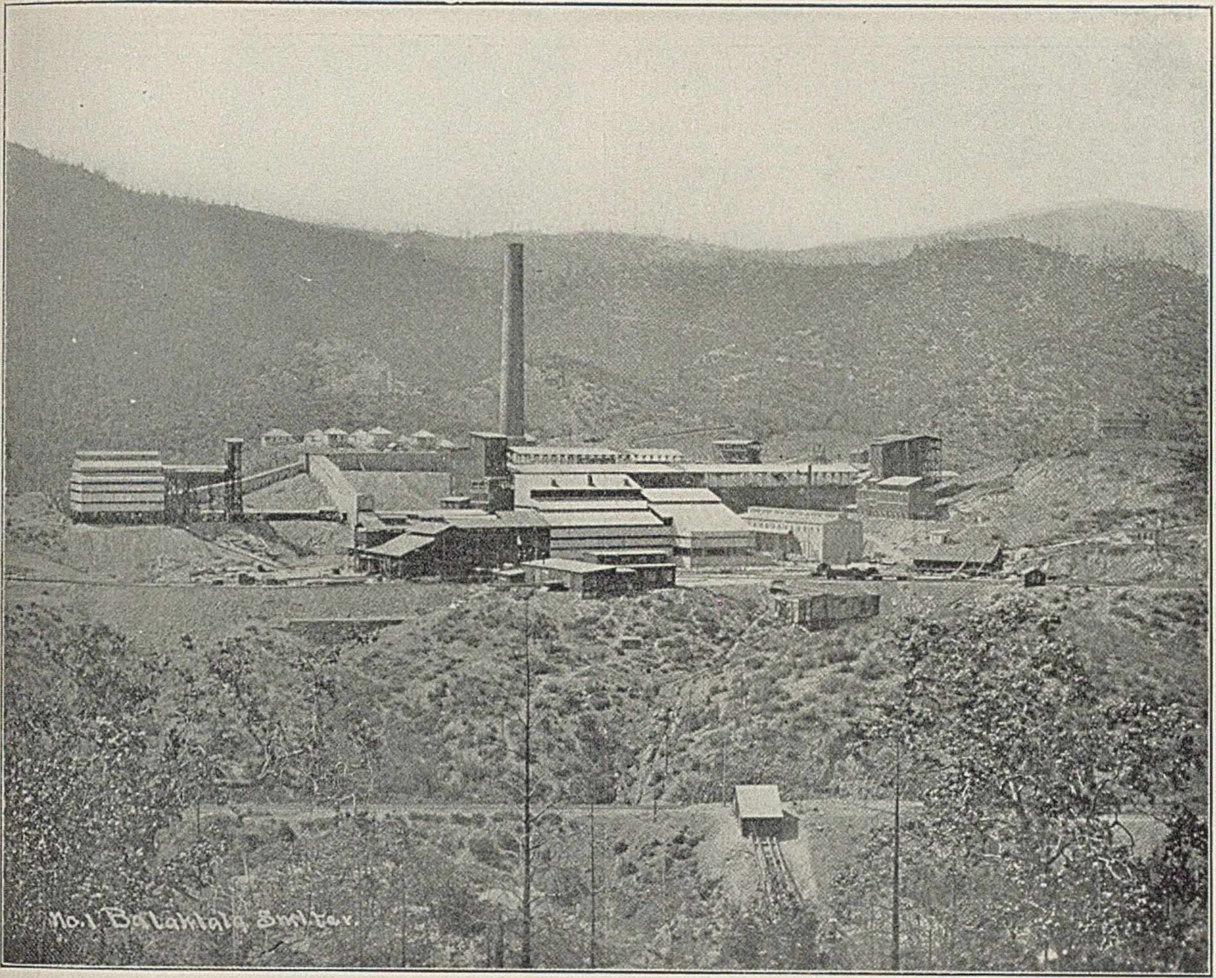

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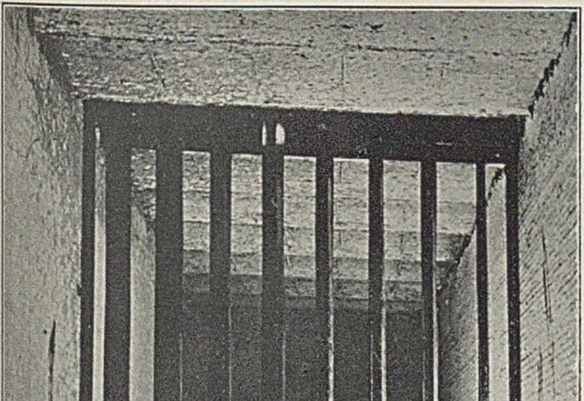

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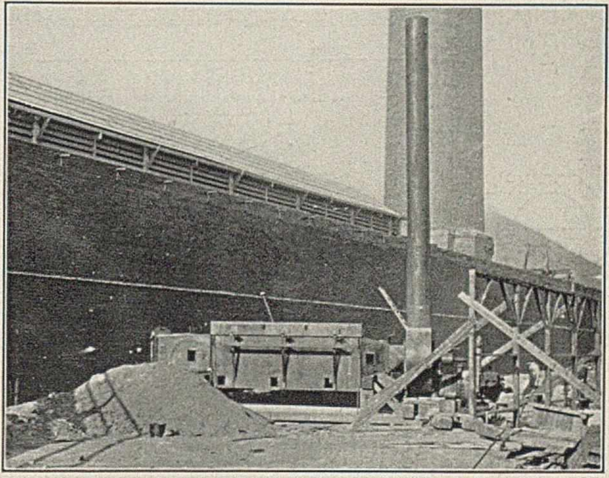

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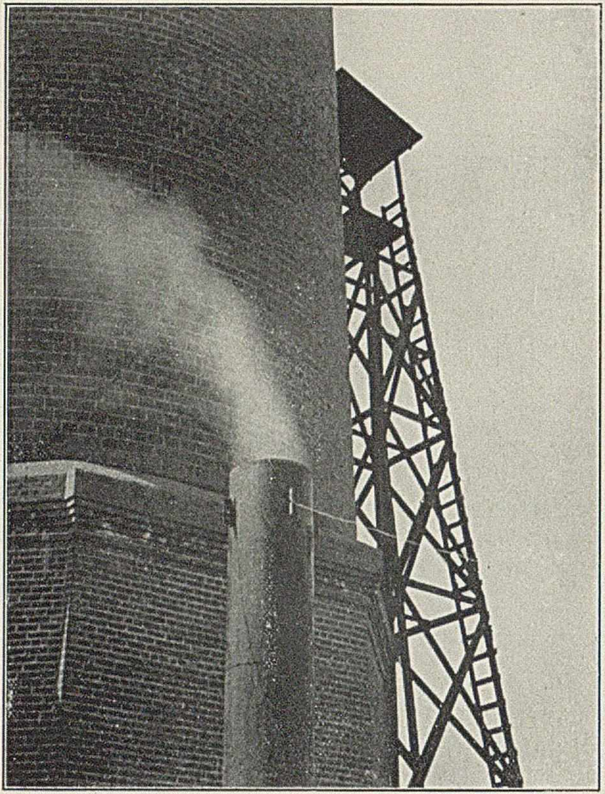

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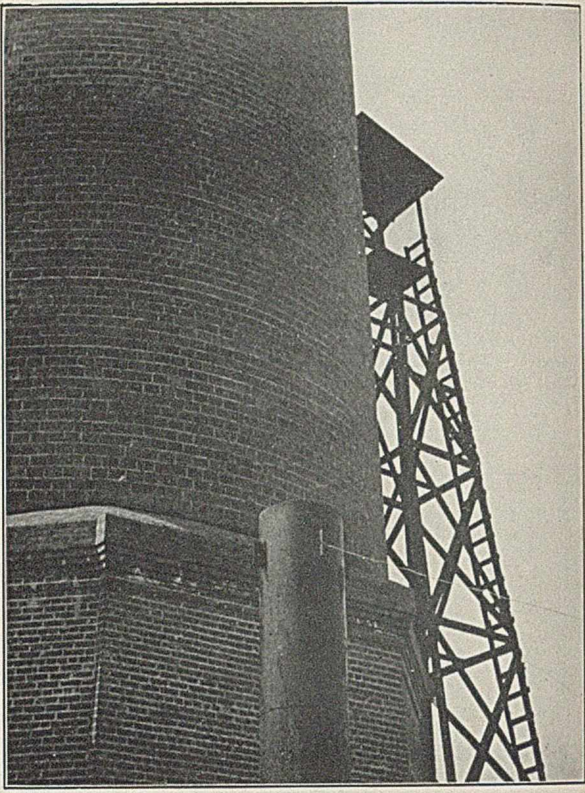
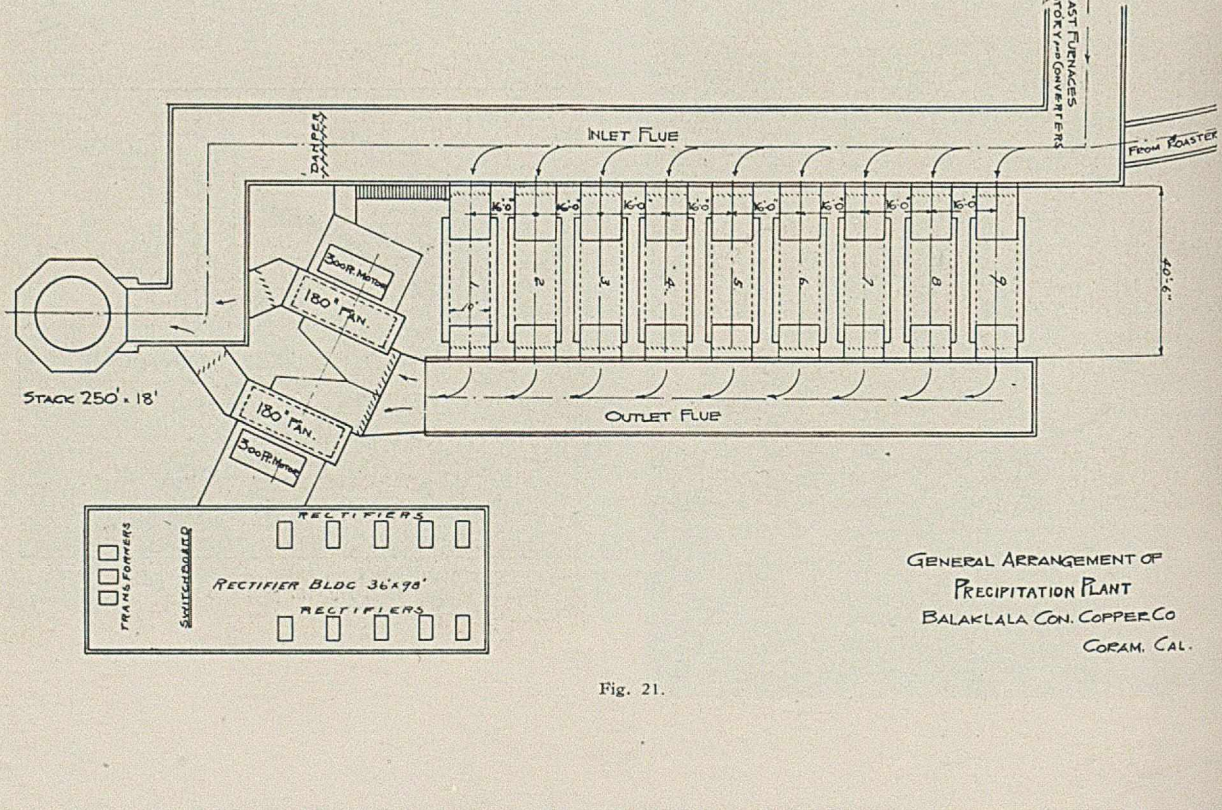


Fig. 20



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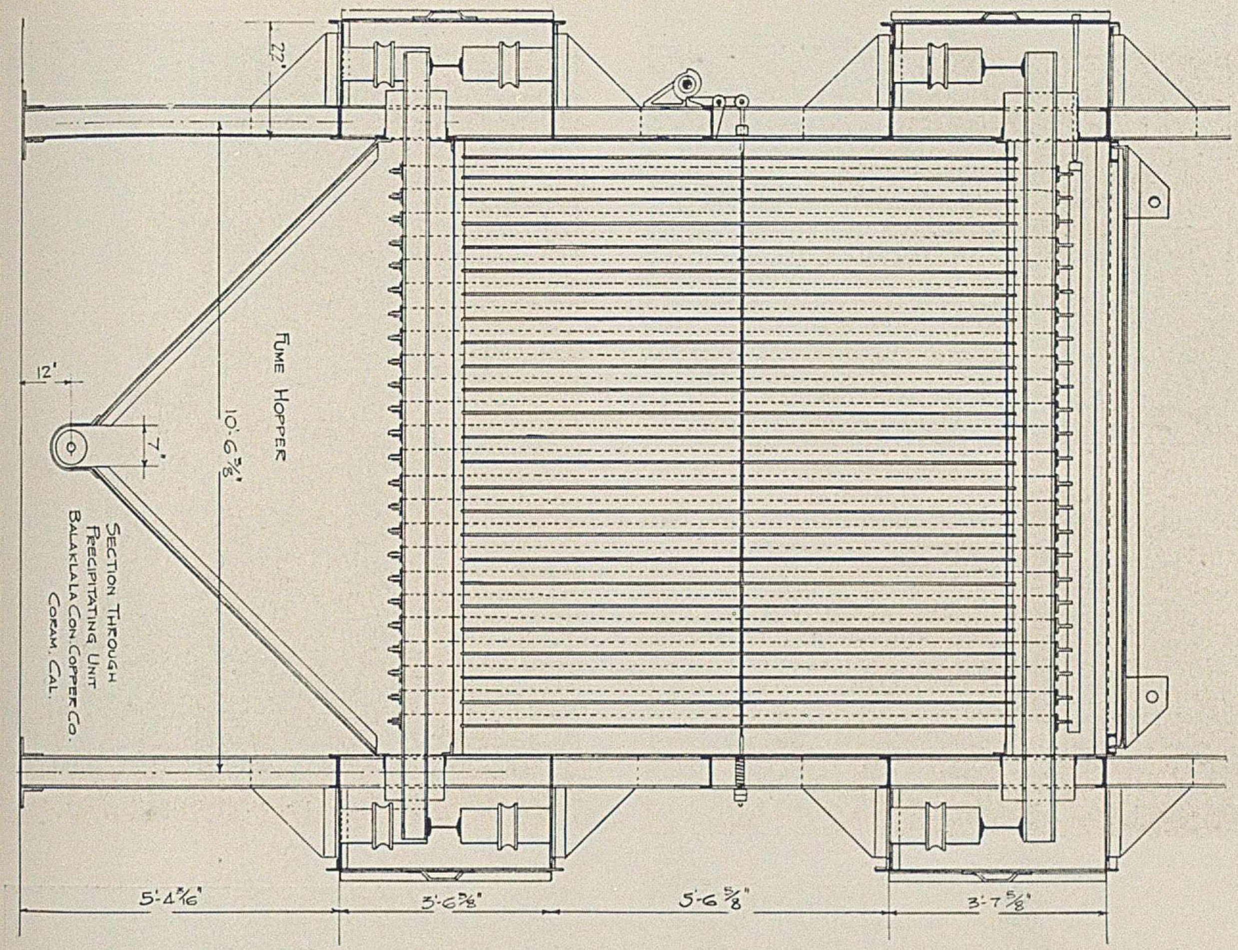

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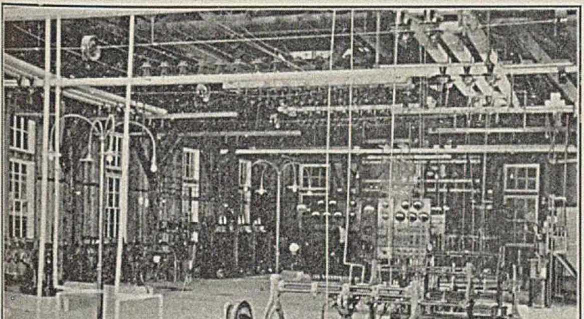

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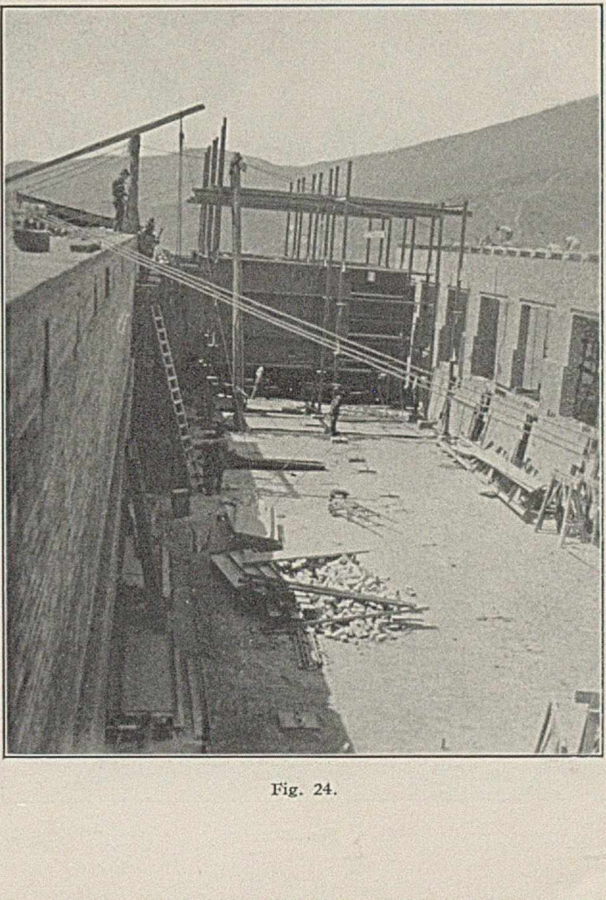

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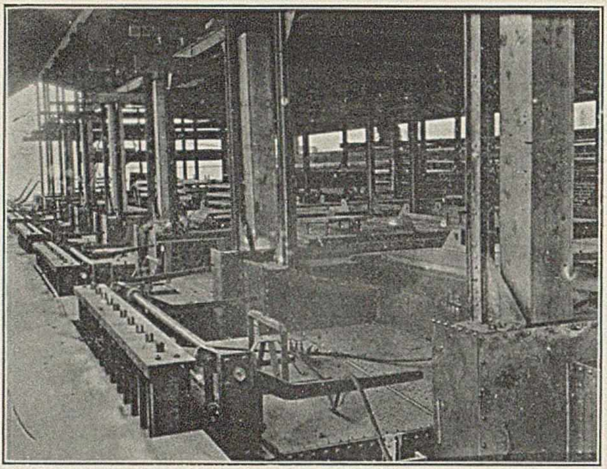

Fig. 25.

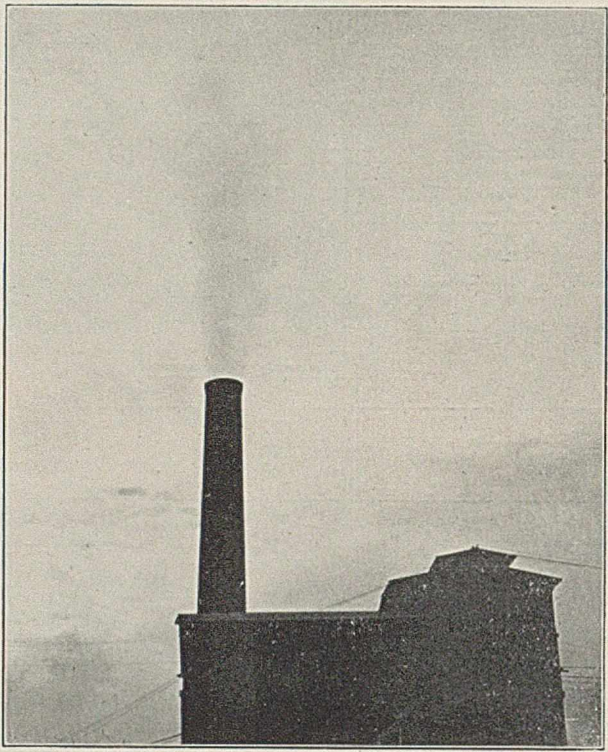

Fig. 27.

Fig. 29.

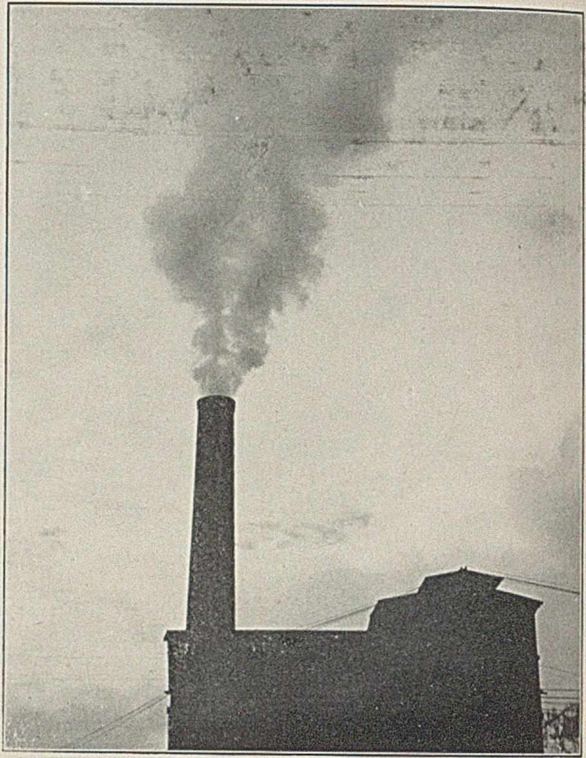

Fig. 26.

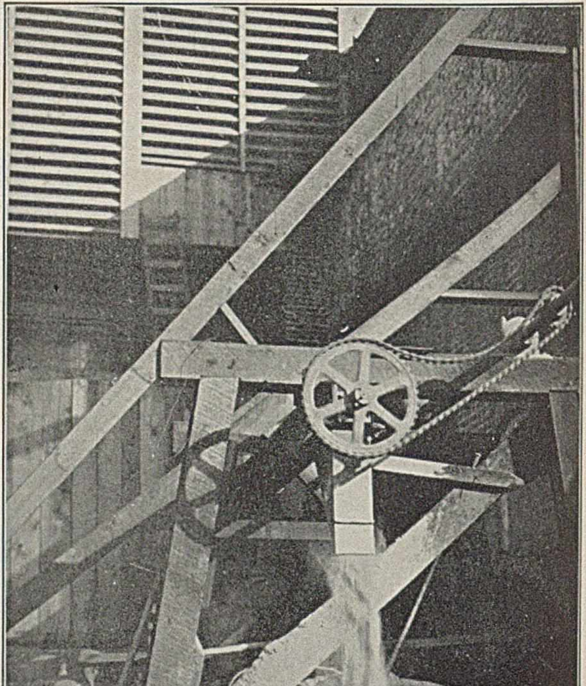

Fig. 28.

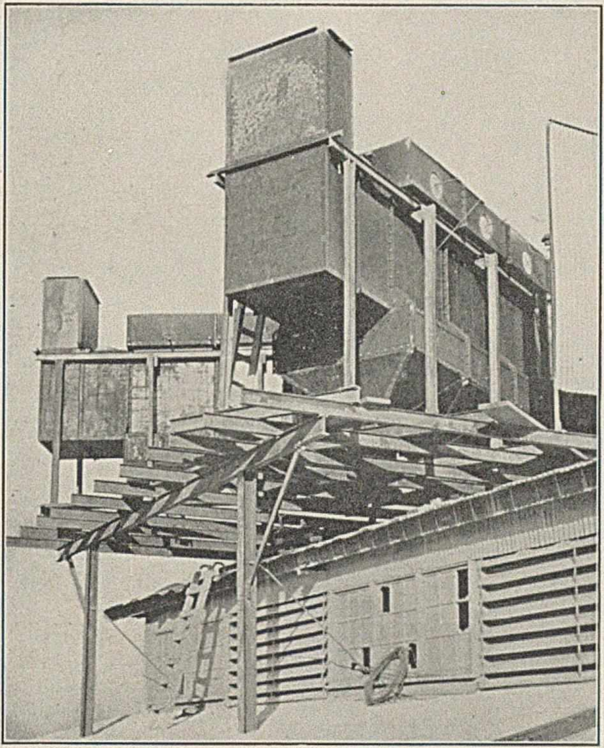

Fig. 30.

pared with corresponding figures furnished by some other good specimens of clays previously examined, the opinion formed is that many of them could hardly be surpassed in purity and quality. An important and interesting fact will be at once noted regarding the relative values of these deposits; *viz.*, with a few exceptions the specimens are remarkably uniform in character and on the whole may be considered as representing a high standard of perfection now reached in the progress of a great industry.

On comparing the figures of the clays marked No. 6 to No. 8, with those yielded by the samples obtained from other deposits, it is evident that there is a great difference in the proportion of iron contained in these minerals. A corresponding difference appears in the general character of the clays, notably when compared with those marked Nos. 1 to 4, and those marked Nos. 9 to 12, which are finer and possess a much better color. The latter variation may be partly owing to a difference in the nature and extent of the surrounding beds, or to some local circumstances affecting the cleaning of the material and the nature of the clay produced. The presence of a comparatively high percentage of alkalies in the clays Nos. 5 and 8 points to the fact that the clay is associated with an unusually large quantity of unaltered feldspar and some micas, while the potash content found on analysis indicates the presence of "muscovite," one of the characteristic minerals of the crystalline rocks, granites, etc. This information leads one to suppose that the clay has been mined near some point of gradation of the true kaolin and the primary bed: a corresponding increase of the constituents of the original rock is noticed, which serves to confirm this impression.

With regard to the question of the properties imparted to papers by the use of different kinds of fillers, one can hardly differentiate between values of the best qualities: at least, when dealing with high-class grades, such as the above mentioned. One might go further, however, and say that more attention should be given by consumers to the question of the state of fineness of the clays acquired for the purpose of loading. For example, clays are not uncommonly found on the market which to all intents and purposes are equal in purity and color to the well-known brands of standard clays, but, on a physical examination, they are proved to contain as much as 8 to 12 per cent. of grit, and sometimes even 18 per cent. Again, the question of difference in price is often very little, the rate being but slightly lower than that demanded for really high-grade material.

It will be readily understood from this digression that the absolute analytical figures, unless interpreted by a skilled chemist, do not accurately gauge the entire value of the clay, because the component parts of the foreign débris, usually associated with clay, bears a close relationship to the ratio of the constituent elements in the true kaolin itself. It behooves buyers, therefore, to attach due importance to the classification which is based on the composition furnished under this system of mechanical separation of the gritty particles.

Aynsome Technical Laboratories,
Lancashire, England.

A SCHEME FOR THE RAPID ANALYSIS OF CEMENT.

By Clarence N. Wiley and W. A. Ernst.

Received June 15, 1911.

Chemists who are engaged in the manufacture or testing of Portland cement have long wished that they could obtain a complete analysis of a cement, the composition of which was in question, without proceeding with the tedious and lengthy method generally employed. This method, in order to be accurate, calls for the solution of the cement in HCl, evaporation to dryness, followed by a short baking in order to render the silicic acid entirely dehydrated and insoluble. This evaporation must be carried out with more or less care, because if the evaporation is made at too great a temperature or in too hasty a manner, and extreme care is not taken, the gelatinous silicic acid, in being freed from its water, will spatter and danger of loss is incurred. The operation requires at best from three to four hours, and if all of the silicic acid is not dehydrated, a loss is bound to occur through silica passing through the filter.

The old method for the separation of iron and alumina, by means of fusion with potassium acid sulphate, is also a source of annoyance to the busy chemist. Fusion must be carefully watched until the liquid stage has been reached, and even then, if the heat is not carefully adjusted, frothing or boiling over is frequent. To make this fusion requires time and attention taken from other, perhaps more important, work. The solution of the cake is again an occasion of delay and the reduction of the iron present, to be properly accomplished, requires several hours and, if the iron is in large quantity, even longer.

The determination for magnesia also consumes much time and it is the general custom to allow the granular crystalline precipitate of magnesium ammonium phosphate to completely subside so that filtration may be speedily accomplished.

A complete analysis of cement, therefore, covers a period of two days' time, although it can be done in the course of one day by careful manipulation. The authors have been searching for some time to find a method whereby accurate results could be obtained in a much shorter time. They had already adopted the schemes for the determination of magnesia and the separation of iron and alumina, which will be described later, but had found no suitable method for the rapid accurate determination of silica.

Some time ago there appeared in *Tonindustrie Zeitung*, **35**, 265, a method described by C. Hentschel, whereby silica can be accurately separated from cement by means of acetic acid and in a very short time. Here, at last, appeared the solution of our problem, and upon the first trial of this method we knew that the operation of cement analysis could be accomplished in a few hours' time.

The method described by Hentschel is as follows:

"One gram of cement is ground to powder in a porcelain dish; a little water and 10 cc. acetic acid are added. The mixture is then heated under constant stirring for about 15–20 minutes, till the cement has settled and no particles are floating around any more. Now more distilled water and as much dilute HNO_3 are added as is necessary to keep the iron and the silicates of aluminum in solution. The mixture is heated again for 5 minutes. It is then filtered off with accompanying decantation of the residue silica, washed in hot water and filtered again. If sufficient care is taken, the filtered silica will always be free from iron and aluminum silicates. After washing the silica is ignited and then weighed. After heating in the water bath, the solution must be treated with HNO_3 and not HCl, as this would prolong the test. The determination can be made within one and one-fourth hours, whereas any of the other methods take at least 3 to 4 hours."

After repeated trials, the authors have decided that there is no difference in the time of operation, whether HNO_3 or HCl be added to the liquid after solution by acetic acid. Also, it has been determined that but 5–6 minutes are required for digestion if 0.5 gram of material is used and the results on the smaller amount are equally accurate.

The entire method for the complete analysis of Portland cement now in use by the writers is as follows: Weigh 0.5 gram of cement into a porcelain casserole, add water and then 10 cc. glacial acetic acid. Stir with a glass rod until all lumps are broken up, then place on the hot plate and digest, stirring from time to time until no particles of cement remain. This requires about 5 minutes, and care should be taken that the contents do not boil over. To this solution add a dilute solution of HCl until the reddish color is dissipated. Filter and wash thoroughly with hot water, ignite the precipitate, blast for a few minutes, cool and weigh. After a little experience this operation can be completed in 30 minutes.

The filtrate from the silica is now made up to 200 cc. in a graduated flask and aliquot portions separated. To the first is added a few drops of HNO_3 and then NH_4OH until the iron and alumina are precipitated as hydrates. Set the solution aside for a few minutes on the hot plate until subsidence takes place, filter, wash, ignite and weigh as oxids. Alumina and iron are separated in the second portion by means of the Zimmermann-Reinhardt method. Heat the solution to boiling, reduce the ferric chlorid by adding, drop by drop, a solution of stannous chlorid[1] until the solution becomes colorless. Cool, make up to 300 cc., and add 25 cc. $MnSO_4$ solution.[2] Stir vigorously, add 10 cc. $HgCl_2$ (saturated solution) and titrate the solution at once with $KMnO_4$.

The filtrate from the first portion is now made up to about 400 cc., the lime precipitated at $Ca_2C_2O_4$, filtered, washed and titrated with $KMnO_4$ in the usual manner.

The filtrate from the lime is boiled down in an evaporating dish to about 200 cc., acidified with HCl and washed into an Erlenmeyer flask. Add sodium ammonium phosphate solution and about 5 cc. NH_4OH and cool in running water, shaking vigorously, until the precipitate begins to form. Then add about 15 cc. of NH_4OH and shake for about 10 minutes. Allow the precipitate to settle for about 5 minutes and filter. Wash with the usual solution, ignite and weigh as $Mg_2P_2O_7$.

While the above procedure has been carried on, another sample has been started for the determination of sulphuric anhydride. In this case take 1 gram of cement, digest with acetic acid as before, and add dilute HCl before filtering. The filtrate is heated to boiling and a few cc. of alcohol are added. $BaSO_4$ is precipitated by means of $BaCl_2$ solution and the beaker stood on the hot plate for one-half hour, at the end of which time all of the $BaSO_4$ will have subsided and filtration can be speedily accomplished.

From a large number of determinations we have found that it requires from 2 to 2.5 hours to make a complete analysis of cement and our results have agreed very closely with those obtained by means of the usual method. These results are sufficiently accurate for control work and the great saving in time makes this short method of much value. In the routine of the cement works laboratory, the daily analysis of the finished cement becomes very monotonous because of the fact that it may be considered "post-mortem" work, by which is meant that the composition of the cement cannot now be altered. Where large clinker storages are in use, the clinker may not be ground for several weeks after it is discharged from the kilns. It is thus seen that analysis of the finished cement is of very little value except for purpose of record and comparison with the physical tests.

Following are given several results of analyses made by both methods:

	Regular.			Acetic acid.		
	(1)	(2)	(3)	(1)	(2)	(3)
SiO_2	21.42	22.74	21.50	21.34	22.94	21.40
Al_2O_3	7.38	7.24	7.66	7.34	6.98	7.76
Fe_2O_3	2.60	2.72	2.84	2.60	2.72	2.84
CaO	62.40	61.46	62.18	62.40	61.85	62.33
MgO	2.41	2.26	2.51	2.52	2.26	2.45
SO_3	1.33	1.45	1.27	1.34	1.45	1.27
Ig. loss	1.54	1.38	1.14	1.54	1.38	1.14

Nos. 1 and 3 were completed in 2.5 hours and in No. 2 the SiO_2, R_2O_3 and CaO results were obtained in 45 minutes after the sample was weighed. We have obtained results of complete analyses which have checked closer than the above, but these are given as they represent the average of our experience. Determinations of SiO_2 completed in 20 minutes check as follows with SiO_2 evaporations:

Regular.			Acetic acid.		
(1)	(2)	(3)	(1)	(2)	(3)
21.54	22.94	21.56	21.50	23.00	21.65

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[1] Stannous chlorid solution: 25 grams stannous chlorid are dissolved in 100 cc. concentrated HCl and diluted with water to 1 liter.

[2] $MnSO_4$ solution: 67 grams crystalline $MnSO_4.4H_2O$ are dissolved in 500–600 cc. water, 138 cc. phosphoric acid (sp. gr. 1.70) and 130 cc. concentrated sulfuric acid (sp. gr. 1.82) are added and the mixture diluted to 1 liter.

Efforts have been made to apply this acetic acid scheme for the decomposition of raw material, shale and clay, and limestone, but so far have not been successful. Evaporation after fusion must be practiced to render the silica insoluble, but it is our hope to find a method whereby this determination may be considerably shortened.

Laboratory of the
Atlantic & Gulf Portland Cement Co.,
Ragland, Ala.

THE DETERMINATION OF SULPHUR IN COAL BY MEANS OF JACKSON'S CANDLE TURBIDIMETER.

By Henry F. Muer.

Received May 5, 1911.

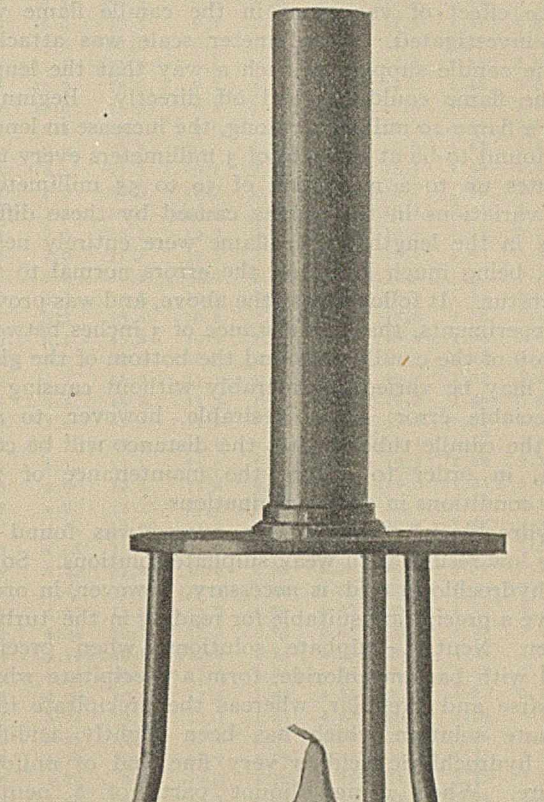
The candle turbidimeter is an apparatus originally devised by D. D. Jackson for the purpose of measuring the turbidity of water, and thereby furnishing a means of comparing different waters in that respect.[1] The simplicity and ease of operation of this apparatus led to its adoption as a standard for that purpose.[2] Further experiments demonstrated the possibility of calibrating the apparatus for measuring the turbidity produced by certain precipitates, such as barium sulphate and calcium oxalate, thus indicating the amount of sulphate, or lime, present in the tested solution. Tables of values were prepared and the apparatus was adopted by the U. S. Geological Survey for use in the field assay of water.[3]

The apparatus comprises a support for a standard candle, in which the candle is kept at a constant height by means of a spring. This is set upright in a base, to which is attached the support for the removable holder of the graduated tube used to measure the depth of the turbid solution necessary to efface the image of the candle flame. Naturally, the more turbid the liquid, the less will be required to efface the image of the flame.

Although the results obtained photometrically cannot be expected to show the same exactness as the gravimetric methods, such an apparatus will, if properly used, give very satisfactory results, and is especially advantageous in routine work when large numbers of samples have to be examined daily and rapidly. Such a case is the determination of "volatile" sulphur in coal. By means of the bomb calorimeter and the candle turbidimeter this may be determined in about ten minutes, whereas by the gravimetric method the result would not be obtained in less than two hours. This apparatus is equally useful in the routine determination of the SO_3 content of cements and boiler waters.

When the writer began the use of the candle turbidimeter in routine coal work it was deemed desirable to make frequent gravimetric check determinations in order to note possible errors. In the course of these control tests it was found that the results obtained with the turbidimeter did not always correspond with the gravimetric results. The differences seemed greater than was desirable, and an investigation was begun in order to learn the cause.

A re-standardization of Jackson's table was first attempted. For this purpose a sodium sulphate solution was prepared and carefully standardized gravimetrically. It was of such a strength that 1 cubic centimeter contained 1 milligram of sulphur, or 4.43 milligrams of sodium sulphate. The flasks and burettes chosen were all in agreement with each other, but when aliquot parts of the sulphate solution were acidified and diluted to 100 cubic centimeters, and tested with the turbidimeter, it was



Jackson's candle turbidimeter.

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[1] *Techn. Quarterly*, **13**, 278 (1900).

[2] Stand. Meth. Water Anal., Am. Pub. Health Assn., 1905.

[3] *U. S. Geol. Sur. W. S. Paper* **151**, 1905.

found that the results did not at all points agree with the original table of sulphur values published by Jackson,[1] and that the results obtained at different times were not consistent. The study was then continued in order to ascertain the reasons for the variations and inconsistencies.

The effect of variations in the candle flame was first investigated. A millimeter scale was attached to the candle support in such a way that the length of the flame could be read off directly. Beginning with a flame 20 millimeters long, the increase in length was found to be at the rate of 3 millimeters every two minutes up to a maximum of 50 to 55 millimeters. The variations in the results caused by these differences in the length of the flame were entirely negligible, being much less than the errors normal to the apparatus. It follows from the above, and was proven by experiments, that the distance of 3 inches between the top of the candle tube and the bottom of the glass tube may be varied considerably without causing an appreciable error. It is desirable, however, to adjust the candle tube so that the distance will be constant, in order to ensure the maintenance of the same conditions in all determinations.

Hydrochloric acid in large excess was found to cause low results with weak sulphate solutions. Some free hydrochloric acid is necessary, however, in order to give a precipitate suitable for reading in the turbidimeter. Neutral sulphate solutions, when precipitated with barium chloride, form a precipitate which is coarse and irregular, whereas the precipitate in a sulphate solution which has been slightly acidified with hydrochloric acid is very fine and of uniform texture. When using aliquot parts of a neutral sulphate solution, the acid should not be added until the portion taken has been diluted nearly to 100 cubic centimeters and well mixed. Failure to observe this precaution was found to be coincident with variable results.

The discrepancies between the turbidimetric and gravimetric results in the case of the coal solutions were at first thought to be caused by the presence of nitrates in the solutions examined. The disturbing effect of these in gravimetric sulphur determinations has frequently been noted.[2] The presence of nitrates in the solutions, in amounts equal to or exceeding the sodium sulphate present, was found to cause slightly high results in the turbidimetric estimation of the sulphur. The error thus caused, however, is too small to be taken into account.

The principal cause of the variations noted was found to be the difference in size and hardness of the barium chloride crystals used for the precipitation of the sulphur. It appears that the texture of the barium sulphate resulting from cold precipitation is very much affected by the rate at which it is formed in the solution, and will be the finer the more slowly it is formed, and *vice versa.* Hence large crystals of barium chloride which dissolve more slowly form a barium sulphate of finer texture, which, when suspended in the liquid, will efface the image of the flame much sooner than a coarser one more rapidly formed. This was actually found to be the case, and the regularity of this effect is well shown by the following table:

TABLE I.—EFFECT OF DIFFERENT SIZES OF BARIUM CHLORIDE CRYSTALS.

Data:

Solution—100 cc. contained 10 mg. sulphur.
Barium chloride used for each test—2 grams.
The size of the barium chloride is that remaining successively on each sieve of the series as numbered.

Size sieve.	Reading. Cm.	Size sieve.	Reading. Cm.	Size sieve.	Reading. Cm.
2	2.1	16	3.5	36	3.8
4	2.2	20	3.5	40	4.3
8	2.4	24	3.5	50	4.5
10	2.6	30	3.7	60	4.5
				100	4.6

The sieves used in sizing the barium chloride for the above tests were the standard sieves used in mechanical analysis of sand, except numbers 2, 4, and 8, which were made from wire screening. Since all of the above tests were made on the same solution, it will be noted that the error due to the difference in the size of the barium chloride is considerable.

It was also found that in the case of the smaller sizes of barium chloride differences in manipulation made rather large differences in the readings. The variations in the results were greater the smaller the barium chloride crystals used. The following is a case in point:

The solution used contained 10 milligrams of sulphur in 100 cc.; the barium chloride used was of sieve size 30. When the solution was placed in a glass-stoppered bottle and shaken after adding the barium chloride, the resulting reading was 3.8 centimeters. But when the solution was placed in a beaker, the barium chloride added, and the mixture poured back and forth into another beaker until the barium chloride was dissolved, the reading was 2.8 centimeters. It is evident, therefore, that in photometric sulphur work it is necessary to adhere strictly to the prescribed procedure.

In view of the above observations many attempts were made to obtain a barium chloride of a standard size which might be duplicated at any time. Although the screening out of any particular size presented no difficulty, the results obtained from different lots of the salt were not as concordant as was desired. Several experiments indicated that this was apparently due to varying hardness and efflorescence of the crystals, whereby the rate of solubility was much affected.

In order to eliminate the errors caused by the varying physical properties of the barium chloride, solutions of the salt were prepared and used in further tests. It was then found that with a concentrated solution of barium chloride the range of the table was materially altered. If a solution contained more than 10 milligrams of sulphur in 100 cubic centimeters, the solution required to be diluted to 200 cubic centimeters in order to obtain a precipitate of sufficiently fine texture to produce a distinct end point. The lower part of the table, however, was

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[1] *J. Am. Chem. Soc.*, **33**, 799.

[2] *Ibid.*, **31**, 55 (1909); **32**, 613 (1910); *Chem. Abs.*, **3**, 1623; THIS JOURNAL, **2**, 199 (1910).

not greatly affected. But the precipitate produced by the solution of barium chloride was in all cases coarser and more irregular in texture than that obtained by means of solid barium chloride.

The addition of a small amount of oxalic acid[1] to the barium chloride solution effected a considerable improvement in the character of the precipitate, rendering it much finer, and made it possible to obtain a direct reading in one operation from a solution containing as low as 1 milligram of sulphur in 100 cubic centimeters. With such a precipitating solution it was found possible, within a limited range, to reproduce given results at any time, provided the method were followed exactly. As in the case of solid barium chloride, differences in the method of manipulation gave different results, but by no means as great as before.

The same was true of variations in the amount of free hydrochloric acid in the sulphate solution. If much more than the prescribed amount of free hydrochloric acid was present, it caused low results, the magnitude of the error depending upon the proportion of the excess of acid to the concentration of the sulphate solution. An excess of oxalic acid, however, caused high results, the extent of which also depended on the excess of acid and the concentration of the sulphate solution. The general effect of the oxalic acid was to contract the table, especially in the lower values.

It was found, however, that a barium chloride-oxalic acid solution of a given formula would not answer for the entire range of the table. A solution which gave good results in the lower values would not do for the higher ones. In fact, it was almost impossible to obtain a good precipitate beyond the 5-milligram point. The precipitate formed by means of a solution of barium chloride was formed so rapidly that it was very coarse, and the effect of the oxalic acid was gradually lessened as the strength of the sulphate solution increased. This was also partly due to the fact that as the oxalic acid content of such a precipitating solution increased, it required increased amounts of free hydrochloric acid to prevent separation of barium oxalate. Beyond a certain point these two acids neutralized one another so far as their effect on the barium sulphate formation was concerned; hence the result was practically the same as when using a simple barium chloride solution.

The best, most regular, and most accurate results were finally obtained by the use of barium chloride in the form of tablets[2] weighing 1 gram each, compressed without the use of a binder. The advantages of using barium chloride in this form are: convenience in handling, and the certainty of having a uniform weight and volume of the precipitant in each test. By this means the variations in results due to the differences in the size and hardness of the barium chloride crystals are practically eliminated. The precipitate produced by means of these tablets is uniform and gives a good end point for all parts of the table. The table obtained by means of these

TABLE II.—TURBIDIMETRIC SULPHUR TABLE.

For use with Jackson's candle turbidimeter.
Sulphur and SO_3 contained in 100 cc. precipitated.

Depth. Cm.	S. Mg.	SO_3. Mg.	Depth. Cm.	S. Mg.	SO_3. Mg.	Depth. Cm.	S. Mg.	SO_3. Mg.
1.0	20.0	50.0	9.1	2.28	5.70	17.1	1.49	3.73
1.1	18.0	45.0	9.2	2.26	5.65	17.2	1.49	3.73
1.2	16.5	41.3	9.3	2.25	5.63	17.3	1.48	3.70
1.3	15.0	37.5	9.4	2.23	5.58	17.4	1.47	3.68
1.4	13.5	33.8	9.5	2.21	5.53	17.5	1.47	3.68
1.5	12.5	31.3	9.6	2.19	5.48	17.6	1.46	3.65
1.6	11.2	28.0	9.7	2.18	5.45	17.7	1.45	3.63
1.7	10.0	25.0	9.8	2.16	5.40	17.8	1.44	3.60
1.8	9.5	23.8	9.9	2.15	5.38	17.9	1.44	3.60
1.9	9.0	22.5	10.0	2.13	5.33	18.0	1.43	3.58
2.0	8.5	21.3	10.1	2.11	5.28	18.1	1.43	3.58
2.1	8.0	20.0	10.2	2.10	5.25	18.2	1.42	3.55
2.2	7.6	19.0	10.3	2.09	5.23	18.3	1.41	3.53
2.3	7.3	18.3	10.4	2.07	5.18	18.4	1.41	3.53
2.4	7.0	17.5	10.5	2.06	5.15	18.5	1.40	3.50
2.5	6.7	16.8	10.6	2.04	5.10	18.6	1.40	3.50
2.6	6.5	16.3	10.7	2.03	5.08	18.7	1.39	3.48
2.7	6.3	15.8	10.8	2.02	5.05	18.8	1.38	3.45
2.8	6.1	15.3	10.9	2.01	5.03	18.9	1.38	3.45
2.9	5.9	14.8	11.0	2.00	5.00	19.0	1.37	3.43
3.0	5.7	14.3	11.1	1.98	4.95	19.1	1.37	3.43
3.1	5.5	13.8	11.2	1.97	4.93	19.2	1.36	3.40
3.2	5.4	13.5	11.3	1.95	4.88	19.3	1.35	3.38
3.3	5.2	13.0	11.4	1.94	4.85	19.4	1.35	3.38
3.4	5.1	12.8	11.5	1.93	4.83	19.5	1.34	3.35
3.5	5.0	12.5	11.6	1.92	4.80	19.6	1.34	3.35
3.6	4.85	12.25	11.7	1.91	4.78	19.7	1.33	3.33
3.7	4.75	12.00	11.8	1.90	4.75	19.8	1.32	3.30
3.8	4.63	11.75	11.9	1.89	4.73	19.9	1.32	3.30
3.9	4.52	11.50	12.0	1.88	4.70	20.0	1.31	3.28
4.0	4.43	11.25	12.1	1.87	4.68	20.1	1.30	3.25
4.1	4.33	11.00	12.2	1.86	4.65	20.2	1.30	3.25
4.2	4.24	10.75	12.3	1.85	4.63	20.3	1.29	3.23
4.3	4.16	10.50	12.4	1.84	4.60	20.4	1.28	3.20
4.4	4.08	10.25	12.5	1.83	4.58	20.5	1.28	3.20
4.5	4.00	10.00	12.6	1.82	4.55	20.6	1.27	3.18
4.6	3.93	9.83	12.7	1.81	4.53	20.7	1.26	3.15
4.7	3.86	9.65	12.8	1.80	4.50	20.8	1.26	3.15
4.8	3.79	9.48	12.9	1.79	4.48	20.9	1.25	3.13
4.9	3.72	9.30	13.0	1.78	4.45	21.0	1.25	3.13
5.0	3.66	9.15	13.1	1.77	4.43	21.1	1.24	3.10
5.1	3.60	9.00	13.2	1.76	4.40	21.2	1.23	3.08
5.2	3.54	8.85	13.3	1.75	4.38	21.3	1.23	3.08
5.3	3.49	8.73	13.4	1.74	4.35	21.4	1.22	3.05
5.4	3.43	8.58	13.5	1.73	4.33	21.5	1.21	3.03
5.5	3.38	8.45	13.6	1.73	4.33	21.6	1.21	3.03
5.6	3.33	8.33	13.7	1.72	4.30	21.7	1.20	3.00
5.7	3.28	8.20	13.8	1.71	4.28	21.8	1.20	3.00
5.8	3.24	8.10	13.9	1.70	4.25	21.9	1.19	2.98
5.9	3.20	8.00	14.0	1.70	4.25	22.0	1.18	2.95
6.0	3.15	7.88	14.1	1.69	4.23	22.1	1.18	2.95
6.1	3.11	7.78	14.2	1.68	4.20	22.2	1.17	2.93
6.2	3.07	7.68	14.3	1.67	4.18	22.3	1.16	2.90
6.3	3.03	7.58	14.4	1.66	4.15	22.4	1.16	2.90
6.4	2.99	7.48	14.5	1.66	4.15	22.5	1.15	2.88
6.5	2.95	7.38	14.6	1.65	4.13	22.6	1.15	2.88
6.6	2.92	7.30	14.7	1.64	4.10	22.7	1.14	2.85
6.7	2.88	7.20	14.8	1.63	4.08	22.8	1.13	2.83
6.8	2.85	7.13	14.9	1.62	4.05	22.9	1.13	2.83
6.9	2.82	7.05	15.0	1.62	4.05	23.0	1.12	2.80
7.0	2.79	6.98	15.1	1.61	4.03	23.1	1.11	2.78
7.1	2.76	6.90	15.2	1.60	4.00	23.2	1.11	2.78
7.2	2.73	6.83	15.3	1.60	4.00	23.3	1.10	2.75
7.3	2.70	6.75	15.4	1.59	3.98	23.4	1.09	2.73
7.4	2.67	6.68	15.5	1.59	3.98	23.5	1.08	2.70
7.5	2.64	6.60	15.6	1.58	3.95	23.6	1.08	2.70
7.6	2.61	6.53	15.7	1.57	3.93	23.7	1.07	2.68
7.7	2.59	6.48	15.8	1.57	3.93	23.8	1.06	2.65
7.8	2.56	6.40	15.9	1.56	3.90	23.9	1.05	2.63
7.9	2.54	6.35	16.0	1.56	3.90	24.0	1.05	2.63
8.0	2.51	6.28	16.1	1.55	3.88	24.1	1.04	2.60
8.1	2.49	6.23	16.2	1.54	3.85	24.2	1.03	2.58
8.2	2.47	6.18	16.3	1.54	3.85	24.3	1.03	2.58
8.3	2.44	6.10	16.4	1.53	3.83	24.4	1.02	2.55
8.4	2.42	6.05	16.5	1.53	3.83	24.5	1.02	2.55
8.5	2.40	6.00	16.6	1.52	3.80	24.6	1.01	2.53
8.6	2.38	5.95	16.7	1.52	3.80	24.7	1.01	2.53
8.7	2.36	5.90	16.8	1.51	3.78	24.8	1.00	2.50
8.8	2.34	5.85	16.9	1.50	3.75	24.9	1.00	2.50
8.9	2.32	5.80	17.0	1.50	3.75	25.0	1.00	2.50
9.0	2.30	5.75						

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[1] THIS JOURNAL, **1**, 690.

[2] These tablets were prepared on order by the Fraser Tablet Co., of Brooklyn, N. Y.

tablets is somewhat different from that originally published by Jackson and is given above.

The method of operation used in the preparation of this table, and which should be used in all determinations by means of this apparatus, is as follows:

The aliquot of the solution to be tested is measured into the turbidimeter tube, diluted to near the 100 cc. mark, shaken, then acidified with 1 cc. of 1:1 hydrochloric acid, made up to the mark, and mixed well by shaking. One of the barium chloride tablets[1] is then dropped in and the tube closed by means of a clean rubber stopper. The tube is then tilted up and down, causing the tablet to roll back and forth through the solution by gravity.

When the precipitation appears to be complete, the remainder of the tablet may be dissolved by rapidly rotating the tube; but violent shaking should be avoided, since it would have a tendency to cause aggregation of the precipitate. The turbid liquid is then transferred to a beaker, the candle lighted, a small quantity of the liquid poured into the glass tube to prevent overheating and cracking, and the tube put in place. More of the liquid is then poured in, allowing it to run down the side of the tube, rapidly at first, until the image of the flame becomes dim, then more slowly, waiting a moment after each addition until the liquid in the tube is quiet, and continuing thus until the *image* of the flame just disappears. The depth of the liquid in centimeters is noted. The mixture is then returned to the beaker, poured back and forth from beaker to tube two or three times, and read again as before.

Having thus obtained empirically a set of readings corresponding to sulphate solutions of graded strength, the relation between these values was made the subject of study. The weights of barium sulphate contained in each volume of liquid obscuring the flame at the determined points were plotted as abscissas against the centimeters depth of the liquid as ordinates, and it was found that between the 2.5 centimeter and the 17.0 centimeter marks these weights formed a practically straight line. Between these two points the amount of barium sulphate required to obscure the flame increases slightly and is directly proportional to the depth of liquid. From this line the following formula was deduced:

$$S = 0.6 + \frac{15.3}{C}$$

where S is the amount of sulphur, in milligrams, and C is the depth in centimeters of the turbid liquid, between 2.5 cm. and 17.0 cm.

Below the 2.5 cm. mark there was a sudden and sharp deviation of the line, showing that the amount of barium sulphate required to hide the flame below this point increased rapidly in *inverse* proportion to the depth, a condition opposite to that previously described. This is probably due to the fact that the bottom of the turbidimeter tube forms a lens, whose focus is probably at or near the 2.5 cm. mark on the tube. This lens effect will also explain why variations in the size of the flame make no appreciable difference in the results, as previously shown, since the image of the flame will always be focused at the 2.5 cm. mark, no matter what its size may be. The readings below the 2.5 cm. mark are also complicated by the fact that the solutions whose readings fall below this point are so strong that they form a dense precipitate which settles rapidly. Above the 17.0 cm. mark the amount of barium sulphate required to hide the flame becomes gradually less. The decrease is, however, very slight for the remainder of the tube.

By means of the above information the values of the Turbidimetric Sulphur Table were all co-ordinated. The accuracy of this table is shown by the conformity of results obtained by precipitating varying amounts of the same solution (see Table III). These results were obtained in routine analysis of coal by the writer, and by Messrs. C. B. Phipps and J. A. Powders, chemists of this laboratory.

TABLE III.—COMPARISON OF TURBIDIMETRIC AND GRAVIMETRIC RESULTS ON VARIOUS COAL SOLUTIONS.

Test No.	Aliquot taken.	Turb. reading. Cm.	Turb. sulphur. Per cent.	Grav. sulphur. Per cent.
1	1/4	10.5	0.82	0.86
2	1/4	5.1	1.44	1.40
3	1/4	1.7	4.00	
	1/10	4.5	4.00	4.03
4	1/4	4.1	1.76	
	1/10	13.2	1.76	1.74
5	1/4	3.4	2.04	
	1/10	11.3	1.95	1.93
6	1/4	3.5	2.00	
	1/10	11.2	1.97	1.95
7	1/4	3.9	1.84	
	1/10	12.5	1.83	1.82
8	1/4	3.9	1.84	
	1/10	12.2	1.86	1.83
9	1/4	3.5	2.00	
	1/10	10.8	2.02	2.01
10	1/4	2.8	2.44	
	1/10	8.5	2.40	2.52[1]
11	1/4	4.1	1.76	
	1/10	13.6	1.73	1.83[1]
12	1/4	2.7	2.52	
	1/10	8.0	2.51	2.59[1]
13	1/4	4.4	1.63	
	1/10	16.0	1.56	1.60

In the Turbidimetric Sulphur Table the figures obtained by readings less than 2.5 centimeters are to be regarded as only approximately correct. In such a case it is preferable to take a smaller proportion, bringing the reading between 2.5 cm. and 17.0 cm.

As a result of this investigation, the procedure in the case of the coal sulphurs has been modified at this laboratory, and is now conducted as follows:

After the combustion in the Mahler bomb the latter is rinsed with serveral portions of distilled water, amounting in all to about 150 cubic centimeters. This is filtered if necessary, and then titrated with $N/10$ sodium carbonate, using methyl orange as

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[1] On standing for some time, some of the tablets become coated with a thin layer of effloresced salt. This should be removed by gently rubbing between the fingers before using the tablet. It is not advisable to keep the tablets in a moist atmosphere to prevent this efflorescence, as they become extremely hard and difficult to dissolve.

[1] Barium sulphate contaminated, apparently with iron.

indicator. The titrated solution is then made up to 200 cc. The amount of acidity found is used as a guide in selecting the aliquot for a sulphur determination. In the case of anthracite coals, the amount taken is one-fourth to one-half; in the case of soft coals from one-fourth to one-tenth of the whole. This portion is measured into the turbidimeter tube, diluted, mixed, and treated as described above. The precipitated solution is read at least twice, and the readings usually check exactly, unless they fall in the upper part of the tube, where they may differ by a centimeter without materially altering the results. In this case readings may be averaged. The amount of sulphur corresponding to the depth of liquid in the tube is found in the table, and multiplied by the proper factor, depending on the aliquot of the original solution taken. The average time required for these tests, including the cleaning of the vessels used, was found by the writer to be 10 minutes per test.

All dilutions must be made before precipitation, for otherwise the results will not be concordant for different dilutions.

PRACTICAL NOTES ON THE CANDLE TURBIDIMETER.

The flame should be protected from drafts, since it is almost impossible to obtain a good end point with a flickering flame. The wick should be kept trimmed so that the flame will be between 30 and 40 millimeters long, in order to prevent the deposition of soot on the bottom of the glass tube.

The glass tube should be kept clean. The barium sulphate adheres to the glass and cannot be rinsed out, but must be removed by means of a brush.

The readings should be taken in diffused daylight. The eye should be held quite near the top of the graduated tube, sighting in such a way that the image of the flame appears in the center of the bottom of the tube.

Since the 100 cc. mark on different tubes varies from 16.6 to 17.6 cm., if the sulphate solution contains less than 1.5 milligrams of sulphur in 100 cc., more than 100 cc. must be taken for the test in order to obtain enough of the turbid liquid to efface the image of the flame. The procedure is just the same as when 100 cc. or less are used, but the sulphur value found in the table is the amount contained in 100 cc. of the solution.

SUMMARY.

This investigation was made in order to determine the causes of observed variations between the gravimetric results of sulphate determinations and those obtained by means of Jackson's candle turbidimeter. It was found:

1. That variations in the size of the flame or of the distance between the top of the candle tube and the bottom of the glass tube made no appreciable difference in the results.

2. Nitrates in the solution, in quantities such as are found in coal analyses, do not affect the results.

3. A large excess of free hydrochloric acid tends to give low results in weak sulphate solutions. Aliquots of neutral solutions should not be acidified until they are diluted nearly to 100 cc., since addition of all the acid to the undiluted portion was found to be followed by variable results.

4. The chief cause of the difference above referred to was found to be difference in the size and hardness of the barium chloride crystals used. The remedy found to be effective was the use of barium chloride in tablet form, whereby the weight and volume of the precipitant, as well as the texture of the precipitate, is rendered uniform in all tests.

5. By using the candle turbidimeter according to the method recommended in this paper, uniform and sufficiently accurate results may be obtained, and the method has been found very useful for making daily routine tests in large numbers. This applies to the determination of sulphur in coal, cement, and boiler waters. The sulphate in the latter may be determined without concentration if present in quantity of more than 37 parts per million of SO_3. For amounts less than this the water must be concentrated by evaporation.

Department of Water Supply,
Mt. Prospect Laboratory,
Borough of Brooklyn,
City of New York.

THE ACCURATE TECHNICAL ESTIMATION OF THE CALORIFIC VALUE OF ANTHRACITE COAL.

By A. G. Blakeley and E. M. Chance.

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Though much has been published upon the subject of fuel calorimetry in general, it is nevertheless true that but little has been written upon that phase of this subject dealing with anthracite coals. Moreover, the value of that which has been published is in a large measure discounted because the coals examined were not an example of the usual merchant sizes. Thus in the paper published by Parr and Wheeler[1] the two anthracites described contained but 11 per cent. and 13 per cent. of ash respectively. Palmenburg, on the other hand,[2] has published the results of an examination of a series of much more representative coals, which range from 9 to 27 per cent. ash, and which may be considered as covering practically the whole range of the merchant coals. It is frequently stated in the literature of this subject, that with high ash anthracites it is necessary to apply a correction for unburned carbon. Under the conditions which usually obtain, this statement is undoubtedly true, and while we may know that an error is ever present, the methods suggested for its correction are of but doubtful value. Such methods include the weighing by difference of the unburned carbon[3] and the mixing of the coal to be burned with a smaller quantity of a substance of relatively high calorific value.

This second well-known method[4] has recently been brought forward by Palmenburg as an original solution of this troublesome question. While this method will

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[1] This Journal, **1**, 573.

[2] *Ibid.*, **2**, 404.

[3] Parr and Wheeler.

[4] "Engineering Chemistry," T. B. Stillman, 4th Ed., 1910, pp. 131 and 139; "Fuel, Water and Gas Analysis," J. B. C. Kershaw, 1907, p. 49; "The Calorific Power of Fuels," H. Poole, 2nd Ed., 1907, p. 68.

doubtless give accurate and concordant results, it is only with the greatest care and skill on the part of the operator that such a desirable issue can be expected. The writers have found that with this method the bituminous coal underlying the anthracite is rapidly raised to a high temperature, and that the large volume of gases thus produced are likely to project small particles of the anthracite out of the nickel capsule and thus permit them to escape combustion. Thus, after a combustion it is no uncommon thing to find small particles of unburned coal lying upon the floor of the bomb. Another source of error worthy of attention is that a greater error is incurred in weighing a small quantity of a coal of high heating value than in weighing a large quantity of coal of low heating value, and that this whole error in weighing is calculated as error in the heating value of the anthracite. Thus the errors in weighing and sampling in both the anthracite and its kindler are concentrated as error in the heating value of the anthracite itself. Moreover, this error is multiplied 1¹/₄ times as 0.8 gram of the anthracite is taken instead of 1 gram. Of course it is understood that these errors are generally small, but the writers hope to show that they are entirely avoidable.

A few determinations by the method of the addition of a kindler are appended compared with determinations by our routine method.

TABLE A.

Number.	Per cent. Soft coal.	B. T. U.	Asbestos method. B. T. U.
C-2241	30.31	10440[1]	.....
"	31.02	10690[1]	10740
"	32.68	10720[1]	10770
C-3022	31.37	9860[1]	10010
"	30.20	9920[1]	10040
C-2300[2]	.....	....	14800
"	.....	....	14850

A total of approximately 1 gram of the anthracite and kindler was used for each determination.

When first the Atwater calorimeter was applied to the determination of the calorific value of anthracites in this laboratory, the usual difficulties were encountered. Upon observation it was noted that while the upper or exposed surface of a high ash anthracite might be completely burned to ash, the lower stratum, or that part in immediate contact with the nickel capsule, would, in the vast majority of cases, be completely unconsumed. Thus it would seem that the real cause of the incomplete combustion was the chilling of the coal by the rapid conduction of heat through the nickel capsule and heavy platinum wire. The thermal insulation of the coal from the nickel capsule was then tried, with most satisfactory results. This insulation was brought about by lightly tamping into the bottom of the capsule a layer, about 3 mm. thick, of soft, previously ignited, asbestos. By this slight modification we have been enabled to burn completely and without difficulty coals containing as much as 40 per cent. of ash. The coal burns completely, leaving the ash either as a porous mass or a small vitreous globule. In either case the residue is free from unburned carbon as is proved by its failure to lose weight when dried and then ignited.

Briefly the procedure is as follows:

A nickel capsule, 15 mm. in height by 25 mm. in width, is chosen, and a fair-sized pinch of soft, thoroughly ignited, asbestos is placed in it. This asbestos is then lightly tamped in place with some blunt instrument such as the butt end of a fountain pen. This mat of asbestos may be readily formed with the pen so as to present a concave depression with the center, perhaps 2 mm. lower than the edges. The mat at its thinnest point, its center, should be not less than 2 mm. thick. The coal, which should at least pass a screen of 80 meshes to the linear inch, after weighing in counterpoised scoop or bottle is then poured into the capsule, which is placed in the bomb, and the usual routine of combustion pursued, except that a pressure of oxygen of 25 atmospheres is used.

It will be seen at once how slight is this divergence from the usual routine. The increased accuracy to be gained is not so obvious. To test the accuracy of the determinations by this method we calculated from the determined calorific value of the coal the heating value per pound "unit coal," by the formula of Parr and Wheeler.[1]

This scheme has been found admirably adapted to such a purpose, for though the heating value per pound unit coal of anthracites from different localities may vary widely that from the product of the same breaker will adhere more closely to a mean, an exception being the occasional intermixture of badly weathered coals with the usual freshly mined material. A few of these results may not be out of place as illustrative of these statements. It should be noted that these results are taken from the daily routine and are in no case the result of work performed with a view to future publication.

When reviewing such a table as the following the fact should be borne in mind that the formula by which the values were obtained is but an approximation having no absolute accuracy and that the errors

TABLE B.

Test No.	Colliery and information.	Per cent. moisture.	Per cent. volatile matter.	Per cent fixed carbon.	Per cent. ash.	Per cent. sulfur.	Heating value per lb. dry coal in B. T. U.	Heating value per lb. unit coal in B. T. U. (Parr and Wheeler).
C 2521[2]	Gilberton boiler tests.	7.64	5.44	68.98	17.94	0.81	11950	15160
2508[2]		9.96	3.34	60.37	26.33	0.83	10400	15320
2365[2]		9.87	3.52	62.05	24.56	0.69	10760	15280
3040[2]	Hammond boiler tests.	6.61	4.79	62.94	25.66	0.78	10640	15170
3039[2]		7.78	4.32	64.23	23.67	0.71	11010	15270
1760[2]		5.21	5.23	68.26	21.30	0.45	11400	15070
1759[2]		5.99	5.28	65.73	23.00	0.54	11260	15190
2099[2]	Wadesville.	9.27	5.38	71.21	14.14	0.65	12390	14920
2153[2]		10.49	4.94	66.11	18.46	0.65	11600	14950
1291[2]	Boston Run tests.	4.61	4.41	60.29	30.69	0.80	9720	14940
1220[2]		9.20	2.94	58.00	29.86	1.26	9510	14830

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[1] Poor burn.

[2] Soft coal used as kindler.

[1] *Bull.* 37, University of Illinois, Engineering Experiment Station.

[2] As these coals were fired wet, the samples were preserved in airtight containers, the moisture being determined prior to grinding.

TABLE B (*Continued*).—VEIN SAMPLES.

Test No.	Lift.	Per cent. moisture.	Per cent. volatile matter.	Per cent. fixed carbon.	Per cent. ash.	Per cent. sulfur.	Heating value per lb. dry coal in B. T. U.	Heating value per lb. unit coal in B. T. U. (Parr and Wheeler).
C 2381	E 5th	2.82	5.85	87.88	3.45	0.56	15100	15680
2382	6th	2.06	6.92	85.20	5.82	0.59	14530	15550
2388	W 8th	1.39	7.27	83.06	8.28	0.59	14040	15410
2637	W 5th	2.50	6.47	73.27	17.76	0.52	12570	15670
2638	E 5th	2.06	7.46	78.88	11.60	0.52	13620	15630
2639	W 4th	2.80	6.93	74.06	16.21	0.34	12880	15720
2640	W 6th	2.45	6.44	80.95	10.16	0.50	13860	15630
2641	W 3rd	1.94	7.85	50.17	40.04	0.35	8650	15490
2642	W 1st	1.81	7.35	69.37	21.47	0.40	11960	15670

TABLE B (*Continued*).

Test No.	Size of coal.	Per cent. moisture.	Per cent volatile matter.	Per cent. fixed carbon.	Per cent. ash.	Per cent. sulfur.	Heating value per lb. dry coal in B. T. U.	Heating value per lb. unit coal in B. T. U. (Parr and Wheeler).
C 2572	Stove........	1.70	6.45	79.33	12.52	0.57	13410	15560
C 2573	Chestnut	2.10	6.38	76.14	15.38	0.54	12830	15470
C 2574	Pea.........	2.51	7.20	71.14	19.15	0.56	12230	15540
C 2575	Buckwheat .	1.39	6.45	73.86	18.30	0.58	12490	15640
C 2576	Rice.........	2.13	6.69	71.40	19.78	0.57	12290	15750
C 2577	Barley.......	2.44	6.90	69.80	20.86	0.50	12120	15780
C 2776	Broken......	2.95	5.57	80.75	10.73	0.55	13660	15530
C 2777	Flat jig stove	2.66	6.40	74.27	16.67	0.56	12670	15570
C 2778	Stove........	2.65	6.12	78.35	12.88	0.53	13290	15520
C 2779	Chestnut ...	3.04	5.84	77.67	13.45	0.56	13250	15640
C 2780	Pea.........	2.92	6.42	72.60	18.06	0.54	12440	15590
C 2781	Buckwheat .	2.89	6.64	72.60	17.87	0.54	12490	15610
C 2782	Rice.........	2.92	5.92	74.52	16.64	0.52	12690	15600
C 2783	Barley.......	2.68	6.46	74.59	16.27	0.55	12750	15580
2792	Stove........	2.25	8.09	78.73	10.93	0.54	13760	15670
2793	Chestnut....	2.12	6.78	78.18	12.92	0.51	13350	15590
2794	Pea.........	1.86	6.67	71.66	19.81	0.50	12230	15670
2795	Buckwheat	0.66	6.25	75.58	17.51	0.46	12640	15630
2796	Rice.........	1.96	7.07	71.30	19.67	0.49	12160	15550
2797	Barley.......	2.28	6.77	75.21	15.74	0.47	12810	15530

of the proximate analysis as well as those of the actual calorimetric determination are reflected in the heating value per pound unit coal.

For the sake of comparison the values published by Palmenburg (*Loc. cit.*, p. 406) have been calculated to heating values per pound unit coal, by the formula of Parr and Wheeler. The values published have been assumed to have been determined on, or calculated to, the dry coal.

TABLE C.

No.	Per cent. Ash.	Heating value per lb. unit coal (Parr and Wheeler).	Determination from which taken.
328	26.58	14790	second
330	20.19	14970	first
330	20.19	15080	second
330	20.19	15030	mean
333	14.36	14790	mean
438	14.29	14840	mean
440	25.20	14990	mean
442	20.26	14890	mean
444	23.62	14900	mean
462	15.22	15010	mean
399	21.23	14880	mean
400	21.67	14940	mean
494	8.99	15130	mean

It may be well to note that the above results were obtained with the Atwater calorimeter, the water equivalent of which was determined by burning samples of naphthalene and hippuric acid as recommended by Atwater in his original article.[1]

Although having no direct bearing on the method, it may be of interest to state here that this particular Atwater calorimeter has been slightly modified by us for convenience in manipulation. The screw cap socketed for a spanner on the original apparatus, has been replaced by a screw cap bearing a hexagon head. Thus by substituting a box wrench for the original spanner, the annoying tendency to slip has been removed. The stirring motor together with an upright some 42 cm. high have been mounted upon a piece of oak board, free to move upon the calorimeter table. This upright supports a walking beam, one end of which is connected by a driving rod direct to the crank of the motor, while the other end of the beam may be thrust into the ring of the stirrer, thus giving the stirrer a positive movement much to be preferred to the more or less uncertain motion imparted to it by the usual string and pulley device.

LABORATORY OF THE PHILADELPHIA & READING
COAL AND IRON COMPANY, POTTSVILLE, PA.

PREPARATION OF NEUTRAL AMMONIUM CITRATE SOLUTIONS BY THE CONDUCTIVITY METHOD.

By ROBERT A. HALL.

Received May 8, 1911.

In their investigations of the proportions of aqueous solutions containing ammonia and citric acid,[2] Hall and Bell found that the neutral point of the solution could be detected by conductivity measurements, and this suggested the application of the conductivity method as a possible means of preparing the neutral ammonium citrate solution required in fertilizer analysis for the determination of the citrate-insoluble phosphoric acid in a fertilizer. In order to ascertain the possibility of readily and easily preparing neutral ammonium citrate by the application of the conductivity method the following experiments were made by the author of this article.

A citric acid solution was prepared of such a citrate content that when neutralized by ammonia its specific gravity would be greater than 1.09 at 20°; that is, 370 grams of pure citric acid[3] were dissolved in ammonium hydroxide of 0.90 sp. gr. and water, until the solution was near the point of neutrality, yet leaving the solution acid to litmus paper. Care was taken that the volume was not over one liter. The solution was allowed to stand over night to cool. It was again tested with litmus paper to see that it was distinctly acid. Also, small portions, one to two cc., were withdrawn with pipettes and roughly titrated with a diluted ammonia solution in order to ascertain the approximate amounts of ammonia solution necessary to make the citrate solution distinctly alkaline to litmus. The diluted ammonia solution used was prepared by taking the concentrated am-

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[1] *J. Am. Chem. Soc.*, **25**, 659.

[2] *Ibid.*, **33**, 711.

[3] Method of Analysis; *Bull.* **107**, Bureau of Chemistry, p. 1.

monium hydroxide, sp. gr. 0.90, and diluting exactly ten times, that is, 100 cc. were diluted to one liter. A sufficient amount of this solution was prepared to have enough for the making of the solution for the conductivity measurements and also for addition to the larger bulk of the acid ammonium citrate solution, of the calculated amount, as shown by the conductivity measurements, for complete neutrality. 100-cc. lots of the nearly neutralized ammonium citrate solution were withdrawn with pipettes and put in 200 cc. volumetric flasks. Definite amounts of the diluted ammonia solution were measured into these differ-

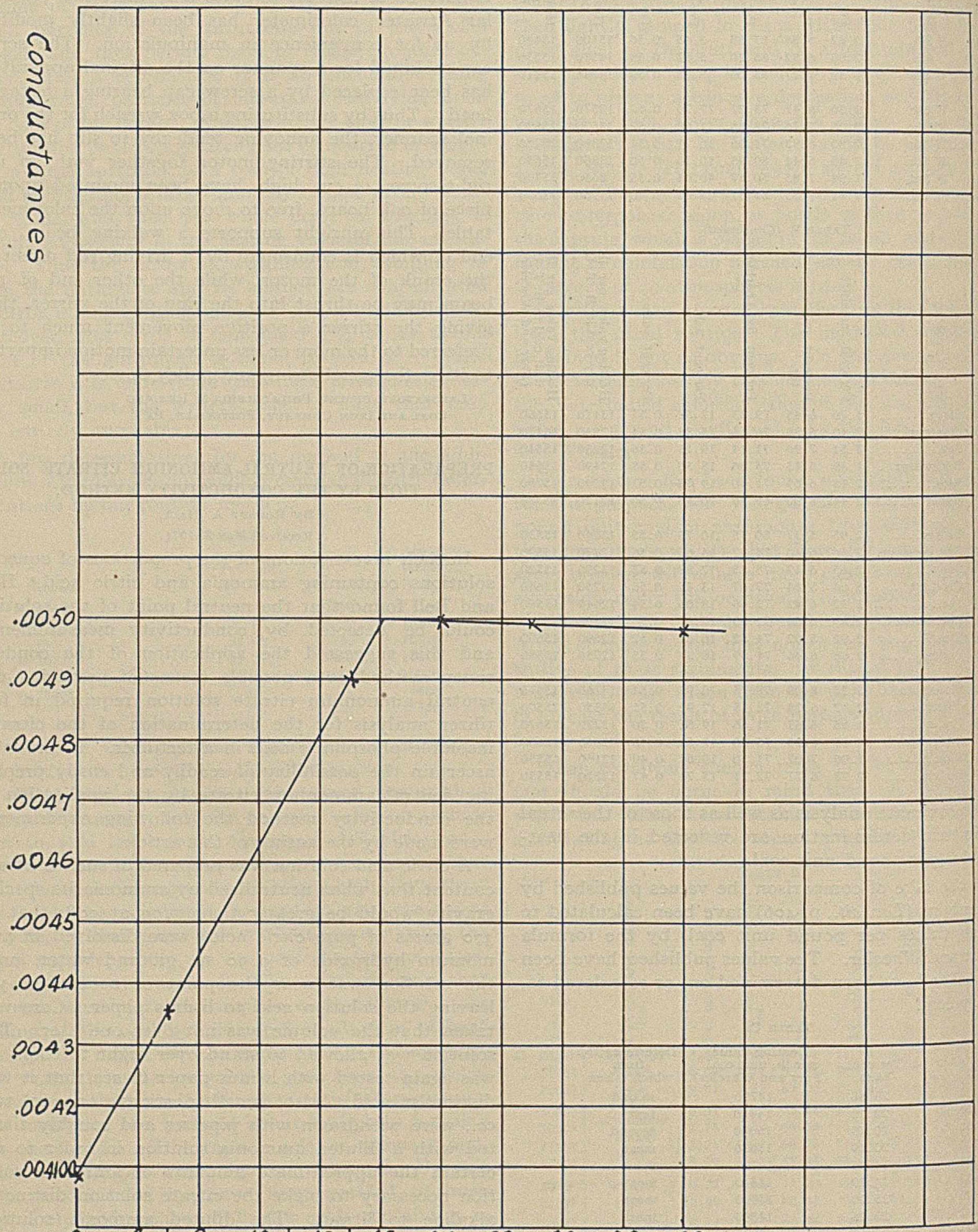

Fig. 1.

ent flasks. Water was then added to the mark, the solution thoroughly mixed, and the flasks placed in an electrically controlled thermostat. The temperature of this thermostat was maintained at 25°, plus or minus 0.01°. When these solutions had come to the temperature of the bath their conductivities were determined with a Wheatstone bridge in the usual way. The conductivity cell used was the H. C. Jones type for concentrated solutions. The conductances were plotted against the cc. of the ammonia solution used. It was easy to read from the curve thus obtained the number of cc. of the ammonia solution needed to neutralize exactly 100 cc. of the acid ammonium citrate solution used. This amount of the diluted ammonia solution was then measured into a 200 cc. flask containing 100 cc. of the citrate solution and water added to the mark. After thorough mixing, the flask was placed in the bath and allowed to come to bath temperature. Its conductivity was then ascertained. Its conductance showed it to have the amount of ammonia necessary for exact neutralization. The solution, when tested with corallin, methyl orange, methyl red, and neutral litmus paper (Squibb's), gave no evidence of the presence of excess of either acid or base. Also, the solution was shaken out with chloroform, the chloroform separated from the citrate solution and shaken with water and the water tested for ammonia.[1] No ammonia was found. Hence it was concluded that a neutral ammonium citrate solution had been prepared with accuracy and certainty.

Specific gravity determinations were also made of the solution used in these conductivity determinations and the densities plotted against the cc. of ammonia. The curve showed that the neutral solution as prepared by the conductivity had the highest specific gravity.[1]

In Table I is given the data obtained in these measurements, and in Fig. 1 the conductances are plotted against the cc. of ammonia solution used:

TABLE I.

Solution No.	Cc. ammonia.	Conductivity.
1	0.00	0.004085
2	6.00	0.004353
3	18.00	0.004900
4	24.00	0.004997
5	30.00	0.004991
6	40.00	0.004980
7	20.30	0.004999

The neutral solution as prepared above had a specific gravity greater than 1.09 at 20°. It was therefore an easy matter to dilute with distilled water and in the usual way bring to the required density.

In order to investigate the possibility of the use of the conductivity method of preparing neutral ammonium citrate solution by the chemist who has not the use of an electrically controlled thermostat, or a thermostat regulated by any other method wherein a constant temperature is secured, a series of experiments were made in which the use of the regulated thermostat was dispensed with; that is, the electrical control was cut off and the temperature of the bath was allowed to vary with that of the room. However, a time for experimentation was chosen so that there was a minimum of variation of room temperature. In brief, the experiments were conducted under such conditions as can be had in any laboratory where a room fairly well protected from the usual weather variations and from the presence of those entering and leaving the room during the time of the experiment can be had. In the place of the thermostat a tub of water could have been used for the bath.

The solutions were prepared as above, placed in the bath and allowed to come to the temperature of the bath. Erlenmeyer flasks of suitable volume and of such sized mouth as to admit of easy entrance of the electrodes of the cell were placed in the bath, so that when the solutions were being changed in the cells the electrodes could be placed in these flasks and be kept at the temperature of the bath, thus preventing the slight lowering of temperature due to the evaporation of the water on the electrodes. The conductivity measurements were made as rapidly as possible (each series was run in less than one and one-half hours), the cells and electrodes being carefully washed each time with the new solution. This rinsing was repeated three times for each change of solutions. During the short intervals of waiting necessary for the cell and its solution to come to bath temperature again after the handling the conductances were computed and the curve plotted, so that as soon as possible after the last reading was made the last point in the curve was located and the curve completed. It was found further that by plotting the bridge readings against the cc. of ammonia solution used that the same results were obtained as by plotting the conductances against the cc. of ammonia solution. In this way it was possible to make the series of six measurements in a very short time, usually less than one and one-half hours being required, and thus minimize the probability of any great change of room temperature. From the curve was read the amount of ammonia solution needed to be added to 100 cc. of the acid ammonium citrate in order exactly to neutralize it. This amount of ammonia was run into a 200 cc. flask containing the solution previously measured out, water added to the mark, and the solution thoroughly mixed. The flask was then placed in the bath and brought to the temperature of the bath. The conductivity measurement was then made. It was found that the bridge reading obtained corresponded exactly to the bridge reading on the curve for neutral ammonium citrate solution. The same amount of ammonia was then run into another 100 cc. lot of the ammonium citrate solution and this solution made up to a specific gravity of 1.09 at 20°. When these solutions were tested with indicators and chloroform, as above, they gave no evidence of containing either acid or free ammonia in excess.

The bath was now brought again to a temperature of 25° and maintained there by the electrical control

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[1] Hall and Bell, *Loc. cit.*

while the conductivity measurements were repeated. These gave a curve showing the neutral point to be the same as that found at room temperature.

In Table II are given the data of the measurements made at room temperature. In Fig. 2 the bridge-readings are plotted against the cc. of ammonia solution used:

TABLE II.

Solution No.	Cc. ammonia.	Bridge-reading.
1	0.00	49.40
2	10.00	52.01
3	18.00	54.09
4	24.00	54.80
5	30.00	54.75
6	36.00	54.70
7	20.80	54.84

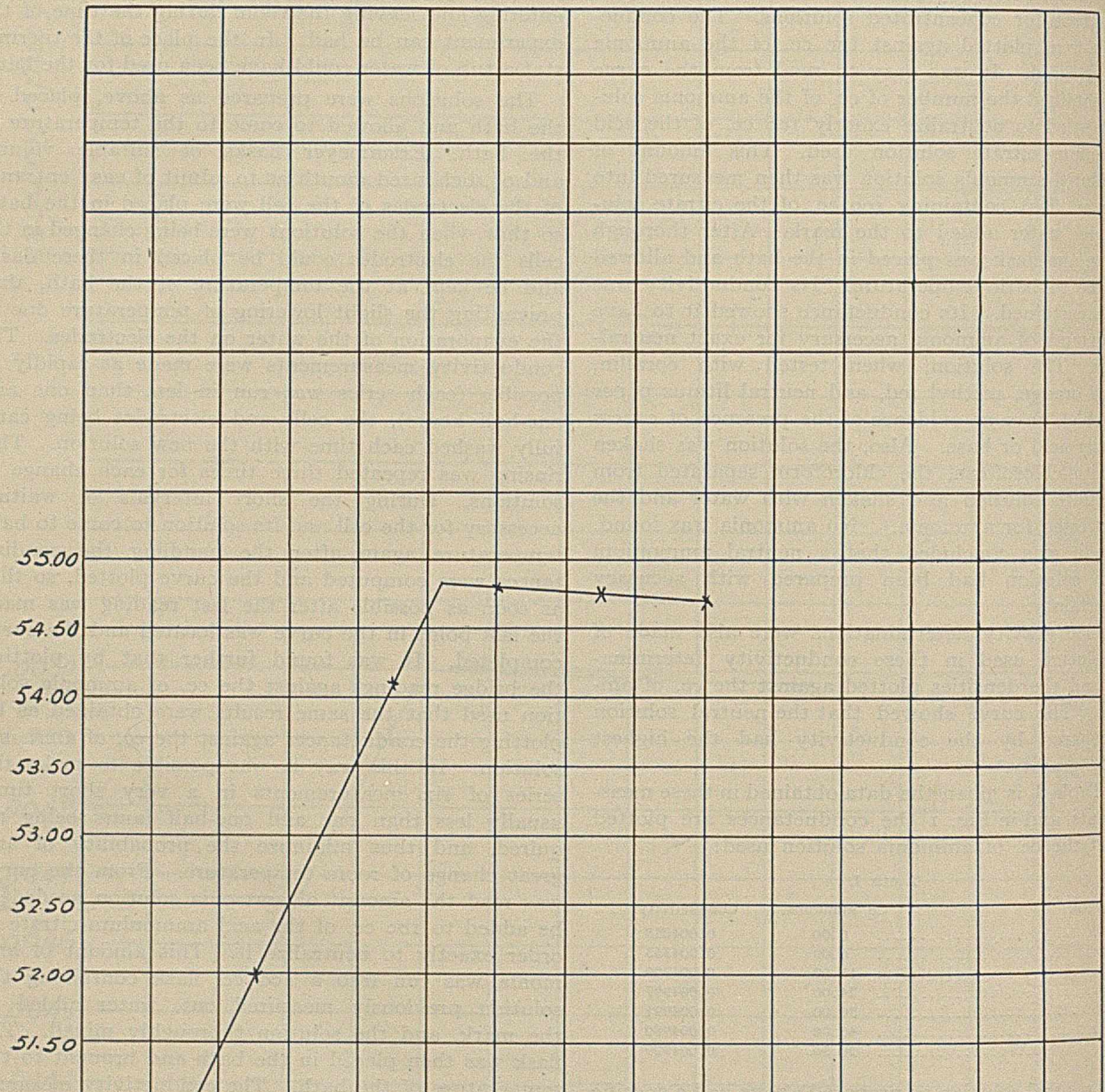

Fig. 2.

An effort was made to ascertain the possibility of preparing a neutral citrate solution by adding an excess of ammonia and afterwards removing this excess by extractions with chloroform.[1] Although repeated extractions were made, there was always free ammonia remaining in the citrate solution. This was to be expected, as the ammonia is so much more soluble in water than in the chloroform. Moreover, had it been possible to extract all the free ammonia from the solution the chloroform that would have remained in solution in the citrate solution would have precluded the use of this method for the preparation of neutral ammonium citrate for the fertilizer analysis, as the chloroform would be decomposed, forming free hydrochloric acid, which would interfere with the determination of the citrate insoluble phosphoric acid.

CONCLUSION.

It has been shown that the conductivity method of preparing neutral solutions is applicable to the preparation of exactly neutral ammonium citrate solutions of such a density that they can, after neutralization, be diluted with distilled water and brought to a density of 1.09 at 20°. This method can be applied under conditions such as can easily be obtained in any laboratory and therefore seems worthy of adoption as an "Official Method" of preparing the exactly neutral ammonium solution required in fertilizer analysis for the determination of the citrate insoluble phosphoric acid content of the fertilizer. For the regulated thermostat there may be substituted a tub of water. However, a thermostat of constant temperature is preferable, for then there is no necessity of the measurements being carried out so quickly as when the measurements are made in a bath at room temperature.

Department of Chemistry,
University of North Carolina,
Chapel Hill, N.C.

A POLARISCOPIC METHOD FOR THE DETERMINATION OF MALIC ACID AND ITS APPLICATION IN CANE AND MAPLE PRODUCTS.

By P. A. Yoder.

Received April 17, 1911.[2]

In the following report there is developed, from extensive original data, a polariscopic method for the estimation of active malic acid which is applicable to a wide range of mixtures without previous isolation or purification of the malic acid. Methods are also developed for a partial separation of malic acid which makes the method of estimating it applicable to an additional wide range of natural products and artificial mixtures. Some applications of the method in the examination of cane and maple syrups are reported. Supplemental to this are notes on a method for tartaric acid, less fully worked out, and a plan for applying these methods to determine both these acids in a mixture of the two, without previous separation of them. This was worked out incidental to an investigation on the acid constituents in sugar cane.

The methods described in the literature for determining the organic plant acids are in many particulars far from satisfactory, even when applied to fruit juices or fermentation products, for which most of them were worked out. In sugar cane juice and its products, new difficulties are encountered. With perhaps none of the commonly occurring organic plant acids have the methods hitherto in use[1] proved more unsatisfactory than with malic acid. In the cane juice, besides the inconvenience occasioned by the large amount of sugar present, the aconitic acid, which is a prominent constituent, introduces special difficulties in that its salts with such bases as are usually available for the separation of organic acids are not widely different from those of malic acid. Therefore a method for its determination which is at once accurate and applicable to a wide range of mixtures will doubtless be welcomed by the many analysts who have occasion to deal with products containing it, such as maple products, fruit juices, fermentation products, etc., as well as by investigators who seek to ascertain for the first time its occurrence or non-occurrence in various substances.

Among analytical operations described in the literature referring to malic acid are several processes, depending upon group reagents, yielding results that are arbitrarily reported as malic acid or more properly as "malic acid values," without presuming in them any ultimate determination of malic acid. Thus a convention has been in vogue in cider and vinegar analysis of computing and reporting the total non-volatile acids, or organic acids, as malic acid.[2]

In the older text-books the method of R. Kayser[3] was commonly given for malic acid in wines. This method is based upon the assumption, that the malate is the only soluble salt of a non-volatile organic acid that barium chloride forms in wine in the presence of sodium carbonate and freed from alcohol. This is true, however, only of a relatively narrow class of natural products. Succinic, citric and aconitic acids besides others all form water-soluble salts with barium, hence in their presence this method could not be applied.

A method somewhat similar to the last but with calcium substituted for the barium, as proposed by Leach[4] for wine and vinegar analysis, has similar limits to its range of usefulness.

In the examination of maple products and suspected adulterations and imitations of maple products it is usual to determine the amount of calcium precipitated by the neutral solution in the presence of alco-

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[1] Hall and Bell, *Loc. cit.*

[2] This paper is an abridgment of a paper by the author on the same subject presented at the 42nd general meeting of the American Chemical Society, July 12, 1910.

[1] Schmidt and Heipe, *Z. anal. Chem.*, **21**, 534–541 (1882); *Bull.* **107**, (revised), Bureau of Chem., U. S. Dept. of Agr., p. 80; G. Joergensen, *Z. Unters. Nahr.-Genussm.*, **13**, 241 (1906); **17**, 396–412 (1909); *Chem. Abs.*, **1**, 1448 (1907); **3**, 1781 (1909); F. Mutellet, *Annales des Falsifications*, **2**, 383–6. Some notes on such means of separating organic acids and on estimating others of them than malic acid forms the subject of a separate paper.

[2] Allen's "Commercial Organic Analysis," 4th Ed., **1**, 187, 505.

[3] *Ibid.*, 3rd Ed., **1**, 512; König's *Untersuchung landw. u. gewerblich wichtiger Stoffe*, 2nd Ed., p. 588. (The newer editions of both these works omit Kayser's method for malic acid.)

[4] Leach's "Food Inspection and Analysis," 2nd Ed., **1909**, pp. 702, 768.

hol to the extent of 75 or 85 per cent.[1] The alkalinity of the ash from this precipitate, computed as per cent. malic acid, gives the so-called "malic acid value." This is a very convenient operation and at present serves a very useful purpose when it is merely a question of distinguishing between pure maple products and those adulterated by the addition of relatively pure cane sugar or glucose. If, however, it is a question of detecting in maple products the addition of substances having impurities such as occur in cane molasses or syrup, it has little value, as will be shown further on in this report.

The results from a determination of a "lead number" by precipitation with lead subacetate, as in the methods for maple products according to Hortvet,[2] Winton,[3] or Winton and Ross,[4] can also have a close relation to the amount of malic acid present only in those exceptional cases in which there is present no considerable amount of other precipitate-forming organic or inorganic acid, as in maple sugar products and these mixed with pure sugars.

It is a common experience with optically active substances that slight changes in their composition or in the combination into which they have entered are accompanied by changes in their rotatory power. Thus salts of active acids or bases, alcoholates and esters of active alcohols, etc., we would expect to have different rotatory powers from those of the free compounds although the elements or groups entering into combination with them may not be active. A place among such combinations very exceptional in the extent of this change in the rotatory power is taken by the compounds formed by certain active dicarboxylic oxy-acids with a few of the rarer elements, especially with molybdenum, tungsten and uranium, in that the activity is increased many fold. Thus P. Walden,[5] who was the first to discover that this property belonged also to uranium, reported that it increased the levo-rotatory power of malic acid over 500-fold and that of tartaric acid 20-fold. A. F. Holleman[6] studied the effect of uranyl nitrate on saccharic acid. H. Itzig[7] studied the compounds of uranium with tartaric and malic acids, seeking primarily to determine the constitution of these uranium compounds. Rimbach and Schneider[8] further studied the molybdenum and uranium compounds of quinic acid. H. Grossmann[9] furnishes us with more details concerning the effect of uranyl compounds on some of these oxyacids and also made an extensive study of their effect on the rotatory power of a number of sugars. While this remarkable property of the uranyl compounds with the dicarboxylic oxyacids at once suggests the possibility of basing upon this property quantitative methods for the estimation and identification of individual members of the group of acids, no such method has yet been published as far as I have been able to find. Seeking to elaborate such a quantitative method which should enable me to make reasonably quick and accurate estimations of malic acid in the sugar-cane products, I carried out many series of tests to answer the questions suggested by the sub-headings which follow under the heading "Experimental Basis." Some of these were apparently answered in advance by the data of the investigators cited above, but as my results were in part contradictory to those given by the above, and were in part obtained under different conditions, I shall here give the conclusions based upon my own experimental data. Space does not permit presenting here all the rather extensive tables of the data involved.

In the collection of these data, the polarizations were made with a Schmidt and Haensch quartz wedge, double compensation instrument with readings on the sugar scale. As the limit of accuracy with clear solutions was 0.05 to 0.1 unit on the Ventzke scale, and somewhat more with solutions deeply colored yellow or brown from the uranium compounds, a corresponding latitude must be allowed in the conclusions.

I. EXPERIMENTAL BASIS FOR THE METHOD.

1. The Maximum Effect.—Under various conditions, approximately the same increase was occasioned in the levo-rotatory activity of the malic acid. In the most accurate determinations made of the rotation of the uranium-malic acid compound, using a "Kahlbaum" preparation of the acid, it was found that at 20° C. a 1 per cent.[1] malic acid solution, converted to the uranium compound, has a levo-rotation of 29.7 units on the Ventzke sugar scale, if white light from a Welsbach gas light is used, and 28.9 units when yellow, sodium light is used. From this we have for white light

$$[\alpha]^{20} = -515$$

and for yellow sodium light,

$$[\alpha]^{20}_{D} = -501.$$

The free malic acid, *i. e.*, without the addition of a uranyl compound, has a rotatory power so low that in a concentration like those used with the uranyl compounds, *viz.*, not much above 0.1 normal, the delicacy of the polariscope used did not suffice for very accurate determinations. With a 3.043 per cent. solution, the rotatory power was found equivalent to approximately 0.13 on the Ventzke scale computed for a 1 per cent. solution, or

$$[\alpha] = -2.25.$$

Comparing this number with —515 above, we find that the uranium causes a 229-fold increase in the rotatory power.[2]

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[1] *J. Am. Chem. Soc.*, **30**, 1285 (1908); Official and Provisional Methods of Analysis, *Bull.* **107** (revised), Bureau of Chem., U. S. Dept. of Agr., p. 74.

[2] *J. Am. Chem. Soc.*, **26**, 1523 (1904); *Bull.* **107** (revised), Bureau of Chem., U. S. Dept. of Agr., p. 73.

[3] *J. Am. Chem. Soc.*, **28**, 1204 (1906).

[4] *Circular* **53** (1910), Bureau of Chem., U. S. Dept. of Agr.

[5] *Ber. d. chem. Ges.*, **30**, 2889 (1897).

[6] *Rec. des. travaux chimiques des Pays-Bas et de la Belgique*, **326**, 1898.

[7] *Ber. d. chem. Ges.*, **34**, 3822 (1901).

[8] *Z. physik. Chem.*, **44**, 467 (1903).

[9] *Z. d. Ver. deutsch. Zuckerind.*, **55**, II, 650, 941, 1058 (1905).

[1] For brevity's sake the term "per cent.' is used here and in what follows to mean grams per 100 cc.

[2] Walden (*Ber. d. chem. Ges.*, **30**, 2889–90 (1897)) reports $[\alpha]_D$ for malic acid equal to about —0.77 and $[\alpha]_D$ for malic acid with uranium added equal to —475. The latter number does not vary greatly from the corresponding result from my data, *viz.*, —501. From Schneider's formula for malic acid (Landolt's, *Das optische Drehungs-Vermögen*, 2nd Ed., p. 178. $[\alpha]^{20}_{D} = 5.89 - 0.0896q$), the specific rotatory power of a 1 per cent. solution is —2.98. Necessarily with such a low activity, the results of different experimenters must vary greatly.

2. *Influence of Concentration of the Malic Acid.*—In a series of tests with various concentrations up to 1.3 per cent., it was seen that with a plentiful supply of the uranium compounds, *i. e.*, with 1.25 or more atoms of U to each molecule of malic acid, the variation in specific rotatory power due to the concentration of malic acid, if there be any variation, is within the limits of the experimental error in these tests. With a scant supply of uranium, *e. g.*, 1.04 atoms, the results are all too low, but there is a tendency towards higher results with more dilute solutions.

3. *Influence of Kind of Uranyl Compounds Used.*—Provided it is soluble and capable of reacting with the malic acid and no interfering by-product is formed, the kind of uranyl compound used has little or no influence. Uranyl acetate and sodium and potassium uranates were used. In using the uranates (prepared from the acetate or nitrate by precipitation with sodium or potassium hydroxide and incomplete washing) the alkalinity imparted by these salts had to be neutralized to get the maximum effects. The uranyl nitrate, used alone with malic acid, is unsuited because the by-product, nitric acid, interferes, as will be shown under "Interference of Foreign Substances." For convenience of application and for a wide range of conditions giving the maximum effects, uranyl acetate is preferred. Commercial preparations of sodium uranate and of uranic acid were found unsuited for the reaction. The uranyl acetate used in most of the work contained 51.56 per cent. uranium (theoretical for $(UO_2)(C_2H_3O_2)_2.2aq.$, 56.04 per cent.). It did not completely dissolve in weak acids like malic acid, necessitating filtering before polarizing. By recrystallizing from a hot filtered solution, and drying the crystals at a temperature not above 50°, I succeeded in preparing crystals which dissolved completely.

4. *Influence of the Quantity of the Uranyl Compound.*—The proportion of 1 atom U to 1 molecule of malic acid, which we may presume is the theoretical amount required, will not suffice to call forth the maximum rotation. Using successively larger amounts, the action increases gradually until about 1.25 atoms U to 1 molecule malic acid is reached, after which it remains constant. Presumably, by the law of mass

TABLE 1.

Effect of other acids and of alkali upon the rotatory power of the malic-acid-uranium compound. In each case, unless otherwise stated, the concentration of the malic acid was 0.1 *N*. Polarizations are computed on a 1 per cent. solution.

The uranium was added as uranyl acetate and, unless otherwise stated, in the proportion of 1.25 atoms U to each molecule malic acid. The acidity numbers refer to standards in Table III of shades of methyl orange, depending upon the concentration of H ions.

No. of line.	Other acids added. cc. normal acid to 15 cc.		Cc. normal KOH added to 15 cc.										
			0	1.0	1.5	2.0	2.5	3.0	4.0	4.5	5.0	6.0	7.5
1	None	Acidity	2	11	14	14	...	...	...	...	...	...	...
		Polarization	29.28	28.26	27.45	27.99	...	...	...	...	...	...	...
2	3 cc. acetic	Acidity	2	...	...	11	...	13	13	14	14	14	...
		Polarization	29.24	...	...	29.06	...	28.36	27.75	26.63	25.93	25.29	...
3	6 cc. acetic	Acidity	...	...	4–5	...	...	7	...	11	...	12	...
		Polarization	27.05	...	29.08	...	...	28.58	...	28.47	...	27.84	...
4	3 cc. formic	Acidity	1–2	2–3	...	3–4	4–5	6	11	...	13	14	...
		Polarization	26.11	28.72	...	28.82	29.00	29.45	28.79	...	26.66	24.74	...
5	3 cc. lactic	Acidity	1–2	2–3	...	3–4	4–5	6–7	...	...	...	...	...
		Polarization	21.16	27.26	...	28.26	28.29	28.29	...	...	...	...	...
		Polarization	20.99	27.57	...	...	...	27.91	...	...	...	...	...
6	3 cc. succinic	Acidity	2	2–3	...	7	9	11	...	...	...	...	...
		Polarization	27.76	...	...	...	...	27.91	...	...	...	...	...
7	3 cc. citric	Acidity	2	...	4	...	...	11	...	13–14	...	...	...
		Polarization	10.47	...	16.54	...	...	19.40	...	...	...	...	...
		Polarization	10.52	...	...	...	...	19.28	...	17.66	...	...	...
8	3 cc. citric (1)	Polarization	...	...	...	...	...	26.14	...	...	...	...	...
9	3 cc. citric (2)	Polarization	23.24	...	30.19	...	...	29.23	...	27.60	...	...	...
		Polarization	...	...	30.30	...	...	...	...	...	...	...	...
10	3 cc. citric (3)	Polarization	...	...	...	...	...	29.26	...	...	...	...	...
11	3 cc. aconitic	Polarization	25.26	...	...	29.15	...	...	...	...	...	...	...
12	3 cc. mucic	Polarization	...	...	...	...	...	27.90	...	...	...	...	...
13	3 cc. acetic and 3 cc. lactic	Acidity	1–2	2–3	...	...	...	5	...	7–8	...	11–12	13–14
		Polarization	21.30	26.72	...	...	...	27.26	...	26.69	...	27.91	27.15
		Polarization	...	25.74	...	...	...	27.34	...	27.57	...	27.14	27.28
14	3 cc. acetic and 3 cc. lactic (2)	Polarization	26.71	28.22	...	...	...	28.76	...	28.32	...	27.89	27.26
15	3 cc. sulphuric	Acidity	1	...	...	1	1	2	11	14	...	...	...
		Polarization	1.37	...	...	24.56	...	28.49	28.35	27.69	...	...	...
		Polarization	...	...	...	...	...	28.39	...	...	...	...	...
16	3 cc. hydrochloric	Acidity	1	...	...	1	1	2	10–11	14	...	...	...
		Polarization	0.78	...	...	21.87	...	29.03	28.44	27.57	...	...	...
17	3 cc. nitric	Acidity	1	...	...	1	1	2	...	...	...	...	...
		Polarization	0.34	...	...	...	...	28.09	...	...	...	...	...
18	3 cc. sulphuric and 3 cc. acetic	Acidity	...	...	...	1	...	1–2	4	...	7	11	14
		Polarization	0.48	..	...	21.26	...	27.94	28.26	...	28.12	28.02	26.90
19	3 cc. hydrochloric and 3 cc. acetic	Acidity	...	...	...	1	...	1–2	4	...	7	11	14
		Polarization	0.32	...	...	19.93	...	27.94	29.39	...	28.48	28.39	26.92
20	3 cc. nitric and 3 cc. acetic	Acidity	...	...	...	...	...	1–2	...	...	...	...	...
		Polarization	0.75	...	...	...	...	28.00	...	...	...	...	...

(1), (2) and (3)—The amount of uranium acetate in these is increased to 1.67 atoms in (1), 2.1 atoms in (2) and 2.5 atoms in (3) of U to one molecule of malic acid.

action, an excess of the uranyl compound is required to drive the reaction to completion.

5. *Interference of Foreign Substances.*—It is evident from the foregoing that with pure solutions of malic acid we can use the increased rotatory power imparted by uranyl compounds for quantitatively determining the amount with a degree of accuracy limited practically only by the accuracy of the volumetric measuring apparatus. But our difficulty has been to get the malic acid in a pure state without loss. We wish a method of estimating it after only a partial purification, such as we can readily effect. To determine to what extent such accompanying substances like small amounts of sugars or of bases and other acids interfere I carried out many series of tests from which some characteristic ones pertaining to acids and alkalies are collected in Table I.

(*a*) *Acids and Alkalis.*—From Table I, the following results are to be noted:

With no foregin acid added, the base, potassium hydroxide, interferes but little until enough is added to neutralize the malic acid (line 1).

The addition of two equivalents of acetic acid does not interfere nor is there any marked interference with the same partly or wholly neutralized, *i. e.*, with the addition of potassium acetate (line 2).

Four equivalents of acetic acid are sufficient to interfere perceptibly, but by partly neutralizing this, the maximum effect is again secured, which is but slightly reduced upon complete neutralization of the acetic acid added or its equivalent of malic acid (line 3).

In the cases of added formic or lactic acid, there is also a considerable range in the degree of neutralization through which it does not interfere seriously (lines 4 and 5).

The few trials made with succinic, aconitic and mucic acids leave it probable that with more tests a similar range of non-interference might be found.

The presence of two equivalents of the strong mineral acids almost completely destroys the effect of uranyl acetate. When these are neutralized, however, *i. e.*, when neutral salts are added, there is again little or no interference.

In another series of tests, not included in this table, in which sodium uranate was the reagent in place of uranyl acetate, the results ran similar except that, as may be expected, the sodium uranate exercises its neutralizing effect, as does the addition of its equivalent of potassium hydroxide.

Table II presents the results of a series of tests to determine the effect of larger amounts of potassium acetate and also the effects of the presence of the acetates of barium and calcium with and without an excess of acetic acid. Assuming no notable effect upon the rotatory power of the uranium-malic-acid compound by dilution, these tests with different amounts of added substances were made, for convenience, by additions of small measured volumes of strong solutions to definite volumes filled into the dry polariscope tube. For these additions a polariscope tube with tubulature and

TABLE II.

Further data on the effects of potassium acetate and acetic acid, and data on the effects of calcium and barium acetates and acetic acid upon the rotatory power of the malic-acid-uranyl compound.

No. of test, composition of original mixture, and temperature of tests.	Additions.		Polariscope readings.		Percentage which the rotatory power is of that of same concentration without additions.
	2 × N acetic acid.	2 × N KOH.	Actual.	Equivalent computed on original concentration and temperature.	
No. 348.—8 cc. malic acid sol. A + 0.8832 gram uranyl acetate made up to 20 cc. tested at 30° C.	0	0	18.87	.....	.....
	3	0	16.70	19.20	101.6
	3	0.5	16.32	19.17	101.5
	3	1.0	15.94	19.13	100.7
	3	1.5	15.46	18.94	100.3
	3	2.0	15.06	18.82	99.6
	3	2.5	14.53	18.52	98.0
	3	3.0	14.16	18.41	97.5
	11.2	3.0	10.25	17.51	92.7
	11.2	4.3	9.85	17.48	92.5
	11.2	5.6	9.56	17.58	93.1
	11.2	6.9	9.12	17.37	92.0
	11.2	8.2	8.79	17.31	91.6
	11.2	9.5	8.45	17.19	91.0
	11.2	10.8	8.28	17.38	92.0
No. 374.—0.09 gm. moist malic acid crystals + 0.6 gram uranyl acetate made up to 15 cc. Tested at 30° C.	0	0	15.42	.....	.....
	3	0	13.10	15.72	102.9
	3	0.5	12.49	15.40	99.9
	3	1.0	12.04	15.25	98.9
	6	1.0	10.21	14.97	97.1
	6	1.5	10.08	15.12	98.1
	6	2.0	9.61	14.74	95.6
	9	2.0	8.28	14.35	93.1
	9	2.5	8.06	14.24	92.3
	9	3.0	7.91	14.24	92.3
	9	3.5	7.73	14.17	91.9
	9	4.0	7.60	14.19	92.0
	9	5.0	7.33	14.17	91.9
	9	6.0	7.25	14.50	94.0
	9	9.0	6.34	13.95	90.5
		20% sol. barium acetate.			
No. 375.—4 cc. of malic acid sol. B + 0.56 gram uranyl acetate made up to 12 cc. Tested at 26° C.	0	0	23.02	.....	.....
	0	2	18.51	21.59	93.8
No. 376 4 cc. of malic acid sol. B + 0.56 gram uranyl acetate + 1.6 cc. 20 % barium acetate sol. made up to 12 cc. Tested at 26° C.	0	1.6	22.32	22.32	97.0
	0.5	1.6	21.37	22.26	96.7
	0.5	3.6	18.32	22.13	96.1
No. 377.—4 cc. of malic acid sol. B + 0.84 gram uranyl acetate + 1.6 cc. 20% barium acetate sol. made up to 12 cc. Tested at 27° C.	0	1.6	21.61	21.63	94.0
	0.5	1.6	20.96	21.85	94.9
	1.0	1.6	20.20	21.90	95.1
	1.5	1.6	19.51	21.97	95.4
	2.0	1.6	18.87	22.04	95.7
	2.5	1.6	18.04	21.82	94.8
	3.0	1.6	17.39	21.76	94.5
		10% calcium acetate.			
No. 378.—4 cc. of malic acid sol. B + 0.56 gram uranyl acetate + 1.6 cc. 10% calcium acetate sol. made up to 12 cc. Tested at 26° C.	0	1.6	22.81	22.81	99.1
	0.5	1.6	22.00	22.92	99.6
	1.0	1.6	21.05	22.80	99.0
	1.5	1.6	20.26	22.79	99.0
	2.0	1.6	19.50	22.75	98.8
	2.0	3.6	16.33	21.77	94.6
	3.0	3.6	15.10	21.39	92.9

No. 379.—4 cc. of malic acid sol. B + 0.84 gram uranyl acetate + 1.6 cc. 10% calcium acetate sol. made up to 12 cc. Tested at 24.5° C.	0	1.6	22.73	22.72	98.7
	0.5	1.6	21.92	22.80	99.0
	1.0	1.6	21.13	22.86	99.3
	1.5	1.6	20.42	22.94	99.7
	2.0	1.6	19.72	22.98	99.8
	2.5	1.6	19.06	23.00	99.9
	3.0	1.6	18.22	22.74	98.8
	4.0	1.6	17.02	22.66	98.4
	4.0	3.6	14.72	22.05	95.8
	5.0	3.6	13.65	21.59	93.7

with a bulb-tube set upon the tubulature (see Fig. 1) was found very convenient.

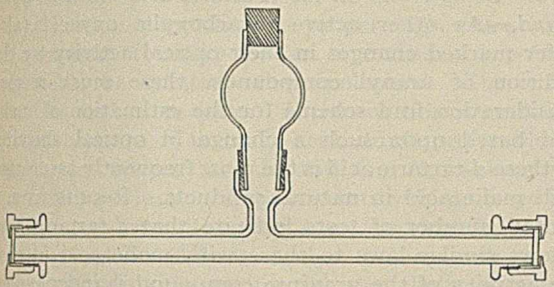

Fig. 1.

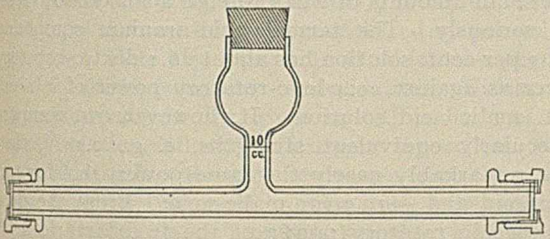

Fig. 2.

This device proved very serviceable also in making additions to solutions derived from syrups, to find the maximum rotatory power, as will be noted further on in this report. This method of procedure gave results more strictly comparable, except for the possible slight influence of volume or concentration, than those in Table I. This table brings out what is not clearly evident from Table I, that acetic acid alone, added in moderate quantity, can slightly increase the rotatory activity. As the quantity of potassium acetate is increased, the rotatory power gradually falls (tests Nos. 348 and 374), but a considerable proportion can be present without any reduction that in technical analysis need be considered very serious. With calcium acetate (Nos. 378 and 379) the effect is also a relatively slight lowering. With barium acetate (Nos. 376 and 377) the tests commenced with larger amounts, *viz.*, 1.6 cc. 20 per cent. solution or 320 mg. to 12 cc. or roughly 1.5 times the barium acetate equivalent of the malic acid. In the absence of free acetic acid, we find its depressing effect upon the rotatory power greater with a greater excess of uranium. With acetic acid in a quantity for maximum rotatory power, it polarizes 95.7 per cent. in No. 377 and 97 per cent. in No 376 of what the same strength of malic acid solution without the barium salt does.

Referring again to Table I, we note that with all these additions of acids, excepting citric and possibly the mixture of lactic and acetic acids, there is a range in the degrees of neutralization through which they do not interfere seriously. Can we find a general means of detecting this degree of neutrality and of establishing it in unknown mixtures containing these foreign acids with malic acid?

Looking through the series we find that the stronger the acids (in H ions) the lower the non-interference range in neutralization can reach. Thus free acetic acid shows less tendency to interfere than the stronger acids, formic and lactic. Succinic acid in this respect comes between acetic and lactic or formic. The three mineral acids are far more effective than the organic acids in interfering with the rotatory activity of the malic-acid-uranium compound. In their electrical conductivities, which may be taken as a measure of ionization and of concentration of H ions, these acids stand in the same order as in their interfering power, *viz.*, for normal solutions, hydrochloric (100), nitric (99.6), sulphuric (65.1), formic (1.68), lactic (1.04), succinic (0.581), and acetic (0.424).[1] In this list we find also citric (1.66) and malic (1.34) acids.

To study the relations between concentrations of H ions and rotatory activity and in analyses to establish a degree of acidity for maximum rotatory activity, an indicator, such as methyl orange, of low sensitiveness towards weak acids, may conveniently be used. Standard tints for comparison were established as exhibited in Table III.

TABLE III.

Standards of acidity or concentration of H ions, in tints with methyl orange. Each number has 10 cc. normal acetic acid, 2 drops of methyl orange solution and other additions as indicated, and is made up to 30 cc.

No. of standard.	Additions.	No. of standard.	Additions.
1	2 cc. normal H_2SO_4	8	3.0 cc. normal KOH
2	Nothing	9	3.5 cc. normal KOH
3	0.5 cc. normal KOH	10	4.0 cc. normal KOH
4	1.0 cc. normal KOH	11	5.0 cc. normal KOH
5	1.5 cc. normal KOH	12	6.0 cc. normal KOH
6	2.0 cc. normal KOH	13	8.0 cc. normal KOH
7	2.5 cc. normal KOH	14	12.0 cc. normal KOH

Glancing through Table I for the cases in which the polarization reached its maximum, say from 28.00 up, we see that in no case where the acidity corresponds to No. 1, did it reach that limit, and that in nearly all cases where the acidity corresponded to Nos. 3 to 12, it reached this maximum. Very exceptional was the behavior with citric acid, line 7, and to a less extent also that of the combined addition of lactic and acetic acids, line 13. Since these were such striking exceptions, we seek the cause elsewhere than in the degree of acidity, and, sure enough, the addition of more uranyl acetate, lines 8, 9, 10 and 14, shows that the low results were due to an insufficiency in this reagent. Speculating upon the reason why these acids should require such a large proportion of uranyl acetate, we note that both the citric and the lactic acids are oxyacids and we recall in this connection that of the active dicarboxylic acids, it is also the oxyacids that show the remarkable sensitiveness to uranyl compounds in greatly increased optical activity. This points to the hypothesis that the uranyl group readily

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[1] Ostwald's "Outline of General Chemistry," 1st ed., pp. 360-1.

enters the molecule at the alcohol hydroxyl, and that therefore the citric and the lactic acids have a power of using up the uranyl and holding it away from the malic acid, which the acetic, formic, succinic, etc., acids do not possess. This view would support the hypothesis of Walden,[1] who proposed the formula of the active acid with (UO_2OH) displacing the H of the alcoholic hydroxyl group, and it argues against the view held by Itzig,[2] that it displaces a carboxyl H.

In the polarization of malic acid the presence of other active dicarboxylic oxyacids not represented in these tables, since these themselves show marked changes in their optical activity on addition of a uranyl compound, must of course, cause an interference of a different kind than that caused by the acids here listed. Of these, tartaric acid will receive some consideration below under a practical method of estimation and under some notes on tartaric acid.

(*b*) *Sugars.*—In tests with the usual proportions of malic acid and uranyl compounds and with a sugar, it was found that the sugars (sucrose, dextrose and levulose were tried) had no appreciable influence upon the rotatory activity of the malic-acid-uranium compound, even though present to the extent of 3 per cent. or of five times the quantity of malic acid, the independent activity of the sugar used being, of course, taken into consideration. H. Grossman[3] has studied in detail the action of uranyl compounds upon sugars and finds but slight changes, especially in the acid solution.

6. *Influence of the Time of Standing after Mixing Upon the Rotatory Power.*—Several hours have no notable influence, but several days cause a lowering.

7. *Influence of Temperature.*—Very careful tests, recorded in Table IV, indicate that the influence of the temperature is somewhat more than what is accounted for by the expansion of the water solution. The rotatory power for the same number of grams per 100 true cc. decreases as the temperature rises. In a 1 per cent. solution this is, on an average, 0.03 degrees Ventzke per degree C. rise in temperature.

TABLE IV.

Influence of temperature and kind of light used upon the rotatory power of the malic-acid-uranium compound. All numbers in line 1 were of the same solution, of a concentration of 0.11207 normal at 20°, and all those in lines 2 and 3 were of another solution, of a concentration of 0.10682 normal at 20°. In each number polarized below or above 20° a correction was made for the contraction or expansion from the volume at 20° and the polarization given in each case is that calculated for a solution at that temperature having 1 gram malic acid in 100 true cc.

No. of line.	Light used	Temperature of polarization. 10°	15°	20°	25°	27.5°	30°	35°
1	Welsbach polarization	.....	.....	29.22	.....	29.02	.....	28.91
2	Welsbach polarization	30.04	29.96	29.72	29.56	29.35	29.30	29.15
3	Sodium polarization	.....	28.99	28.95	28.84	.....	28.60	.....

8. *Influence of Heating when Mixing.*—Heating the mixture up to boiling (to hasten the solution of uranyl acetate) has no influence on the results.

9. *Influence of the Kind of Light Used in Polarizing.*—As before noted, with the intensely yellow or brown uranium compound in the polariscope, the field could not be adjusted quite uniform in shade and color, thus showing a dispersion or absorption unlike that of the compensating quartz wedge. This is not enough to seriously interfere with the accuracy of the results, but to get data with the standard polariscopic light I also made parallel polarizations with sodium light (line 3, Table IV). Sharper readings can be made with a good sodium flame, and these readings run about 0.8° Ventzke lower for a 1 per cent. solution than with the white Welsbach light.

10. *Some Notes on the Tartaric-acid-uranium Compound.*—As other active dicarboxylic oxyacids also suffer marked changes in their optical activity by the addition of uranyl compounds, these must receive consideration in a scheme for the estimation of malic acid based upon such a change in optical activity. Of these *d*-tartaric acid is the most frequently associated with malic acid in natural products. Results from a limited number of tests indicate that *d*-tartaric acid follows similar laws to those with malic acid in that the activity of the uranium compound is independent of the kind of uranyl compound used, that somewhat more uranium is needed than in the ratio 1 : 1, and that small amounts of weak foreign acids do not interfere seriously. The tartaric-acid-uranium compound in a 1 per cent. solution has about 26.1 dextro-rotatory power as against 29.4 levo-rotatory power of a 1 per cent. malic acid solution. If, however, we compare molecularly equivalent strengths, *e. g.*, 0.1 *N*, they have remarkably nearly the same power, 19.6 for tartaric acid and —19.7 for malic acid. From the data the specific rotatory power of the free tartaric acid, with white light at 27.5° C., is

$$[\alpha]^{27.5} = 16.3$$

as against

$$[\alpha]^{20}_{D} = 14$$

usually given for yellow light at 20° C.

For the uranium compound, computed on the free tartaric acid, I find for white light and quartz compensation

$$[\alpha]^{27.5} = 453$$

as against the maximum

$$[\alpha]_{D} = 303$$

reported by Walden[1] for yellow light. I thus find a 28-fold increase instead of 20-fold, as reported by Walden.

II. METHOD FOR THE QUANTITATIVE DETERMINATION OF MALIC ACID AS FINALLY ADOPTED.

With the foregoing data before us we have the basis for establishing a quantitative method for estimating malic acid, based upon the change in its optical activity on conversion to the uranium compound, under the conditions for the maximum change. What preliminary preparation the substance needs, of course depends upon its composition.

1. *Procedure with Only Non-interfering Substances Present.*—This applies to solutions which may contain, besides malic acid, *a*, neutral active or inactive substances, like the sugars in small quantities, or *b*, other

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[1] *Ber. d. chem. Ges.*, **30**, 2889 (1897).

[2] *Ibid.*, **34**, 3822 (1901).

[3] *Z. d. Ver. deutsch. Zuckerind.*, **55**, II, 1058 (1905).

[1] *Ber. d. chem. Ges.*, **30**, 2890 (1897).

acids in small quantities, say up to a strength of 0.2 *N* or to a strength not exceeding double that of the malic acid present if the latter is above 0.1 *N* (excepting optically active dicarboxylic oxyacids and acids destroying or precipitating either the malic acid or the uranyl compound). I shall consider two methods of procedure, of which one or the other will be preferred according to circumstances, such as the amount of solution available, the apparatus available, what is known concerning the composition of the solution and its condition as to acidity or alkalinity, etc.

(*a*) Procedure in which the proper degree of acidity for maximum rotatory power is established beforehand and the solution then polarized. The acids should be in the free state. If the solution is probably stronger than 0.2 *N* in malic acid, dilute preferably to a strength between 0.1 *N* and 0.2 *N*, making up to a definite volume. A convenient volume is 50 cc. To an aliquot part of it (say 10 cc.) add both methyl orange and phenolphthalein, then titrate with 0.1 *N* potassium hydroxide, noting the point between which the methyl orange passes through the shades between those of the two methyl orange standards, first, in $^1/_4$ *N* acetic acid and, second, in $^1/_3$ *N* acetic acid in which $^1/_4$ of the acid has been neutralized by potassium hydroxide. Note also the point at which the phenolphthalein shows complete neutralization. Unless the polarization tube is dry, rinse it with a little of the original solution, fill and polarize in the 20 cm. tube for the reading P. Return the portion from the polariscope tube to the main portion and take another aliquot portion (20 cc.) of this solution, add uranyl acetate in a quantity that will allow about 1 atom uranium to every atom of displaceable H of the acids (*i. e.*, about 0.046 g. Kahlbaum's crystalline uranyl acetate, containing about 51.6 per cent. uranium, for every cc. 0.1 *N* potassium hydroxide required for complete neutralization of this portion). Dissolve the uranyl acetate, then add potassium hydroxide in form of 0.1 *N* or *N* solution in the proportion necessary to secure a degree of neutralization within the range as determined in the above titration with methyl orange as indicator. Make up to definite volume (25 cc.). Filter through a dry filter, if necessary, and polarize in a 20 cm. tube. Increase the reading in the ratio that the volume of this portion was increased (by $^1/_4$, if 20 cc. were made up to 25 cc.) for the reading P′.

From the difference between the rotatory power with and without the uranyl acetate, *i. e.*, by the increase in the levo-rotation, calculate the malic acid, from the basis that in a 1 per cent. solution of malic acid, polarized in a 2 dcm. tube, at 20° C., the increase in levo-rotation is, with white light and quartz compensation, 29.6° Ventzke (or 10.25 circular degrees) and with yellow sodium light, 28.8° Ventzke (or 9.99 circular degrees). If the polarization was made at any other temperature than 20° C., correct this reading in degrees Ventzke by multiplying by $1 + 0.001\ (t - 20)$, in which t is the degrees C. Putting this into a formula and letting t = temperature C., L = length of polariscope tube in dcm., P = the polarization of the mixture without uranium and P′ = polarization of the same strength mixture with uranium, the formula for the per cent. malic acid in that strength solution is for white light—

(1) Per cent. malic acid

$$= \frac{(P' - P) \times [1 + 0.001(t - 20)]}{-29.6 \times {}^1/_2 L}$$

or for yellow light

$$(2) \quad = \frac{(P' - P) \times [1 + 0.001(t - 20)]}{-28.8 \times {}^1/_2 L}$$

or for yellow light with the circular scale

$$= \frac{(P' - P) \times [1 + 0.001\ (t - 20)]}{-9.99 \times {}^1/_2 L}.$$

If the malic acid in 50 g. of the material analyzed is contained in a volume of 50 cc., as proposed below for syrups, and if 20 cc. of this solution are diluted to 25 cc. for polarizing and the reading increased by $^1/_4$ for P′, then to find the per cent. malic acid, multiply the difference in readings (P′ — P), with the sign changed, by 0.0338 if white light and the Ventzke scale were used, by 0.347 if yellow light and the Ventzke scale were used, and with 0.1001 if yellow light and the circular scale were used. These constants are calculated for the temperature 20°. The correction for other room temperatures may be neglected in ordinary analyses.

Notes on the Above Method. *1.*—If the acids are not all in the free state in the start, but are partly neutralized, so that the titration of a portion of the solution with phenolphthalein as indicator will not indicate the total acids, then the solution, after suitably neutralizing, may be divided into aliquot parts, adding to one portion a medium amount of uranyl acetate and to another equal portion, somewhat more uranyl acetate. Should the latter portion give higher results than the former, then additional portions may be treated with different amounts of uranyl acetate, until a maximum effect is produced. Or, more advantageously, a definite volume of the solution with a conservative amount of uranyl acetate in solution is introduced into a dry polarization tube provided with a tubulature. After polarizing, a small weighed quantity of wholly soluble, dry, crystalline uranyl acetate is added and, after dissolving, the solution again polarized. Allowing for an increase in volume of 0.04 cc. for every 0.1 gram uranyl acetate added, if the new reading is higher, then additional amounts of uranyl acetate are added, until a maximum effect is produced or the solution is cold saturated with uranyl acetate.

2. In case the test portion with methyl orange gives a shade of pure yellow or almost pure yellow, showing alkalinity, neutrality, or a point nearer neutrality than the shade of the second standard mentioned, then the titration may be made with 0.1 *N* acetic acid to a point within the range mentioned and a corresponding amount of acetic acid added to the main portion.

3. In case the original solution is colored so that the methyl orange shades are not pure, the neutralization of an excess of acidity may be carried to a stage

at which the color has distinctly begun to change, or in case of an alkaline solution, the neutralization in one portion is carried to a point where the change is complete, then in the portion to use it is stopped just before it is complete.

In the last two cases it is more advantageous to work according to the procedure next to be given.

(*b*) Procedure in which the proper acidity is established by trial polarizations after successive additions of alkali or acid. The solution of suitable strength is prepared, the polarization without uranium is made, and the right amount of uranyl acetate is determined and added as in the preceding procedure. The polarization of the uranyl compound is made in a tube with a tubulature, to which is attached a tube or bulb-tube to increase its capacity, as previously described. Into this tube, previously dried, a measured volume of the solution is placed and polarized. To the mixture in the tube is added from a burette (preferably of small diameter) in successive portions of 0.5 cc. each, either double normal potassium hydroxide or double normal acetic acid solution, according as the original mixture is too strongly acid or too nearly neutral or alkaline, mixing and polarizing after each addition. When the maximum rotatory activity is reached and exceeded, allowing for the increase in volume when comparing the readings, this maximum, computed for the volume before dilution, is used to calculate the per cent. malic acid as directed in the previous procedure. A suitable conservative quantity of liquid by this method is 25 cc. If the liquid used in polarizing before adding the uranyl acetate is poured back, 20 cc. of the solution may remain to be pipetted into another 25 cc. flask and there treated with uranyl acetate and made up to 25 cc.

Notes on the Above Method.—In the majority of solutions from natural products to be examined for malic acid, I consider this second method more advantageous. In exceptional cases where each addition of the reagent (especially of potassium hydroxide) causes a precipitate which has to be filtered off before polarizing, this method can, of course, not be applied unmodified. Such a case I had in a solution of acids from cane syrup, prepared by use of the lead salts, and without the previous removal of phosphoric and possibly other acids that may form a precipitate with uranyl compounds. By choosing a different means of separating the malic acid (see below) I could avoid this admixture and use this latter method in the polarizing. Where many such polarizations are to be made, I would deem it expedient to provide one's self with a polarization tube that has a fixed volume marked on a suitable neck of the tubulature, which might conveniently be 10 cc. (see Fig. 2). Above this neck should be a bulb large enough to hold about 10 cc. additional, with a short neck large enough to admit of wiping the bulb dry inside above the mark, and this neck should be provided with a close-fitting rubber stopper. With such a tube and sufficient of the solution to be polarized, the necessity of drying the tube is avoided in that it may be rinsed with a portion of the solution, then filled to the mark, wiping away any that may adhere to the inside walls above the mark.

2. *Procedure with Interfering Substances Present.*—Either of the above two general procedures, as shown by the preceding data, is applicable to a wide range of mixtures, yielding results very near the true value of the malic acid, when there is present even a considerable portion of such substances as the sugars, or acetic, lactic, succinic, citric, hydrochloric, nitric, or sulphuric acids. With certain other substances which interfere, or with very large amounts of these present there is necessary some preliminary operation to eliminate the interfering substances or to reduce the amount of foreign acids and neutral optically active substances. How most advantageously to make these separations and the details of any method will depend upon the nature of the accompanying substances, upon which of these it is desired also to determine, upon the apparatus and reagents available, and upon the urgency of economizing in sample, reagents, or time. What follows on this subject is meant rather in the way of data and suggestions than in the hope of describing in detail a method that will be the most advantageous for any wide range of natural products. In the next section will then be described, in detail, methods for syrups based upon the data.

From an excessive amount of sugars, of acetic or nitric acids, or of other bases, the malic acid may readily be separated as a lead salt and afterwards set free by hydrogen sulphide. The tartaric acid may be removed more or less nearly completely as the acid potassium tartrate, the calcium tartrate, or the barium tartrate. To test the efficiency of several proposed methods for separating malic acid from sugar (in syrups, cane juice, etc.) and to work out the details of methods, I carried out a series of tests on its precipitation as lead, barium, and calcium salts with various amounts of alcohol.

It is generally assumed by analysts and writers of text-books on organic analysis that lead acetate or subacetate, and a volume of alcohol equal to that of the original solution, would precipitate quantitatively a group of organic acids, including malic acid. A series of tests made by me does not bear out this assumption, and the loss is especially great, 18 per cent., with sugar solutions. S. H. Ross,[1] in his study of the Winton "lead number" method of distinguishing between pure and adulterated maple products, also noted a tendency of sugar solutions to hold back lead. He proposed to "correct the solvent action of the sugar" by the addition of a small quantity of potassium sulphate. I find that with the addition of the proportion of potassium sulphate recommended by Ross, and lead-subacetate in limited quantity, but more than enough for the malic acid present, the loss of malic acid increases to 67.2 per cent. when no alcohol is used, and 38.5 per cent. when 1.8 volumes of alcohol is used. These facts suggest that probably in the experiments of Ross the potassium sulphate improved the results, not by correcting the incomplete precipitation of certain constituents of the syrup, but rather by compensating for it, and that therefore a numerical

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[1] *Circular* **53**, Bureau of Chemistry, U. S. Dept. of Agr., p. 8.

addition to the results, corresponding to the solubility of the lead precipitate in a sugar solution of equal strength, would answer the purpose quite as well.

For complete precipitation of malic acid from sugar solutions with lead acetate or subacetate, more alcohol is needed than an equal volume. 3.6 volumes of 95 per cent. alcohol with an excess of lead acetate (27.8 grams sugar, 35 cc. water, 0.1605 gram malic acid, 1.5 cc. lead acetate solution of specific gravity 1.25, and 125 cc. of 95 per cent. alcohol) effected an almost complete (98 per cent.) precipitation of the lead malate, as determined by the polariscopic method after liberating the acid from the lead by means of hydrogen sulphide. The subacetate was found not quite so advantageous. In certain tests with maple syrup in which only one volume of alcohol was used in the precipitation with lead acetate, the results were 0.04 per cent. lower, thus showing a loss of about 7 per cent. of the malic acid present. In a series of tests with lead acetate as precipitant, having decreasing amounts of sugar, but with the sum of sugar plus water the same, the more dilute solutions showed the highest losses of malic acid.

Of calcium acetate and barium acetate in equivalent amounts and with like amounts of alcohol, the latter gave the more nearly complete precipitation, the results with the barium acetate and 14 volumes of 95 per cent. alcohol (27.8 grams sugar, 29 cc. water, 0.1537 gram malic acid, 8.3 cc. 16.2 per cent. barium acetate solution, and 414 cc. 95 per cent. alcohol) being apparently as good as those with lead acetate and 3.6 volumes of alcohol. In reality the precipitation with barium acetate in tests made was probably more nearly complete than that with the lead, the low results being accounted for in the slight depressing effect of the byproduct, potassium acetate, which was present when polarizing the uranium-malic-acid compound. However, the recovery by either method is sufficiently near complete to serve ordinary practical purposes. Either method would effect a separation with but insignificant loss, of malic acid from sugars or nitric and acetic acids. By the barium acetate method of precipitation and subsequent solution in water we may at the same time separate it from hydrochloric and lactic acids, which would not be precipitated; from sulphuric, phosphoric, or oxalic acids, whose barium salts are insoluble in water; and from interfering excesses of succinic and citric acids, whose barium salts are difficultly soluble in water. If much tartaric acid were present, it would mostly be separated in the same operation. Similar advantages for separation from these other acids are possessed by calcium acetate. Tests with aconitic acid showed that its calcium salt is soluble in cold water but is precipitated almost completely by the addition of an equal volume of alcohol, while calcium malate solutions of strengths up to 0.25 per cent. were not precipitated by the addition of an equal volume of alcohol.

Tests on the precipitability of tartaric acid as a calcium salt, by the addition of an equal volume of alcohol, showed that when exactly neutralized with calcium hydrate, using phenolphthalein as indicator, then an excess of calcium acetate and an equal volume of absolute alcohol added, there remained in 100 cc. of the supernatant liquor after standing over night 0.0076 gram calcium tartrate, equivalent to 0.0060 gram tartaric acid.

If this method of separating malic acid is applied to mixtures including tartaric acid, approximate corrections in the subsequent polarizations of the malic acid before and after the addition of uranium for the traces of tartaric acid would be 0.01 and 0.3 degree Ventzke, respectively, to be subtracted from P and P′ in the formula, for every 100 cc. of the 50 per cent. alcoholic filtrate finally concentrated into 50 cc. for polarizing.

III. SEPARATION OF MALIC ACID FROM CANE AND MAPLE SYRUPS AND SUGARS AND ITS DETERMINATION BY THE POLARISCOPIC METHOD.

Based upon the data in the preceding sections and upon further facts developed in the examination of syrups as reported below, I recommend either of the following two methods:

1. Lead Acetate Method.—Determine the acidity of the sample by diluting 5 cc. of it with water, adding phenolphthalein, and titrating with 0.1 N alkali. Weigh out 50 grams of the syrup (or $33^1/_3$ grams of sugar, adding to it $16^2/_3$ cc. additional of water). Add to it the necessary amount, as previously determined, of normal or double normal alkali to neutralize the acidity and enough water to make with the added alkali solution 15 cc. After mixing thoroughly (or dissolving in case of sugar), add 10 cc. of lead acetate solution of specific gravity 1.25. Add 150 cc. neutral 95 per cent. alcohol. Shake thoroughly and set aside for three hours or more. Carefully decant the clear supernatant liquor through a suction filter of a diameter of not less than 7 cm. Remove the clear decanted filtrate from the filtration flask, then bring the precipitate itself onto the filter. After it runs clear, pour back onto the filter what at first ran through cloudy and rinse the filtration flask with some of the decanted clear liquor, returning the rinsings onto the filter, then continue the filtration, finally rinsing the precipitation flask and precipitate a few times with 75 per cent. alcohol. Thorough washing is unnecessary. Return the precipitate and filter into the precipitation flask, heat with some water, and shake to disintegrate the precipitate, then treat with hydrogen sulphide to convert the lead into lead sulphide. Repeat the heating and shaking and the treatment with hydrogen sulphide, if necessary, until the whole of the precipitate is acted upon. The precipitate tends to cake during filtration, often causing difficulty in disintegrating it, so that it will be acted upon by the hydrogen sulphide. Filter hot and wash with hot water containing some hydrogen sulphide. Concentrate the filtrate on the water bath to about 30 cc., transfer to a 50 cc. flask and make up to the mark. Determine in this solution the malic acid according to either of the methods given in Section III, Division 1, of this report. Use about 0.7 gram uranyl acetate with 20 cc. of this solution.

Notes on this Method.—(*a*) If the solution is too dark colored to polarize in the 20 cm. tube, either before or after the addition of the uranyl acetate, use a 10 cm. tube or dilute a portion. In four samples of maple syrup which I examined, three of which were unusually dark, I was able to polarize any of them in the 20 cm. tube without further dilution than here planned. In a sample of very dark cane syrup I had to use the 10 cm. tube in order to be able to polarize it. With ordinary light colored syrups or sugars the solution might safely be made twice as strong, *i. e.*, the acids from 50 grams syrup concentrated into 25 cc.

(*b*) If the analyst does not object to the greater care necessary in working with smaller volumes, he can very well make the determinations with only 25 cc. of solution, in which case half the above quantities of substance and of reagents will suffice, thus saving time in filtering.

(*c*) The 0.7 gram uranyl acetate is deemed a safe margin of excess for 20 cc. of the above strength solution of acids from maple or cane syrups. It is twice the theoretical amount needed, if the syrup has 0.50 per cent. malic acid, and if the uranyl acetate has 51.56 per cent. uranium.

(*d*) Where no acids other than those separated from maple products need be expected, the titration of an aliquot part of the solution of the acids may be omitted, since maple products do not yield any interfering strong mineral acids. The cane syrups, however, which I examined had considerable phosphoric and some sulphuric acid, hence the solutions required some alkali for the maximum rotatory power. Because of these, it was more advantageous with cane syrup to use the second method of separating the malic acid, to be described in the next paragraph.

2. *Barium Acetate Method.*—Determine the acidity as in the lead acetate method. Weigh out 25 grams of syrup (or $16^2/_3$ grams sugar, adding to it $8\ ^1/_3$ cc. additional of water). If the acidity was more than a trace, about neutralize with the required amount of powdered barium hydroxide, avoiding an excess (0.0157 gram $Ba(OH)_2 + 8aq.$ for every 1 cc. 0.1 *N* alkali required by the 25 grams of syrup). Add 7.5 cc. 20 per cent. barium acetate solution. Mix and dissolve the barium hydroxide (and the sugar in case a sugar is analyzed). Now add 220 cc. 95 per cent. neutral alcohol and warm on the water bath to incipient boiling, in a flask (preferably Erlenmeyer) provided with a reflux air-condenser, until the precipitate settles readily and the supernatant liquor is clear or nearly clear. About one hour suffices. Decant carefully as far as possible the hot liquor through a filter. Dilute the liquid remaining with some of a hot mixture of 1 part water to 14 parts 95 per cent. alcohol and bring it upon the filter. Rinse as rapidly as possible the precipitation flask and the precipitate three or four times with this strength alcohol (thorough washing is unnecessary), then return the precipitate together with the filter to the precipitation flask, dissolve in about 20 cc. hot water, filter, and wash with hot water. To the filtrate add 1 cc. double normal acetic acid, then concentrate to about 10 cc. Add 2 cc. additional of double normal acetic acid, transfer to a 25 cc. flask, filtering if necessary, and make up to the mark. Determine the malic acid by the second of the methods described in Section III, Division 1, of this report, adding more acetic acid, if necessary for the maximum rotatory power.

Notes on the Latter of the Above Methods.—(*a*) As already noted, this method effects also the separation of the sulphuric and the phosphoric acids, which are likely to occur in cane syrup.

(*b*) The smaller amount of material, 25 grams, is here recommended in order to save alcohol and time in filtering, but if preferred, more liberal quantities may be used, say 50 grams, making up the solution for polarizing also to 50 cc. The first filtering is advantageously accomplished by use of a long-stemmed hot-water funnel. A very efficient hot-water funnel may be improvised by putting a small long-stemmed funnel inside a larger short-stemmed funnel, with hot water in the outer funnel, siphoning off the water from time to time and replacing with hot water. If the alcoholic liquor is allowed to cool, it may yield crystals of sugar, which are then difficult to dissolve in the alcoholic wash liquor.

(*c*) It should be noted that the alcohol for any of these separations should be neutral. The commercial 95 per cent. alcohol is sometimes contaminated with free (volatile) acids to such an extent as to make it necessary to neutralize (conveniently with sodium carbonate) and redistil before using.

(*d*) Care should be exercised not to render the liquid alkaline, as this would be conducive to developing highly colored decomposition products out of the sugars. For the same reason it is best to acidify the water solution of the barium salts before concentrating, and for the additional purpose, that the main part of the sucrose remaining may be inverted so that it will not undergo a change in optical activity during the interval between the polarization without and with the uranium.

(*e*) According to the results in Table II, the polarizations in the presence of the barium compounds are a little low. This suggests that the results might be improved by introducing a correction factor of about 1.03.

3. *Results from Some Cane and Maple Syrups.*—Malic acid was separated from two samples of cane and four authenic samples of maple syrups by both the lead acetate and the barium acetate methods and estimated polariscopically by the second method given. The results are set forth in Table V.

The clarification of Cane Syrup I was accomplished with sulphur dioxide, followed by liming back to near neutrality. At the time of making these tests it had undergone a slight fermentation. Maple Syrup IV was produced from the sap of soft maple trees; the others from sap of hard maple trees. A partial clarification was effected in the manufacture of the maple syrups by mixing an egg or the white of an egg to every four or five gallons of thin syrup, then skimming off after coagulation during boiling. The syrups had been freed by decantation from the so-called "sugar sand" which is always formed in the concentration of the sap. After the separation of the acids from the samples of maple syrup by the lead acetate method, the free acids required no further neutralization to secure the maximum rotatory activity of the uranium compound, there being no strong mineral acids present.

TABLE V.—MALIC ACID DETERMINATIONS IN CANE AND MAPLE SYRUPS AND IN MIXTURES OF THESE.

Syrup and its source.	Degrees Brix.	Per cent. sucrose, single polarization.	Apparent purity (per cent.).	Color.	Per cent. malic acid. By lead acetate method.	Per cent. malic acid. By calcium acetate method.
Cane I, La. Sugar Experiment Station..........	67.3	53.3	79	Dark	0.04[1]	0.04[1]
Cane II, Local Manufacturer	71.5	54.4	80	Medium	0.01	0.02
Maple I, A. H. Miller, Goshen Ind..................	68.7	60.0	90	Light	0.46	0.49
Maple II, M. A. Yoder, Middlebury, Ind...........	68.2	61.0	89	Dark	0.29	0.32
Maple III, M. A. Yoder, Middlebury, Ind...........	....	70.8	..	Dark	0.25	0.26
Maple IV, D. R. Yoder, Goshen, Ind...............	....	34.0	..	Dark	0.53	0.51
Mixture, 1 part Cane I and 1 part Maple I..........	....	....	..	....	0.26	0.26
Mixture, 3 parts Cane I and 1 part Maple I...........	....	....	..	....	0.13	0.13

4. *Detection of Adulterations of Maple Products by the Determination of the Malic Acid by this Polariscopic Method.*—Since the maple products are distinguished by a relatively high percentage of malic acid (0.26 per cent. to 0.53 per cent. in the samples examined), we have by its determination a chemical means of distinguishing it from such substances as cane syrup or impure cane sugar, and to the extent that we can establish a normal by the examination of many samples of maple syrup or sugar from various sources; to that extent we can use the results in judging of the purity of the product, as far as adulteration with pure sugars is concerned. Tests with mixtures of cane and maple syrups give results agreeing sufficiently nearly with the amount of malic acid calculated for the mixture to make it apparent that this method of examination will also afford us a means of determining approximately the proportion of each in a mixture of maple syrup or sugar of known malic acid content, and precipitate-forming substances having little or no malic acid, such as cane syrup or impure cane sugar. More work needs to be done on samples of maple syrup and sugar to ascertain whether such a normal can be established.

For comparison, the "malic acid value" was also determined in Cane I and Maple I syrups by precipitation with calcium acetate, ignition of the precipitate, and calculating the malic acid from the alkalinity of the ash. This gave for Cane I, 1.22 and for Maple I, 0.59. That the "lead number" by Winton's or Hortvet's method would also have been higher in the cane than in the maple syrup could be seen by the bulks of the lead precipitates formed in the procedure for separating the malic acid.

5. *Application of the Methods of Separation and Determination of Malic Acid to Other Products.*—Fresh apple juice and various other natural products are distinguished by their malic acid content. It is therefore probable that this method may be adapted to distinguishing these from their imitations and adulterations. In many other natural products no reliable differentiations have been made of the organic acids present, and it is not improbable that now, with a more delicate method at hand for detecting and determining malic acid, its presence or absence, and its quantity in these may be ascertained and may be found to be a useful means of identifying them or distinguishing between them.

IV. A SIMILAR POLARISCOPIC METHOD FOR THE ESTIMATION OF TARTARIC ACID.

A similar method for tartaric acid can evidently be based upon the change produced in its rotatory power by uranyl compounds. Basing formulas for calculating the per cent. tartaric acid in the solutions polarized upon the specific rotatory powers as found in these experiments, for white light and quartz compensation, *viz.*, $[\alpha]^{27.5} = 16.3$ for the free acid and $[\alpha]^{27.5} = 453$ for the same converted to the uranium compound, using the Ventzke scale,

$$\text{Per cent. tartaric acid} = \frac{P' - P}{25.16 \times {}^{1}/_{2}L}.$$

V. DETERMINATION OF TARTARIC AND MALIC ACIDS IN A MIXTURE OF THE TWO.

Evidently, if in a mixture of these two acids another value besides the rotatory power can be determined, we have the basis for calculating the amount of each present. Thus, if we can determine the total acidity in terms of normal acid due to these two acids and the change in its polarization by treatment with an excess of uranyl acetate, we may develop the formula to calculate the amount of each acid as follows:

Let x = grams malic acid in 100 cc. of the solution.

Let y = grams tartaric acid in 100 cc. of the solution.

Let n = total cc. normal alkali required to neutralize these acids in 100 cc. of the solution.

Let m = change in polarization in a 20 cm. tube in degrees Ventzke occasioned by the uranyl compound. Then

$$n = \frac{x}{0.06703} + \frac{y}{0.07503},$$

and if we take the rotatory power at 27.5° C., *i. e.*, a change of —29.27 in a 1 per cent. malic acid solution and a change of 25.16 in a 1 per cent tartaric acid solution, then

$$m = 25.16y - 29.27x.$$

From these two equations we derive

$$x = 0.03287n - 0.01741m, \text{ and}$$
$$y = 0.03824n + 0.01949m$$

VI. ACKNOWLEDGMENTS.

The foregoing investigation was commenced by me during my engagement with the Louisiana Sugar Experiment Station at Audubon Park, New Orleans, and later continued in private, and this report formulated, using by permission the data collected while in the service of the Experiment Station as well as those collected since. I wish also to acknowledge the faith-

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[1] Sample had started fermenting. An earlier test showed only 0.02 per cent. malic acid.

ful services of Mr. W. G. Taggart, assistant chemist, in carrying out under my direction some preliminary experiments in this problem, leading up to those here reported.

Present Address of the Author,
Bureau of Chemistry,
Washington, D. C.

COCONUT OIL OF HIGH IODINE VALUE.

By W. D. Richardson.

Received July 3, 1911.

Recently several shipments of alleged coconut oil were received by a large concern, and these shipments when analyzed gave iodine values of 18, 20, 24 and 21 respectively. A little later another shipment of alleged coconut oil was received by the same concern from another manufacturer, and this oil showed an iodine value of 20.

One of the principal chemical characteristics of the ordinary coconut oil of commerce, pressed from copra, is its low iodine absorption, the iodine number in a large number of instances being very close to 8 per cent. When, therefore, the high iodine values were found, in the cases of the shipments referred to, an investigation was started, which resulted in finding the cause of the high iodine values.

It was found that the oil in question came from two manufacturers, both located in the United States. Both of these manufacturers, upon being questioned, stated that their oil was pure coconut oil and that nothing but coconuts were used in its preparation. Upon being questioned further they both admitted that their oil was not pressed entirely from copra, but that considerable proportions of the waste material from desiccated coconut factories entered their presses. They stated that they used no unusual methods or extreme temperatures in the preparation of their oil and they failed to understand the reason for their oil showing different constants from the ordinary oil of commerce.

The waste material from the desiccated coconut factories consisted of parings of the rind from the coconut meats, and when this fact was ascertained it was thought best to procure some fresh coconuts and extract the oil from the meats and from the rind, in order to determine whether or not any difference in the oils from the two tissues existed. Accordingly a dozen coconuts were purchased, opened and the rind pared off from the meats. Both lots of the material were then dried separately at low temperatures and the oil extracted by means of ether. The following results were obtained:

	Iodine number. Per cent.	Titer ° C.
Oil extracted from the meats of coconuts....	8.90	23.3
Oil extracted from the rind..................	40.25	25.5

The other constants, such as saponification number, were found to be identical with those obtained in the case of the ordinary coconut oil of commerce. The titer, as shown by the above figures, is slightly higher in the case of the coconut oil from the rind. These figures plainly indicate a considerable difference in composition between the oil from the rind of the coconut meats and from the meats themselves. The rind is such a small percentage of the whole kernel that in all probability the oil derived from this source does not affect to any considerable extent the ordinary oil pressed from copra. On the other hand, when considerable quantities of parings are pressed, either separately or mixed with copra, the iodine value of the resulting oil is considerably increased.

These results are of importance inasmuch as the oils which would be most likely to be used for adulterating coconut oil, would have the same effect upon the ordinary coconut oil of commerce, as does the coconut oil from the rinds.

The present case appears to be another instance of the well-known phenomenon of vegetable physiology, that adjacent tissues in plants may contain oils of very different composition—a fact which is well exemplified in the case of palm oil and palm kernel oil.

The above results indicate that a coconut oil of relatively high iodine value is not necessarily adulterated by a foreign oil, although it can hardly be known as "coconut oil" in the ordinary commercial sense of the term, inasmuch as coconut oil has long been understood in commerce to mean an oil pressed from copra, that is, the whole dried coconut meat.

It was thought that the above facts were of sufficient interest to the oil and fat industries to warrant publication.

Laboratory of Swift & Company, Chicago.

DETERMINATION OF VANADIUM IN STEEL AND IRON.

By B. O. Crites.

Received June 7, 1911.

The determination of vanadium in steel carrying this element in amounts varying from 0.05 per cent. to 0.75 per cent. has been a problem commanding the attention of many of iron and steel chemists for several years.

The methods given in the earlier editions of books on iron and steel analysis have been found almost wholly impracticable and those appearing in the more recent literature have neglected to give any very comprehensive idea of their accuracy or limits of accuracy.

Realizing the difficulties involved in the estimation of rather minute quantities of vanadium in presence of large amounts of iron, it is not the intention of the writer to severely criticize the work of other chemists in their efforts to produce satisfactory methods, but it seems that a discussion of the subject might be of interest at least to chemists who have had only limited experience with this determination.

A method said to have been used by J. Kent Smith in his extensive work on vanadium was first tried by the writer, the method in brief which was as follows:

Four grams of steel were dissolved in sulphuric and nitric acids, the tungsten being separated by the usual methods if present. The nitric acid was expelled by evaporation to the appearance of sulphuric acid fumes, then after dissolving the salts in water, chromium and vanadium were oxidized with slight excess of potassium permanganate solution. After boiling, the excess of potassium permanganate was reduced with manganese sulphate, and the solution made up to a definite volume, filtered, and an aliquot part of the filtrate taken for titration—chromium being titrated with ferrous sulphate and potassium permanganate and finally the vanadium with ferrous sulphate and potassium bichromate. The principle underlying the method is that the vanadium is reduced by ferrous sulphate and oxidized by potassium permanganate in dilute solution but not by potassium bichromate.

After a number of attempts the method was finally abandoned. The end reaction being rather indefinite, there frequently was considerable doubt in the mind of the operator whether any vanadium was present or not.

A method described by Blair[1] was next tried. By this method the vanadium was separated from the iron by fusion with sodium carbonate and sodium nitrate, extraction of the vanadium with water and precipitation from slightly acid solution with mercuric oxide and mercurous nitrate. This precipitate was redissolved and the vanadium finally precipitated with ammonium chloride as directed. The results were unsatisfactory and this method was also abandoned.

The writer then endeavored to work out for himself the details of a method, suggested I believe by Roscoe, which might at least show whether vanadium really was present and the amount.

The method used was as follows:

Five grams of steel were dissolved in nitric acid which was then replaced by hydrochloric acid (tungsten being separated as usual if present) and an ether separation was made to separate the major portion of the iron; the vanadium in the water layer was separated from the iron remaining by large excess of sodium hydroxide, after first replacing hydrochloric with nitric acid. The caustic mixture containing precipitated iron was made up to a definite volume and an aliquot part of the filtrate containing the vanadium acidified and the vanadium precipitated by lead acetate and sodium acetate. The lead vanadate in turn was filtered off, dissolved in hydrochloric acid and evaporated to the appearance of fumes after adding a few cubic centimeters of sulphuric acid. Lead sulphate was filtered off and the vanadium in the filtrate was titrated with $N/100$ potassium permanganate solution.

In order to test its accuracy a standard solution of vanadium was prepared from divanadyl tetrachloride obtained from Eimer & Amend. The solution was standardized as follows:

The contents of a $^1/_8$-ounce bottle of vanadium chloride (divanadyl tetrachloride), $2VO_2.4HCl.3H_2O$, containing 4.051 grams were diluted to 2000 cc.

Twenty cubic centimeters of this solution were withdrawn, 5 cc. strong sulphuric and 40 cc. strong hydrochloric acid added, the solution was boiled down till it fumed strongly, then cooled, diluted to 150 cc. with water, heated to 80° C. and titrated with standard potassium permanganate solution, of which each cubic centimeter was equal to 0.005 gram iron or 0.004578 gram vanadium.

Measured amounts of this solution were then added to plain carbon steel, also to chrome and molybdenum steel and the samples were carried through by the method as described, with the following results:

Vanadium added. Per cent.	Vanadium found. Per cent.	Difference. Per cent.
0.03	0.03	0.00
0.06	0.06	0.00
0.06	0.05	—0.01
0.13	0.12	—0.01
0.13	0.14	+0.01
0.26	0.22	—0.04
0.26	0.24	—0.02
0.26	0.19	—0.07
0.10	0.09	—0.01
0.10	0.08	—0.02
0.10	0.07	—0.03
0.10	0.08	—0.02
0.10	0.10	—0.00
0.10	0.07	—0.03

Attempts to apply the method on samples to which over 0.30 per cent. vanadium was added showed decidedly low results. In such cases it was necessary to fuse the sodium hydroxide precipitate with sodium carbonate and potassium nitrate and determine the vanadium in the water extract, thus complicating the method. While not entirely satisfactory, the results were a very considerable improvement on anything obtained so far by other methods used.

Several months later Blair[1] published a method along somewhat similar lines but with a number of improvements and changes. He made two separations with ether instead of one and omitted the separation of lead sulphate by filtration, this being found unnecessary; a stronger solution of potassium permanganate was also used for the titration. After some practice with the method it was adopted as the best tried so far. The method even in its improved form was still somewhat lengthy and required considerable care in order to obtain anything approaching accurate results. A few of the results obtained are as follows:

Sample.	Vanadium added. Per cent.	Vanadium found. Per cent.	Difference. Per cent.
Carbon steel..................	0.75	0.78	+0.03
Chrome nickel steel............	0.28	0.25	—0.03
Chrome tungsten steel.........	0.195	0.18	—0.015

The principal difficulty was in the analysis of high chromium steels; the chromium seemed to be very difficult to precipitate completely and would often be carried into the vanadium filtrate and thus complicate matters; also, small quantities of organic matter, probably from the filters used seemed to affect the results. These difficulties, of course, could be overcome, but they required considerable care.

C. M. Johnson published a method[2] about this time which was somewhat on the principle of the method used by J. Kent Smith, and described in the beginning of this paper. He omits, however, the use of manga-

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[1] "Chemical Analysis of Iron and Steel," 6th Ed., p. 202.

[1] *J. Am. Chem. Soc.*, **30**, 1229 (1908).

[2] "Chemical Analysis of Special Steels, etc."; p. 8.

nese sulphate to remove excess of potassium permanganate and uses potassium ferricyanide in the solution instead of externally as an indicator. In the judgment of the writer, this is the most practical method available at present. The method as used in our laboratory is practically the same described by Johnson. Two grams of steel are dissolved in dilute sulphuric acid, heated with nitric acid, until the insoluble becomes a bright yellow, if tungsten be present, otherwise simply to oxidize the iron. The solution is diluted, brought to boiling and 3 per cent. potassium permanganate solution added until precipitate of manganese oxide remains after 20 minutes' boiling. This is very important, otherwise low results will be obtained. After cooling, the solution is filtered through asbestos[1] into heavy suction flasks and residue is washed with minimum quantity of very dilute sulphuric acid. The volume of the filtrate must not exceed 300 cc. The end reactions in the titrations to follow will be indefinite if solution is too dilute. The filtrate must be perfectly clear.

The titration of the chromium is the next operation; this is conducted as described by Johnson but it is important to add the standard potassium permanganate until an unmistakable pink persists after 30 seconds' stirring. The oxidation of the vanadium is sometimes a little slow at this point and permanganate must be added till the operator is certain there is a slight excess. The writer uses a solution of potassium permanganate, each cubic centimeter of which is equal to 0.005 gram iron. *N*/10 ammonium ferrous sulphate is used.

The calculation for chromium is as follows:

cc. $KMnO_4$ equal to $FeSO_4$ required for reducing chromium × 0.005 (Fe value) × 0.311 ÷ 2 × 100 equals per cent. chromium.

The volume of the solution now ready for vanadium titration must not be over 350 to 375 cc. One cubic centimeter of a solution of potassium ferricyanide containing 0.020 gram of the salt in 20 cc. of water is added, then standard ammonium ferrous sulphate (same as used for chromium) till the end point is reached. It is well from time to time, during the titration, to add a drop or two of the indicator and note whether a green coloration is produced at a point where the drop mixes with the solution.

A blank should always be run on a steel of similar composition to the sample but without vanadium, and proper deduction made. A standard steel of composition similar to the sample, and to which a definite amount of standard vanadium solution has been added, should also be carried along with the unknown.

Inasmuch as the method described above shows accurately the amount of chromium present in the sample, and separate nickel determination, if nickel be present, can readily be made by the dimethylglyoxime or other of the well-known methods, there is usually no difficulty in preparing synthetic standards and blank of composition similar to the sample under examination, at least sufficiently close for the purpose.[1]

Sample calculation for vanadium:

10 cc. $FeSO_4$ diluted with H_2O and titrated with $KMnO_4$ required 8.5 cc.

1 cc. $KMnO_4$ = 0.005 gram Fe = 0.004578 gram Va.

Blank required 0.7 cc. $FeSO_4$.

Sample required 2.3 cc. $FeSO_4$.

2.3 — 0.7 = 1.6 cc. $FeSO_4$ required for the vanadium.

1.6 × 0.85 = 1.36 cc. $FeSO_4$ (corrected) required for vanadium.

$$\frac{1.36 \times 0.004578 \times 100}{2} = 0.31 \text{ per cent. vanadium.}$$

0.31 per cent. + 5 per cent correction = 0.325 per cent. vanadium.

A few of the results obtained are given below. There seems to be a tendency towards low results, especially in the higher figures. This may be due to a secondary reaction referred to by W. F. Bleeker[2] in his article on vanadium. "If a solution of hypovanadic acid or its salts be added to a solution containing ferric iron, the presence of ferrous iron is immediately observable. According to this we should expect low results, owing to the mass action of the reduced vanadium upon the ferric iron, giving a test for ferrous iron before the vanadium is all reduced."

The results obtained by the writer were about 5 per cent. low. However, if this correction of 5 per cent. is made, a very fair agreement is found. The method is quickly carried through and the end points are sharp.

Sample.	Added vanadium. Per cent.	Found vanadium. Per cent.	Difference. Per cent.	Corrected by 5 per cent. Per cent.
Plain carbon steel.............	0.11	0.123	+0.013	0.129
+0.11 per cent. vanadium......	0.11	0.123	+0.013	0.129
Carbon steel..................	....	.....	......	.....
+1 per cent. molybdenum......	0.55	0.519	—0.031	05.44
+0.55 per cent. vanadium......	0.55	0.506	—0.044	05.31
Chrome nickel steel............	0.33	0.309	—0.021	0.324
+0.33 per cent. vanadium......	0.33	0.309	—0.021	0.324
Chrome tungsten steel..........	0.22	0.21	—0.01	0.22
+0.22 per cent. vanadium......	0.22	0.222	+0.002	0.233
Carbon steel..................	....	.....	....	....
+0.65 per cent. vanadium.....	0.65	0.63	—0.02	0.661
Carbon steel..................	....	.....	....	.....
+0.33 per cent. vanadium......	0.33	0.314	—0.016	0.329
Chrome steel..................	....	.....	....	.....
+0.46 per cent. vanadium......	0.46	0.46	0.00	0.483
Chrome tungsten steel..........	....	.....	....	.....
+0.529 per cent. vanadium.....	0.529	0.508	—0.021	0.533
Chrome tungsten steel..........	....	.....	......	....
+0.46 per cent. vanadium	0.46	0.42	—0.04	0.441

A number of tests were made by both the Blair and Johnson methods, with results as follows:

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[1] The asbestos should be previously prepared in quantity by ignition in a muffle and washing with water.

[1] In this connection it might be well to call attention to the method described by N. M. Randall (*Met. Chem. Eng.*, **8**, 17 (1910)). for quick estimation of chromium in chrome steels and chrome nickel steels and also the method of H. Wdowiszewski (*Chem.-Ztg.*, **34**, 1365) (*C. A.*, **5**, 1378) for chrome in chrome tungsten steels. Both of these methods give excellent results in a remarkably short time.

[2] *Met. Chem. Eng.*, **9**, 209 (1911).

Sample.	Blair method, vanadium. Per cent.	Johnson method, vanadium. Per cent.	Difference Per cent.	Johnson corrected by 5 per cent. vanadium. Per cent.
Chrome tungsten vanadium steel.	0.29	0.287	0.003	0.301
Vanadium steel	0.25	0.208	0.042	0.218
	0.25	0.225	0.025	0.236
Vanadium steel	0.25	0.225	0.025	0.236
	0.25	0.225	0.025	0.236
Chrome tungsten vanadium steel.	0.75	0.705	0.045	0.74
	0.76	0.72	0.04	0.756
Vanadium steel	0.61	0.60	0.01	0.63

Other methods, such as Campbell and Woodham's,[1] in which iron is largely separated from vanadium by converting iron into ferrous sulphate and crystallizing out with strong alcohol and methods described by Auchy[2] were either not as readily applicable as the Johnson method or were not successful in the writer's laboratory. Colorimetric methods, such as described by Slawik,[3] were also unsuccessful.

The Johnson method may be used for the determination of vanadium in iron if it be modified to the extent of fusing with alkali carbonate and a little nitrate, the graphite and silica left insoluble when the iron is dissolved, on account of their tendency to carry vanadium. A blank and standard of similar composition should also be run.

Results on vanadium in iron by Johnson's method (modified).

	Per cent. added. Vanadium.	Per cent. found. Vanadium.	Per cent. Difference.	Per cent. Corrected.
Cast iron	0.22	0.21	0.01	0.22
Malleable iron	0.23	0.21	0.02	0.22

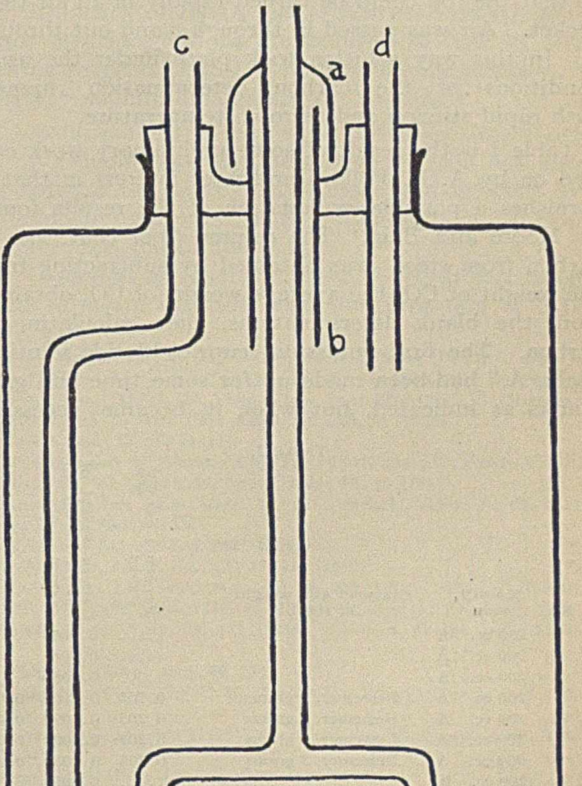
LABORATORY OF OSCAR TEXTOR,
CLEVELAND, O.

THE LOSS OF CARBON DURING SOLUTION OF STEEL IN POTASSIUM CUPRIC CHLORIDE.

By HELEN ISHAM.

Received May 22, 1911.

In a previous article[4] the author, in collaboration with J. A. Aumer, undertook a comparison of the methods for the determination of carbon in steel by direct combustion, and by solution in acidified potassium cupric chloride solution and combustion of the residue. The results led to the conclusion that the direct combustion method afforded values averaging 0.004 per cent. higher than the solution method and that there remained in the burned steel an amount of carbon equivalent to 0.003 per cent. carbon in the original steel, making a total difference of 0.007 per cent. carbon by the two methods, a variation which might well be ascribed to experimental errors. At the same time Moore and Bain[5] published some results on the solution method tending to show that during the solution of steel in potassium cupric chloride solution there is a loss of carbon as gaseous hydrocarbons amounting to 0.04–0.05 per cent. in the steel, or between 7.6 and 3.4 per cent. of the total carbon. Their work consisted in dissolving 3 gram samples of steel, of 0.653 and 1.18 per cent. carbon, in potassium cupric chloride solution at 65° C., passing purified air through the solution as the reaction took place, then through a furnace, and collecting the CO_2 as $BaCO_3$, and determining as $BaSO_4$. The fact that practically the same amount of hydrocarbon gases were evolved from steel of widely varying carbon content, and the fact that comparison of the two methods carried on in this laboratory, taking into account all possible sources of error, had shown a discrepancy which at the greatest was only one-fifth as great as the loss claimed by these investigators to occur when steel is dissolved in potassium cupric chloride, has led the author to repeat that part of the work reported in the first article in which no loss of carbon was found during solution of the steel. The results have shown conclusively that an error amounting to 0.05 per cent. carbon in the steel is out of the question, that the loss is at the most less than 0.01 per cent. carbon in the steel and is in all probability to be explained by difficulties in manipulation and weighing, and that the results of Moore and Bain were in error because of gaseous carbon compounds in the potassium cupric chloride which are evolved at a



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[1] *J. Am. Chem. Soc.*, **30**, 1233 (1908).

[2] THIS JOURNAL, **1**, 455 (1909).

[3] *Chem.-Ztg.*, **34**, 648.

[4] *J. Am. Chem. Soc.*, **30**, 1236 (1908).

[5] *J. Soc. Chem. Ind.*, **27**, 845 (1908).

faster rate when the steel is reacting with the solvent than when air is passing through the solvent alone as in the blank tests. The fact that Moore and Bain used an acidified solution of potassium cupric chloride with nothing in the chain to remove HCl carried from the solution by the current of air may account for the small amount of CO_2 found in the blank runs.

The work as performed in this laboratory has consisted in passing a current of purified air through potassium cupric chloride solution in which the steel was dissolving at room temperature and with constant stirring, then through a combustion furnace, drying it with H_2SO_4 or $CaCl_2$, then absorbing the CO_2 in soda lime tubes. The apparatus used consisted of a chain arranged in the following order: 1, a combustion furnace filled with CuO and heated to redness; 2, a wash bottle filled with KOH (2 : 1); 3, a special bottle in which the solution of the steel took place; 4, a second combustion furnace half filled with CuO, the last half being filled with $PbCrO_4$ and a coil of Ag wire; 5, a drying agent, either conc. H_2SO_4 or $CaCl_2$; 6, soda lime and $CaCl_2$ tubes for the absorption of CO_2; and 7, a safety of $CaCl_2$ or H_2SO_4. The bottle in which the solution took place was fitted with a cork and stirring rod as shown in the figure. The "hood" *a* on the stirring rod dipped into mercury contained in the cup formed by the stopper and the wide glass tubing *b* so that the rod could be turned rapidly in an air-tight socket. Air was passed in through *c* and out through *d*. In this way solution took place under the usual conditions of the carbon determination, namely with rapid stirring and at room temperature.

Table I is the result of some preliminary work carried on by A. R. Pollard and is of interest in that it furnishes a possible explanation of the results found by Moore and Bain. The column "per cent. loss of carbon from steel" was obtained by subtracting from the weight of CO_2 the average weight of CO_2 obtained from the blank determinations, then calculating to carbon. The first potassium cupric chloride solution, "soln. A," had been made up for some time and gave blanks as indicated, but when it became necessary to make up a new solution, "soln. B," the first blank on that solution gave a very large gain in weight and it was only after air had been passed through the solution for 24 hours that the blanks recorded were obtained. The results indicate a loss of carbon of the same order as that reported by Moore and Bain.

TABLE I.

No.	K_2CuCl_4 soln.	Nature[1] and weight of steel.	Per cent. carbon in steel.	Gain in weight of KOH due to CO_2. Gram.	Per cent. loss of carbon from steel.
1	200 cc. A		.....	0.0045	.....
2	200 cc. A		.....	0.0046	.....
3	200 cc. A		.....	0.0050	.....
4	200 cc. A	Bessemer, 5 grams	0.203	0.0100	0.029
5	200 cc. A	Bessemer, 5 grams	0.203	0.0090	0.023
6	200 cc. A	Bessemer, 3 grams	0.203	0.0080	0.030
7	200 cc. A	Bessemer, 3 grams	0.203	0.0080	0.030
8	200 cc. B		.....	0.0032	.....
9	200 cc. B		.....	0.0037	.....
10	200 cc. B		....	0.0035	.....
11	200 cc. B	Basic open hearth, 3 grams	1.048	0.0070	0.033
12	200 cc. B	Basic open hearth, 3 grams	1.048	0.0073	0.035
13	200 cc. B	Basic open hearth, 3 grams	0.608	0.0060	0.024
14	200 cc. B	Basic open hearth, 3 grams	0.608	0.0062	0.025

[1] The iron and steel samples used were those prepared by the Bureau of Standards, and the carbon content given is the average reported by the Bureau of Standards.

Table II shows the results of dissolving steel in acidified potassium cupric chloride solution which is free from gaseous carbon compounds. The solution was made according to the proportions given by Dudley,[1] one pound of crystallized salt being dissolved in 1.3 l. of water and, after air had been blown through the solution for three to four days, 100 cc. conc. HCl added. It was found necessary to continue blowing air through the solution for as much as three days to completely remove the carbon gases, the identification of which has not been attempted. In all cases, those in which no steel was dissolved as well as the others, the solution was stirred vigorously and continuously at about 25° C. In the cases where steel was dissolved the solution was complete in the time specified. The absorption tubes were weighed against tares which were given the same treatment as the tubes except that they were not connected with the chain during a determination.

TABLE II.

No.	K_2CuCl_4 soln.	Nature and weight of steel.	Per cent. carbon in steel.	Change in wt. of soda-lime tubes. Gram.	Duration of run. Hrs.
1	200 cc. C		.....	+0.0011	2
2	200 cc. C		.....	+0.0004	2
3	200 cc. C	Bessemer, 5 grams	0.206	+0.0002	3
4	200 cc. C		.....	—0.0007	1 1/2
5	200 cc. C	Bessemer, 5 grams	0.441	+0.0007	2
6	200 cc. C	Basic open hearth, 5 grams	0.834	+0.0001	3
7	200 cc. C	Basic open hearth, 5 grams	1.048	—0.0006	2
8	200 cc. D		.....	+0.0003	1 1/2
9	200 cc. D	Basic open hearth, 5 grams	1.048	—0.0002	2
10	200 cc. D		.....	+0.0003	3
11	200 cc. D	Bessemer, 5 grams	0.441	—0.0005	2 1/2
12	200 cc. D	Iron C, 5 grams	3.26	—0.0004	2
13	200 cc. D	Iron A, 5 grams	3.67	+0.0001	2

After the first blank, showing a gain of 0.0011 gram in the weight of the soda lime tubes, air was passed through the solution for 12 hours and a second blank determination made which was considered within the limits of accuracy of weighing. The greatest difference between a blank and solution is found in experiments Nos. 4 and 5, and the total difference, 0.0014 gram CO_2, amounts to 0.008 per cent. carbon in the steel. In all other cases the difference between the blank and the solution varies between +0.0008 and —0.0008 gram, the average change in weight of the soda lime in blank runs (omitting No. 1) being +0.0001 and in the determinations in which solution was taking place —0.0001, a result which seems clearly to indicate that there is no evolution of gaseous hydrocarbons during the solution of steel in potassium cupric chloride.

Between Nos. 7 and 8, Table II, the H_2SO_4 (No. 5 in the chain) was replaced by $CaCl_2$ which had been

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[1] *J. Am. Chem. Soc.*, **15**, 533 (1893).

saturated with CO_2. The two iron samples, Nos. 12 and 13 have total carbon as shown in the table; iron C has 0.58 per cent. and iron A 0.77 per cent. combined carbon.

The results obtained have been so entirely uniform that it was deemed unnecessary to continue the work further, and the conclusion reached is that the apparent loss of carbon during solution of steel in potassium cupric chloride at ordinary temperatures is due to gaseous carbon compounds present in the reagent and not to the formation of such from the carbon in the steel. There is no appreciable loss of carbon from the steel.

In the previous article the authors promised further work on the determination of sulphur by direct combustion of steel and evolution of sulphur dioxide and trioxide. All efforts to bring the process to a satisfactory method for the determination of sulphur have failed, because, apparently, the sulphur will not burn out completely from so large an excess of iron.

CHEMICAL LABORATORY, UNIV. OF ILLINOIS,
URBANA, ILL.

CONTRIBUTIONS TO THE CHEMISTRY OF ANAESTHETICS, III: NITROUS OXIDE.[1]

By CHARLES BASKERVILLE AND RESTON STEVENSON.

Received May 25, 1911.

One of the first outcomes of the establishment of the Pneumatic Institute may be given in the historical sentence of Davy, who breathed "dephlogisticated nitrous air" (nitrous oxide), recorded his sensations and the behavior of others after the inhalation: "As nitrous oxide in its extensive operation appears capable of destroying physical pain, it may probably be used to advantage during surgical operations in which no great effusion of blood takes place."[2] In 1844, Drs. Colton and Wells demonstrated this use in dental surgery. It is now used extensively, alone or with other anaesthetics, in general surgery.

This communication records the results of an examination of commercial nitrous oxide, supplied on the American market for anaesthetic purposes, and it presents a new method for the quantitative determination of nitrous oxide.

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A. BIBLIOGRAPHY.

(a) *Preparation.*

1. *Heating NH_4NO_3.*—In 1793, Deimann, von Troostwyer, Nieuwland, Bont and Louwernburgh prepared N_2O by heating NH_4NO_3, and in 1800 Davy[1] published his researches upon this gas. Others[2] have determined, for the decomposition of NH_4NO_3 by heat, the best conditions, such as apparatus, temperature, pressure, moisture, acidity, physical structure, and catalytics. Pelouze[3] prepared N_2O by heating $NH_4NO_3 + H_2SO_4$ to 150°.

2. *Heating Mixed Salts.*—To prevent the explosive formation of N_2O, and to employ cheaper constituents, Watson Smith[4] and others[5] have used the following mixed salts: $KNO_3 + NH_4Cl$; $NaNO_3 + NH_4Cl$; $Pb(NO_3)_2 + (NH_4)_2SO_4$; $NaNO_3 + (NH_4)_2C_2O_4$; $NaNO_3 + (NH_4)_3PO_4$; $2NaNO_3 + (NH_4)_2SO_4$ (especially). N_2O may also be prepared by the decomposition of ammonium nitrosulphate by hot water[6] or by heating NH_4Cl with dilute HNO_3 to 100°.[7]

3. *Reduction of HNO_3 and of Nitrates.*—In 1776, Priestley obtained N_2O by reduction of dilute HNO_3 by metals. Others[8] have shown that it may be made by reaction of the following constituents:

$HNO_3 + H_2O +$ Cu or Zn or Sn or Fe;
$HNO_3 + H_2SO_4 + H_2O +$ Zn or Sn;
$HNO_3 + HCl + SnCl_2$;
$KNO_3 + HCl + SnCl_2$;
$HNO_3 + SO_2$.

It is also found[9] when milk putrefies in the presence of nitrates.

4. *Reduction of HNO_2 and of Nitrites.*—HNO_2 and nitrites in acid solutions are reduced to N_2O by the following reagents: H_2SO_3,[10] hydroxylamine sulphate,[11] $Fe(OH)_2$,[12] sodium amalgam,[13] or $Na_2S_2O_3$.[14]

5. *Reduction of NO.*—In 1772, Priestley discovered N_2O by reducing NO by moist iron.[15] NO has also been reduced to N_2O by Gay-Lussac and others[16] by the following reagents: H_2S, sulphides, Zn, $FeSO_4$, SO_2, sulphites, $SnCl_2$, and NH_3.

6. *Oxidation of Hydroxylamine.*[17]—Hydroxylamine and its salts are oxidized with the formation of N_2O

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[1] Read before the New York Section, May, 1911.

[2] Davy, "Researches Chemical and Philosophical, Chiefly Concerning Nitrous Oxide or Dephlogisticated Nitrous Air, and Its Respiration," London, 1800.

[1] *Loc. cit.*

[2] Hare, *Am. J. Sci.*, **16**, 295 (1829); Porter, *Pharm. J.*, **11**, 62 (1869); Veeley, *J. Chem. Soc.*, August, 1883; *Phil. Trans.*, **1888**, 257; Cazeneuve, *J. Pharm. Chim.*, [5], **11**, 67; Thilo, *Chem.-Ztg.*, **18**, 532; U. S. Dispensatory, 1899; Lidoff, *J. Russ. Phys.-Chem. Soc.*, **35**, 59 (1903).

[3] *Compt. rend.*, **12**, 599 (1841).

[4] W. Smith and W. Elmore, Eng. Pat., 9,023, 1891; W. Smith, *J. Soc. Chem. Ind.*, **11**, 867 (1892); W. Smith, *Ibid.*, **12**, 10 (1893).

[5] Gronvelle, *Ann. chim. phys.*, **17**, 351; Pleischl, *Schw. J.*, **38**, 461; Soubeiran, *Ann.*, **28**, 59 (1838).

[6] W. Smith, *J. Soc. Chem. Ind.*, **1892**, 867.

[7] J. L. Smith, *Am. J. Sci.*, [2], **15**, 240 (1852).

[8] Gay-Lussac, *Ann. chim. phys.*, [3], **23**, 229 (1848); Millon, *J. Pharm. Chim.*, **29**, 179; Schiff, *Ann.*, **118**, 84 (1862); Fr. Mareck, *Jahresber.*, **1885**, 355; Basset, *Chem. News*, **53**, 172 (1886); Compari, *Compt. rend.*, **1888**, 1569.

[9] Schlössing, *Compt. rend.*, **66**, 237.

[10] Rudweber, *Chem. Centr.*, **38**, 22 (1867); Fremy, *Compt. rend.*, **70**, 61 (1870).

[11] Meyer, *Ann.*, **174**, 141 (1875); Guye and Bogdan, *Compt. rend.*, **138**, 1494 (1904).

[12] Dumreicher, *Wien Akad. Ber.*, **82**, 560(1880).

[13] Zorn, *Ber.*, **15**, 1258 (1882).

[14] Meyer, *Z. anorg. Chem.*, **34**, 49 (1903).

[15] See Priestley's "Experiments and Observations on Different Kinds of Air," Vol. I, p. 3; "Memoirs of Joseph Priestley to the Year 1795," 1803, 1.

[16] Gay-Lussac, *Ann. chim. phys.*, **1**, 394 (1816); Schiff, *Ann.*, **118**, 84 (1862); Kulhmoun, *Poly. J.*, **211**, 24 (1874); Gray, *Compt. rend.*, **89**, 410 (1879); Pelouze, *Ann. chim. phys.*, **60**, 162.

[17] V. Meyer, *Ann.*, **174**, 141 (1875); Donath, *Wien. Akad. Ber.*, **75**, 566 (1877); Guye and Bogdan, *Compt. rend.*, **138**, 1494 (1904).

by the following substances: $NaNO_2$, alkaline cupric solution, $Fe_2(SO_4)_3$, iodine, and $AgNO_3$.

7. *From the Air.*—It is claimed that air can be oxidized to N_2O in a tube heated either electrically[1] or by an oxyacetylene flame;[2] and it is claimed that in the presence of H_2 or NH_3 and an oxidizable metal (Cu, Fe, etc.), air, upon heating, forms N_2O, etc.[3]

(b) *Method of Analysis.*

1. *Decomposition into $N_2 + O_2$.*—Priestley decomposed N_2O into $N_2 + O_2$ by heat, and after him, others,[4] using, as sources of heat, gas-heated capillary Pt tube, electrically heated Pt wire, gas-heated porcelain tube, gas-heated Pt and Pd asbestos, silent electric discharge, or spark discharge. In all of these methods, however, it is claimed[5] that other oxides of nitrogen are formed.

2. *Burning with Hydrogen.*—Winkler[6] and others recommended the determination of N_2O by burning it with H_2 in a capillary Pt tube, etc. The reliability of this method has been questioned,[7] because of incomplete combustion and the formation of other oxides of nitrogen.

3. *Explosion with Hydrogen.*—Bunsen[8] used this method to determine N_2O, and after him others[9] decided the proper conditions for the best results. Hydrogen should be present to the extent of 2 or 3 times the volume of N_2O and the presence also of oxygen is recommended. The accuracy of this method has been questioned,[10] because of the formation of other oxides of nitrogen.

4. *Various Methods.*—These various methods have been recommended for the determination of N_2O: passing over ignited charcoal and absorption of the CO_2;[11] explosion with CO:[12] decomposition by electrically heated iron spiral:[13] passing over fused $Na_2CO_3 + Cr_2O_3$ and titration of the Na_2CrO_4 formed;[14] absorption in alcohol.[15]

(c) *Purification.*

Commercial N_2O is apt to contain these impurities: Cl_2, NO, NO_2, HNO_3, NH_3, HCl, CO_2, O_2, N_2, and rare gases of the air. It is purified by passage through solutions of NaOH, $FeSO_4$, and H_2SO_4. Further purification is accomplished by the formation of a hydrate[1] below 0° C. and heating this hydrate; by fractional condensation;[2] and by fractional distillation.

B. EXPERIMENTATION.

(a) *Methods of Analysis Used.*

The following impurities may be suspected in a cylinder of nitrous oxide gas:

1. Solids;
2. Liquids;
3. Gases and Vapors:
    H_2O;
    Halogen Acids, HNO_3, Organic Acids;
    O_3, NO_2, N_2O_3, SO_2;
    NH_3, Organic Bases;
    CO_2, Halogens, Oxides of Chlorine;
    HCN, $(CN)_2$;
    PH_3, SbH_3, AsH_3, H_2S;
    O_2, H_2, NO;
    CO, CH_4, Organic Matter;
    N_2, Rare Gases of the Air.

For these impurities, a qualitative search was first made and then, whenever necessary, a quantitative determination. The following systematic procedure was used.

Experiment 1.

Train:
Cylinder;
Trap + litmus + starch-KI papers;
P_2O_5 U-tubes (1) and (2);
$CaCl_2$ guard tube;
Moistener + litmus + starch-KI papers;
$Ba(OH)_2Aq$ (1);
Na(OH)Aq;
$AgNO_3Aq$;
Alk. Pyrogallol Aq;
2 $CaCl_2$ tubes;
CuO furnace;
$CaCl_2$ U-tubes (1) and (2);
$Ba(OH)_2$ Aq (2);
NaOH tube;
Gasometer.

By this experiment, any solids and liquids were caught in the trap and by the litmus and starch-KI papers tested for acids, bases, halogens and ozone. The moisture was determined quantitatively by the weighed U-tube containing P_2O_5 on glass wool and the accuracy of this determination checked by the second weighed P_2O_5 U-tube. The $CaCl_2$ protected the P_2O_5 tube from absorption of water from the moistener. This apparatus is the same as that used in the examination of oxygen and is shown in Fig. 1[3] in that communication; the gas enters at A, it then passes the wet porous cotton rope B which does not contain enough water to absorb the impurities from the gas, but moistens it enough to enable the impurities in it to react with test papers, and then the gas passes through cones C, D, E, of blue and red litmus and starch-KI papers, repeating the tests made before in the trap tube. The

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[1] Södermann, French Pat., 411,785, 1910.

[2] Pictet, French Pat., 415,594, 1910.

[3] Marston, Eng. Pat., 19,074, 1900.

[4] Berthelot, *Compt. rend.*, **77,** 1448 (1874); *Bull. soc. chim.*, [2], **26,** 101 (1876); *Compt. rend.*, **82,** 1360 (1876); Winkler, *Untersuchung der Industrie Gase*, 1877; Graham-Otto, *Lehrbuch der Chemie*; Lunge, *Ber.*, **14,** 2188; Kemp, *Chem. News*, **71,** 108 (1895).

[5] *Ibid.*

[6] Winkler, *Untersuchung der Industrie Gase*, 1877; Montmartini, *Atti Accad. Lincei*, **7,** II, 219 (1893); Classen, *Angewahlte Methoden*, 1903.

[7] Lunge, *Ber.*, **14,** 2188; Kemp, *Chem. News*, **71,** 108 (1895).

[8] Bunsen, *Gas analytische Methoden*, 1877.

[9] Winkler, *Untersuchung der Industrie Gase*, 1877; Dumreicher, *Wien Akad. Ber.*, **82,** 560 (1880); Hempel, *Ber.*, **15,** 903 (1882).

[10] Lunge, *Ber.*, **14,** 2188.

[11] Winkler, *Untersuchung der Industrie Gase*, 1877.

[12] Kemp, *Chem. News*, **71,** 108 (1895).

[13] Guye and Bogdan, *Compt. rend.*, **139,** 1494 (1904); Jacquerod and Bogdan, *Compt. rend.*, **139,** 49 (1904); Buff and Hoffman, *Ann.*, **113,** 129.

[14] Wagner, *Z. analyt. Chem.*, **21,** 374 (1882); Crookes, *Select Methods in Chem. Anal.*, 1905.

[15] Carius, *Chem. Centr.*, **26,** 433 (1885); Lunge, *Ber.*, **14,** 2188 (1881).

[1] Villard, *Compt. rend.*, **118,** 1096 (1894).

[2] Erdmann und Stolzenberg, *Ber.*, **43,** 1702 (1910); Stolzenberg, *Ibid.*, **43,** 1708.

[3] THIS JOURNAL, July, 1911, p. 474.

nearly saturated $Ba(OH)_2Aq$ showed the presence or absence of CO_2, and after the run this solution was divided into three portions: the first portion acidified with HCl gave a test for SO_3; the second portion with HNO_3+AgNO_3 for halogens, halogen acids, and halogen oxides; and the third portion was set aside. After the run, the NaOHAq (2 : 3) was divided into three portions; to the first portion was added $BaCl_2$ and then HCl in excess, thus testing for CO_2, SO_2, SO_3; the second portion was acidified with HNO_3, then made ammoniacal and $AgNO_3$ added, and finally acidified with HNO_3, thus testing for SO_2, H_2S, halogens, halogen acids, and halogen oxides; the third portion was mixed with the third portion of the $Ba(OH)_2Aq$, and tested for HCN and $(CN)_2$ by boiling with $Fe(OH)_2$ + $Fe(OH)_3$ and acidifying with HCl to form Prussian blue. The $AgNO_3Aq$ repeats some of the previous tests and in addition shows the absence or presence of PH_3, SbH_3 and AsH_3. The gas is tested for O_2 by the darkening of the alkaline pyrogallol Aq; then it is dried by the two $CaCl_2$ tubes and the H_2 and organic compounds are oxidized by the red-hot CuO. The water which is formed is weighed in the $CaCl_2$ U-tube (1) which is guarded by the weighed $CaCl_2$ U-tube (2); and the CO_2 which is formed gives a precipitate in the nearly saturated $Ba(OH)_2Aq$ (2). This last solution is guarded by a tube containing solid NaOH. The gas is measured in the gasometer. From 10 to 18 liters of gas are usually passed in from 3 to 6 hours; the separate bubbles could easily be counted.

Experiment 2.

Train:
Cylinder;
Trap + litmus and starch-KI papers;
$FeSO_4Aq$;
$KMnO_4Aq$;
CuCl + HCl + Aq + $PdCl_2$;
NaOH sol.;
Gasometer.

The trap and test papers used in Experiment 1 were again used in this experiment, so that the tests were repeated in an accumulative manner. The slightly acid solution of $FeSO_4$ tests for NO, and its titration after the run showed the presence or absence of active oxidizing agents—although O_2 would not have affected it.[1] The $KMnO_4Aq$, made by adding one drop of $N/2$ $KMnO_4$ to 500 cc. H_2O, tests for reducing agents. The solution of $PdCl_2$ in an HCl solution of CuCl was diluted with H_2O after each run as a test for CO.[2] The NaOH solution absorbed any HCl from the previous solution before the gas was measured in the gasometer.

In addition to these qualitative determinations, confirmatory tests were made for chlorine by $AgNO_3$ and for hydrogen by anhydrous $CuSO_4$ placed after the combustion furnace.

Experiment 3.—Alkaline pyrogallol showed in each instance no certain absorption of the gas, indicating the absence of oxygen and CO_2 in amounts greater than a trace.

Experiment 4.—NH_3 was determined quantitatively by passing the gas slowly through water to which Nessler's reagent had been added, and comparing the color developed with the ammonia standards such as are used ordinarily in water analysis.

Experiment 5.—It was attempted to determine the N_2O by absorption at 0° in absolute alcohol which had been boiled free from gases. In every instance the gas was practically completely absorbed irrespective of the amount of impurities present. For independent accurate determination, therefore, this method is untrustworthy. Under standardized conditions, however, it might be used as an approximate method for works analysis or factory control.

Experiment 6.—The gas was exploded with about 3 times its volume of hydrogen and the contraction in volume noted—a determination according to Bunsen's method.[1] The duplicate results agree but there is a constant divergence from the true percentage of about—2 per cent. (see *comparison of results*). This method was used by Smith and Leman.[2] It came to our notice in reading the proof.

Experiment 7.—Because of the lack of a reliable method for the accurate determination of N_2O, the authors have devised and tried the following method: Hydrogen was passed over ignited copper in a combustion tube until complete reduction; then the tube was allowed to cool while the stream of hydrogen continued. When cold, the hydrogen was replaced by CO_2, the tube was reheated and the gas sample passed over the Cu, oxidizing it to CuO. The hydrogen was passed until complete reduction and until the moisture was swept out of the tube. The H_2O which was formed was caught in a weighed $CaCl_2$ tube.

This method gave excellent results, but it was simplified and improved as in the following experiment.

Experiment 8.—N_2O was determined by passing the sample of gas over reduced copper in an atmosphere of hydrogen, then reducing the CuO by a stream of hydrogen and collecting the H_2O which was formed in a $CaCl_2$ tube.

In detail, the method is as follows: Hydrogen from a Kipp generator containing zinc and H_2SO_4 (1 : 6), to which 2 drops of H_2PtCl_6Aq have been added, passes through a tower of solid NaOH and a long $CaCl_2$ tube to a hard glass combustion tube. This tube rests upon asbestos in an iron trough heated in a combustion furnace to a dull red color; it is 100 cm. long and contains snugly-fitting rolls of copper gauze aggregating 70 cm. in length. The farther end of this tube is drawn out to a narrow bore, which is inserted into a $CaCl_2$ tube and joined with rubber. This $CaCl_2$ tube is joined to a second similar tube and thence connected with a test tube containing any liquid to show the rate of passage of the gas.

The hydrogen is passed until the copper is completely reduced and the two $CaCl_2$ tubes have reached a constant temperature. Then it is stopped and about 800 cc. of the gas sample of accurately measured volume, temperature, and pressure, are passed through the tube at the rate of about 2 bubbles per second. This requires about 1 hour. The farthest rolls of gauze (about 15 cm.) should not be, and in our

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[1] J. Am. Chem. Soc., July, 1911.

[2] Hempel's "Gas Analysis," trans. by Dennis, **1906**, p. 210.

[1] Hempel's "Gas Analysis," trans. by Dennis, **1906**, p. 195.

[2] *J. Am. Chem. Soc.*, **33**, 1114 (1911).

experiments were never, oxidized. Hydrogen is then passed through at the rate of 3 or 4 bubbles per second until all of the CuO is reduced and all of the moisture driven out of the tube into the $CaCl_2$ tubes, this process requiring about $^3/_4$ hour. The combustion tube and the $CaCl_2$ tubes are then ready for a second determination, to begin with the passage through the tube of the sample of nitrous oxide.

About 2 hours are required for each determination, if many are made consecutively; a single determination made alone would require about 3 hours.

The usual precautions were taken to prevent any leaking of gas, and a trap was used to catch any mercury and prevent its getting into the combustion tube. In our experiments, the second $CaCl_2$ tube remained almost constant, gaining about 1 mg. in weight each time. If as much as a liter of gas is taken as a sample and its volume, temperature, and pressure carefully measured, this method probably would yield results sufficiently accurate for an atomic weight determination. Of course, since this is a determination of the N_2O indirectly by the direct determination of the oxygen present, therefore the H_2O from other oxygen compounds and also the moisture present in gas must be subtracted.

(b) *Results and Conclusions.*

The following table, which is self-explanatory, exhibits the results of our analyses of compressed nitrous oxide as supplied by American manufacturers:

Analysis.

No.	N_2O	H_2O.	CO_2.	NH_3.	O_2.	N_2, etc., by difference.	N_2O by explosion.	N_2O by $Cu+CO_2+H_2$.	N_2O by $Cu + H_2$.
1	99.7	0.13	0	0.006	present	0.16	97.5	99.4	99.7
2	96.6	0.15	0	0.001	present	3.25	95.0	96.2	96.6
3	99.5	0.15	0	0	present	0.35	97.3	99.5	99.5
4	95.9	0.16	present	0	present	3.94	94.1	95.6	95.9

C. RECOMMENDATIONS.

Nitrous oxide which is to be used for anaesthetic purposes should contain at least 95 per cent. of N_2O[1] and no solids, liquids, combustible organic matter, chlorine, or other oxides of nitrogen. The last two impurities may be tested for by slowly passing 10 liters (3 hours) through silver nitrate and ferrous sulphate solutions.

College of the City of New York.

[From the Research Laboratory of Parke, Davis & Co., Detroit, Mich.]

SOAPS FROM DIFFERENT GLYCERIDES.—THEIR GERMICIDAL AND INSECTICIDAL VALUES ALONE AND ASSOCIATED WITH ACTIVE AGENTS.

By H. C. Hamilton.

Received Apr. 1, 1911.

The paper herewith presented is largely characterized by its biological features. It has, however, certain points of a strictly chemical nature. It is therefore presented with the hope of arousing an interest in the chemistry of insecticides and germicides, a subject which has received comparatively little consideration.

In a paper[1] presented before the International Congress of Zoologists in 1907, the writer stated: "We have confirmed the fact that the insecticidal value of soap is very considerable. This might raise the question whether the average coal tar dip on the market, the efficient dilution of which in most cases is not greater than one in seventy-five, does not owe a large part of its efficiency to the soap contained." It is a matter of fact that the average soap is more strongly insecticidal than the average coal tar dip since the bed-bug is killed in most cases by being submerged for one minute in a 1 per cent. solution of soap while few coal tar dips will kill this insect under the same conditions, unless a solution is used one and a half to two times as strong. In spite of this, soap is looked upon merely as a convenient and valuable solvent for other substances which are classed as insecticides or germicides.

When we consider, on the other hand, the germicidal value of soaps, no such high value is inherent in them. They require the addition of an alkali or an antiseptic agent to give them even a nominal value.

As solvents of germicides, however, soaps have in some instances an efficiency greatly out of proportion to their apparent value. For instance, a mixture of carbolic acid and soap, equal parts, has the same germicidal value when diluted 1–75 as the carbolic acid alone, diluted with water 1–100. The quantity of carbolic acid in the soap mixture is such as to give an actual dilution of 1–150, an increase of 50 per cent. in its germicidal value due to the addition of soap.

Tests to determine the germicidal value of the soap alone indicate that the quantity present could not in itself have exerted any action whatever.

The writer recently had occasion to prepare a disinfectant which differed from the common commercial product, in that certain ingredients were added to overcome the disagreeable odor. At the same time the attempt was made to retain the germicidal value with a material reduction in its cost.

One method by which it was planned to accomplish the latter purpose was by the use of a cheaper saponifiable oil. The preliminary work had been done, using linseed oil soap; the physical properties and germicidal values were satisfactory and a formula was worked out. In this formula cottonseed oil was substituted for the more expensive linseed, with no impairment in the physical properties of the resultant product. The germicidal test, however, showed a marked lowering in the value of the product so prepared.

By a process of exclusion the cause of this was finally located in the oil used in making the soap, and a series of tests was carried out to see if any

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[1] Lack of knowledge of the content of real N_2O may seriously interfere with the satisfactorv use of this, the safest, anaesthetic, especially when it is administered by the proper method, namely, mixed with oxygen. If the preparation contains more than 95 per cent. N_2O, the variation in the proportion of the two gases will depend then, n fact, upon the amount of oxygen actually mixed and the percentage is not seriously altered (Gwathmey and Baskerville).

[1] "A Contribution to Our Knowledge of Insecticides."

considerable difference could be detected in the germicidal values of soaps from the different glycerides or whether the difference was apparent only when the soap and an active agent were used in combination.

Table I shows the comparative values of two disinfectants differing in composition only in the oil used for making the soap. Disinfectant A contains linseed oil soap; disinfectant B, cottonseed oil soap.

TABLE I.

		Time in minutes.				
	Dilution.	1.	2.	3.	4.	5.
A	1–200	+	—	—	—	—
	1–250	+	+	—	—	—
	1–300	+	+	+	+	—
B	1–200	+	+	+	+	—
	1–250	+	+	+	+	+
	1–300	+	+	+	+	+

In these tables + stands for growth of organism, – stands for no growth. The organism is grown in bouillon and the culture used is a 24-hour growth of *B. typhosus*. In making the test the culture is thoroughly shaken and filtered through cotton, in order to remove clumps of bacteria which might interfere with the test. The disinfectant is diluted as shown in the table, 1 part in 200, 250 and 300, using about 5 cc. of the diluted disinfectant and 5 drops of the culture, dropped from a standard pipette, which delivers approximately $^1/_{20}$ of a cubic centimeter. After mixing the bacteria with the germicide they are allowed to remain in contact for 1 minute, at the end of which time a loop full of the mixture of bacteria and disinfectant is planted in a tube of sterile bouillon and placed in the incubator for 48 hours. This is repeated at the end of two minutes, three minutes, four minutes, and five minutes. The results, therefore, represent the action of the germicide on the naked bacteria.[1] The object in filtering the bacteria to remove any masses is to obtain the actual germicidal value and not the penetrating value of the product, two properties which are entirely distinct. This method is practically that called the Rideal-Walker method, which is official in Great Britain as a means of standardizing disinfectants.

An article which appeared in the *Medizinische Klinik*, 1910, No. 36, "Concerning the Disinfectant Constituents of Soap," threw no light on this question except in so far as this value is connected with the saturated fatty acids. It was claimed that a soap from palmitic acid or a tripalmitate had antiseptic value in itself greater than that of carbolic acid. A series of experiments was carried out to see if the soaps of the different glycerides differed among themselves in germicidal value.

The following table, Table II, shows the results obtained from a series of tests using *B. typhosus* as the test organism and carried out in a way practically identical with the Rideal-Walker method than which probably not better has yet been found:

TABLE II.

Glyceride.	Oil used.	Dilution.	Result in 5 min.
Trilaurin	Cocoanut	1.40	—
		1–50	+
Tribrassin	Rape seed	1–20	+
Trivalerin	Whale	1–20	+
Trilinolein	Linseed	1–20	+
Triricinolein	Castor	1–20	—
		1–30	+
Tripalmitin	Palm	1–20	+
Triolein	Olive	1–20	—
		1–30	+
	Resin	1–20	+

Insecticidal tests, Table III, were also carried out using the common bed-bug, *Cimex lectularius*, as the experimental organism and following the method described in the paper to which reference was made in the opening paragraph.

The method may be briefly described as follows: The insects are placed in tubes open at both ends, and imprisoned by covering the ends with a porous cloth (India mull). Then by using a hook which will fasten into the cloth, the tube with the insects is quickly plunged into the solution. By rapid agitation, the protective air globules which surround the spiracles can be removed so that intimate contact with the insecticide results. At the end of the period of time, usually one minute, during which time the insect is submerged, it is quickly removed with the hook and the clinging solution shaken off, the capillary action of the cloth tending to draw off all excessive moisture.

It is then transferred to bibulous paper and covered with a clock glass, which allows sufficient air and easy observation.

TABLE III.

		Dilutions.			
Glyceride.	Represented by:	50.	100.	200.	300.
Trilaurin	Cocoanut oil	dead	3 dead 1 alive	3 alive 1 dead	alive
Tribrassin	Rape seed oil	dead	alive	alive	alive
Trivalerin	Whale oil	dead	dead	2 alive 2 dead	alive
Trilinolein	Linseed oil	dead	dead	2 alive 2 dead	alive
Triricinolein	Castor oil	dead	dead	2 alive 2 dead	alive
Tripalmitin	Palm oil	dead	dead	3 alive 1 dead	alive
Triolein	Olive oil	dead	dead	3 alive 1 dead	alive
	Resin oil	dead	2 dead 2 alive	4 alive	alive

These soaps were dissolved in 50% alcohol, so that a certain weight of soap was contained in a definite volume of alcohol, in most cases 1 gram of soap in 3 cc. alcoholic solution.

A study of Table II shows that cocoanut oil soap has the highest value as a germicide. Castor oil and olive oil were the only others tested which had germicidal action in 5 per cent. solution, the others scarcely showing even an inhibiting action on the growth in bouillon.

The insecticidal values indicate that no considerable difference exists in the potassium soaps of the different glycerides, a 1 per cent. solution being efficient

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[1] The germicidal tests were in all cases carried out at approximately 20° C.

in every case but one—that of the soap from rape seed oil. The same soaps mixed with active agents, namely, a rather high-boiling tar acid and a solution of caustic potash, had entirely different effects on the germicidal values from what one would expect. The extended tests on these lines were carried out using only two of the glycerides, trilaurin and triolein, as represented by cocoanut oil and olive oil, because these showed wide variation in their germicidal values without added ingredients and because of the limited time to complete the tests.

Table IV, here shown, is a compilation of the results obtained from tests of these two soaps used:

First, alone.
Second, with cresylic acid.
Third, with alkali (KOH).
Fourth, with both.

Tests were also made for the value of the alkali alone, and of the alkali and cresylic acid together.

The columns headed "Coefficients," Table IV, show the number of times the preparation can be diluted compared with carbolic acid, and retain an equal efficiency.

TABLE IV.

Olive Oil Soap.

	Effective dilution.		Coefficients.	
Combination.	Germicidal.	Insecticidal.	Germicidal.	Insecticidal.
Soap alone.............	1–20	1–100	0.17	5.0
Soap and cresylic acid...	1–500	1–300	4.0	15.0
Soap and alkali.........	1–1100	1–50	9.0	2.5
Soap, cresylic acid, and alkali................	1–1000	1–300	8.3	5.0
Cocoanut Oil Soap.				
Soap alone.............	1–40	1–100	0.33	5.0
Soap and cresylic acid..	1–1000	1–100	8.3	5.0
Soap and alkali.........	1–1100	1–200	9.0	10.0
Soap, cresylic acid, and alkali................	1–1000	1–300	8.3	15.0
Cresylic acid and alkali.	1–400	1–25	3.3	1.25
Alkali (KOH) alone.....	1–1200	1–25	10.0	1.25

In every mixture above described the ingredients are present in equal proportions and in every case the dilutions given are for each ingredient.

The literature on this subject is very contradictory. Some investigators claim that the soap constituents in themselves are valuable and that no difference exists between those from different glycerides. Most of the authors consulted conclude that alkali, volatile oils, or other germicidal agents must be present to give a perceptible value.

Rosenau[1] makes the following statement: "Medicated soaps are for the most part a snare and a delusion so far as any increased germicidal action is concerned; in fact, the addition of carbolic acid and other substances, which have the property of combining with the soap, seems actually to diminish the disinfecting power of that substance."

It should be noted in this connection that without the closest attention to the preparation of the soap, variable results are to be expected. In fact, variations were observed for which no logical reason could be deduced. It is probable that a rigid chemical control of the reactions involved would throw considerable light on the subject and explain many of the discrepancies which now appear to make the literature untrustworthy.

One point should be noted, that bacteriologists have not used the same organism in making their tests. It is a well known fact that bacteria differ greatly in their resistance toward germicides, *B. typhosus* being killed by some germicides in a dilution 4 to 5 times as high as that required to kill *B. pyocyaneus*.

Another point of importance is the effect of hydrolysis on the germicidal value of the soap solution.

The table (Table V) here given is for comparison of the values of a dilution when freshly made and again after 18 hours standing.

TABLE V.

Olive oil soap and cresylic..	1–300	—	—	—	—	–
Same after 18 hours......	1–300	+	+	+	—	–

This shows an evident deterioration probably on account of chemical changes in the solution.

SUMMARY AND CONCLUSIONS.

1. *B. typhosus* is especially susceptible to the germicidal action of alkali (KOH).

2. The combination of soap with an active agent does not invariably enhance the germicidal value of the latter.

3. The germicidal value of the combination of soap and cresylic acid depends on the glyceride used in the manufacture of the soap. One may therefore conclude that the soap exerts a distinct influence on the value of this agent.

4. The germicidal value of the alkali is not increased by any combination used in this series of tests. When combined with cresylic acid, its value is one-third that of the alkali alone.

5. With our present knowledge of the chemistry of these combinations as it affects germicidal and insecticidal values, no safe *a priori* conclusions can be drawn. Even a laboratory test to determine these values must be carried out under rigidly prescribed conditions. Variations in the method may easily make the greatest differences in the results obtained.

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[1] "Disinfection and Disinfectants."

[AGRICULTURAL EXPERIMENT STATION OF THE RHODE ISLAND STATE COLLEGE, KINGSTON, R. I.]

THE AVAILABILITY OF THE INSOLUBLE NITROGEN IN CERTAIN COMMERCIAL FERTILIZERS.[1]

By BURT L. HARTWELL AND F. R. PEMBER.

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Much uncertainty exists in the minds of agriculturists concerning the availability of the insoluble nitrogen in commercial fertilizers, because of the difficulty of recognizing the existence of material of low availability, such as leather, garbage tankage,

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[1] Paper read at the Indianapolis meeting of the American Chemical Society.

and peat, after they have been subjected to certain processes of manufacture.

Since the effect upon plants must be relied upon as furnishing authoritative information regarding the value of manurial substances, it was decided to secure by pot experimentation some knowledge concerning the actual value of the water-insoluble nitrogenous ingredients of certain commercial fertilizers.

Of the brands collected during the regular inspection of 1908, certain ones which had a fairly high percentage of nitrogen in organic matter, and which represented different manufacturers, were selected. Most of them were potato and vegetable fertilizers, and were the higher-priced brands.

They were thoroughly leached with warm water, by decantation and on the filter, to extract especially the nitrates and ammonium salts, but the soluble organic nitrogen was of course also extracted. The residues were dried, the nitrogen determined,[1] and the material used in comparison with dried blood (13.62 per cent. N) and nitrate of soda, on an equal nitrogen basis, as sources of nitrogen for oats, millet, and oats grown successively on the same soil.

Optimum amounts of lime, potassium and phosphorus were provided for each crop in order that the differences in growth might be attributable to differences in the availability of the nitrogen.

Eight-inch Wagner pots and a light soil which it was hoped was naturally deficient in nitrogen, were used. The soil was found to be less deficient than was estimated, however, so that the first crop of oats was too well supplied with nitrogen to enable marked differences in availability to be shown. For the succeeding crops less nitrogen was used, so that less than the optimum amount should be present in those pots which had the uniform application.

The crop results are given in the accompanying table.

The addition of an extra amount of lime to two of the pots of soil which received blood increased the total yield of the three crops only from 302 to 305.9 grams. It is evident, therefore, that the general application of lime was sufficient. On the other hand, when the regular application of nitrogen in the blood itself was increased, the total yield rose to 348.2 grams, indicating that the general nitrogenous manuring was not sufficient for the production of maximum crops. If such had not been the case there would be no proof that an opportunity had been afforded for the materials under comparison to have exerted their full effect.

Although the leaching would remove all of the soluble phosphorus and potassium there would still remain much phosphorus in the reverted and insoluble condition which would exert an effect upon the crop unless this element was so abundantly supplied as to render impossible any additional influence from this source. In consideration of this, a very liberal application of acid phosphate was made for each crop, and yet when 50 per cent. more was added in connection with the general application of nitrogen in nitrate of soda (see the last two series in the table), the total yield was somewhat increased, namely, from 338.9 to 357.5 grams. It is believed, however, on account of the fact that the other nitrogenous materials were less available than the nitrate of soda, that the full requirement for phosphorus was probably fulfilled by that which was added in the general application of acid phosphate; and that, practically what was present in the nitrogenous materials was without effect, especially on the last crop.

Results from an equal amount of nitrogen in nitrate of soda, dried blood, and the water-insoluble nitrogen of certain commercial fertilizers (Nos. 1–12):

	Grams of air-dry crops.				Availability of nitrogen.	
Source of nitrogen.	Oats, total.	Millet, total.	Oats. Total.	Oats. Grain.	By last oat crop, with blood at 80.	By alk. $KMnO_4$ method
None	38.5 48.0	16.7 14.7	25.5 23.5	8.0 8.2	0	
1	64.5 69.0	23.6 21.6	43.5 45.5	14.6 15.7	58	70
2	69.5 83.0	24.3 21.2	42.0 45.0	14.2 14.0	55	59
3	73.5 71.0	24.2 21.5	50.0 51.5	16.8 17.5	76	74
4	78.5 75.0	21.3 23.0	51.0 51.0	17.5 17.9	77	74
5	71.0 78.5	24.0 21.5	52.5 55.0	18.2 19.6	85	78
6	74.5 74.5	27.3 27.7	49.5 49.0	17.3 17.1	72	76
7	78.0 68.0	25.7 23.0	53.0 56.0	18.1 18.2	87	76
8	78.5 85.5	26.0 22.5	45.0 47.0	15.0 15.9	63	73
9	80.5 82.5	21.0 22.0	49.0 51.0	14.3 16.3	74	76
10	76.0 77.5	26.8 22.7	54.5 53.0	17.0 18.6	85	83
11	82.5 77.5	22.9 24.7	52.5 51.0	18.1 17.8	79	83
12	85.0 86.5	25.5 25.8	53.0 51.5	18.9 17.9	81	81
Dried blood	78.0 67.0	27.5 25.8	52.0 52.0	16.7 17.6	80	79
Dried blood + extra lime	77.5 71.0	30.0 25.7	56.2 45.5	20.6 14.7		
Dried blood (extra amount)	91.5 80.0	28.4 31.3	58.0 59.0	20.8 21.8		
Nitrate of soda	86.5 75.0	25.9 27.5	64.0 60.0	24.7 22.6		
Nitrate of soda + extra phosphate	87.5 85.0	28.5 29.0	63.0 64.5	23.2 24.5		

The increase over the check pots, caused by the general application of nitrogen in the dried blood, has been placed arbitrarily at 80 in the table, because of our belief that high-grade blood under conditions favorable to nitrification will cause an average increase in crop of about 80, in comparison with nitrate of soda at 100.

It may be seen by comparing the weights of the crops grown on the different fertilizer residues, with those from an equal amount of nitrogen in dried blood, that with a few exceptions the availability of the nitrogen in them was practically equal to that in blood.

This fact should increase the confidence of the

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[1] The authors are indebted to Mr. J. Frank Morgan for this work.

agriculturist in the quality of the material in the more concentrated commercial fertilizers such as those used in this experiment.

In the following respects the best comparison of the different materials is afforded by the growth of the last crop, namely: the soil itself had become more depleted of its nitrogen; the cumulative effects of three applications of nitrogen were exerted; there was scarcely any evidence that the phosphorus associated with the nitrogenous materials exerted any influence; and the grain was allowed to ripen.

On the basis of the last crop, only five of the twelve fertilizers (Nos. 1, 2, 6, 8 and 9) yielded in each of the two respective pots, less total crop and grain than was produced in either of the pots in which blood was applied. Although the insoluble nitrogen in fertilizers 1 and 2, particularly, was less available than the nitrogen in blood, there is reason for the belief that it was largely from bone and meat tankage instead of from such low-grade material as garbage tankage, peat, and leather.

The directors of certain northeastern stations announced in March, 1910, their intention to have the fertilizers collected in 1911 for inspection, examined by some uniform laboratory method as to the availability of their organic nitrogen; and they appointed a committee of station chemists to recommend a method.

It was very opportune that the vegetation results under discussion had already been secured on the insoluble organic nitrogen of certain fertilizers, and that some of the identical material was on hand. This material was submitted, without any information concerning the crop results, to Mr. C. H. Jones, of the Vermont Agricultural Experiment Station, for the determination of availability by the alkaline permanganate method. The agreement was very satisfactory, but it was considered unfortunate that probably none of these particular fertilizers were made up of low-grade materials. Subsequently, however, a few decidedly low-grade fertilizers were likewise compared, with gratifying results; the vegetation tests are not fully completed and will not be published at this time.

The alkaline permanganate method was the one adopted March 4, 1911, by the agricultural experiment stations of New York, New Jersey and the New England States for "examining the activity of the organic forms of nitrogen," and a circular was printed which includes the details of the method.

In the last column of the accompanying table we have included the results secured by Mr. Jones with the method as adopted. The agreement is quite good even without full recognition of the fact that the limit of error in vegetation experiments must be placed rather wide.

Even the hird crop (oats) equaled 49 grams on the check pots, although the pots to which blood was added yielded 55 grams more; this is taken to represent a range in availability from 0 to 80; it is evident, therefore, that even a variation of 3.4 grams in the weight of the crop from two parallel pots represents a difference of 5 in availability.

With two kinds of crops even on the same soil, the degree of availability will vary considerably, and on different soils the variation may be expected to be still greater. It is probable, for example, that an experiment with rye on an acid soil, in which the predominating microflora is composed of fungi and yeasts, would result in quite a different availability from one with barley on a neutral or alkaline soil in which *bacterial* growth is the more prominent. Two nitrogenous materials might exhibit very different relative availability, depending upon which of the above-mentioned conditions existed.

An availability test even with a single kind of plant and soil may comprise the following: one manuring and one planting; one manuring, and more than one planting; or more than one manuring and as many plantings.

It should be understood, therefore, that a difference of at least ten per cent. in the availability as determined by pot experiments is not of much significance, especially when no standard conditions have been adopted for carrying on vegetation tests.

The degree of availability of a substance, whether determined by vegetation or chemical tests, should be considered only as an approximation which is useful in distinguishing between materials of quite different qualities.

THE NATURE OF SOME COAL DUSTS AND MINE AIR FROM COLORADO MINES.

By John B. Ekeley.

Received May 2, 1911.

In November, 1910, Governor John F. Shafroth appointed a commission, consisting of Victor C. Alderson, president of the State School of Mines; James Dalrymple, state coal mine inspector; R. D. George, state geologist and professor of geology at the University of Colorado; and John B. Ekeley, professor of chemistry at the University of Colorado, to inquire into the condition of the coal mines of Colorado, and the causes of the many accidents in those mines, and to suggest remedial legislation for the consideration of the Eighteenth General Assembly of the State.

The following tables give the analyses of samples of coal dusts and of mine air taken during the investigation trip made by the Coal Mine Commission.

The coal dust samples were passed through 20-, 100-, and 200-mesh sieves, and the fractions analyzed. In the fractions passing through the 200-mesh sieve, the analyses show a slight error, because the very fine dust undoubtedly lost some moisture during the screening operation. However, the results for this fine dust are very interesting, because they show that in all cases the composition was approximately the same as in the coarser portions. The analyses show that the non-carbonaceous part of the dust was of about the same state of division as the coal dust itself.

The air samples were collected by allowing water to run out from completely filled glass bulbs, which were then closed air-tight. This is the method used by Mr. Chamberlin, of the United States Geological Survey. The small amount of water remaining on the inner walls of the bulbs absorbs carbon dioxide so that the amounts of carbon dioxide shown in the analyses are a fraction of a per cent. too low. The striking fact shown by the analyses is the presence, in most cases, of a small amount of methane, even in samples where none was expected. Since it is known that a small amount of methane may act as a primer in an explosion of coal dust, these facts are significant.

ANALYSES OF COAL DUST.

No.	Standard mine.	Mesh.	Moisture.	Volatile matter.	Fixed carbon.	Ash.
1	Main north entry, 250 ft. from hoisting shaft. Road dust.	20	13.2	25.8	33.3	27.7
		100	11.5	24.4	30.1	34.0
		200	8.0	23.9	28.5	40.6
2	Same as No. 1. Dust from timbers.	20	9.7	21.8	25.1	43.4
		100	8.5	20.8	27.2	43.5
		200	8.0	21.3	26.0	44.7
3	Fifth northwest room 8, 25 ft. from working face.	20	15.8	24.6	27.2	22.4
		100	12.4	22.2	21.9	34.5
		200	10.1	22.3	26.8	40.8
4	Fifth southwest.	20	16.9	26.1	44.3	12.7
		100	14.8	26.7	43.5	15.0
		200	14.3	27.0	42.4	16.3
5	Intersection of main south and first southwest entries. Road dust.	20	13.8	24.0	35.9	26.3
		100	10.5	25.3	31.2	33.0
		200	9.1	25.1	29.5	36.3
6	No. 7, parting main south. Road dust.	20	16.8	23.8	37.5	21.9
		100	13.7	22.1	22.0	31.2
		200	12.7	24.5	28.0	34.8
7	Main south at intersection of third east. Dust from timbers and ribs.	20	11.9	22.1	20.1	35.9
		100	11.1	20.2	21.5	37.1
		200	8.9	22.8	29.1	39.2
	Hastings mine.					
8	Dust from main slope 600 ft. in, from timbers and ribs.	20	1.8	28.9	48.7	20.6
		100	1.5	28.6	49.2	20.7
		200	1.3	25.7	51.5	21.5
9	Main slope between second and third entries. Road dust.	20	2.4	27.8	46.2	23.6
		100	1.7	28.3	46.4	23.6
		200	1.4	26.3	48.4	23.9
10	Rope parting in main slope between 4th and 6th south. Road dust.	20	2.1	23.8	34.9	39.2
		100	1.6	24.4	36.8	36.2
		200	1.3	23.6	39.9	35.2
11	7th south, 500 ft. from main slope. Trolley.	20	1.8	17.9	30.6	49.7
		100	1.8	18.9	31.8	47.5
		200	1.4	19.0	33.2	46.4
12	Double parting between 7th and 8th cross-cut of 7th south. Road dust. Trolley.	20	1.9	9.6	16.0	72.5
		100	1.8	12.8	19.9	65.5
		200	1.6	13.0	22.2	63.2
13	Dust from timbers and ribs between 1st and 2nd cross-cut in 7th south.	20	2.2	21.7	32.8	43.3
		100	1.8	21.1	33.9	43.2
		200	0.8	22.0	34.4	42.8
	Delagua mine.					
14	Fine dust from ribs 3rd north entry, not dislodged by explosion.	20	2.4	21.0	39.9	36.7
		100	2.3	20.0	40.3	37.4
		200	1.1	22.1	39.2	37.6
	Primero mines.					
15	1st east mine. Dust from ribs, 700 ft. from entrance.	20	1.0	24.4	47.9	26.7
		100	1.0	24.8	46.4	26.2
		200	0.5	25.3	47.2	26.1
16	1st north mine. Dust from ribs in A-12.	20	2.4	20.5	48.0	24.7
		100	1.7	18.1	54.6	25.6
		200	0.6	21.7	42.1	26.6
	Pictou mine.					
17	Main slope 500 ft. in. Roof and ribs.	20	3.3	25.0	33.2	38.5
		100	3.8	23.1	36.3	36.8
		200	1.8	28.2	33.2	36.8
18	8th north off main entry. Ribs.	20	5.3	25.4	36.2	33.1
		100	5.2	22.9	38.5	33.4
		200	2.3	27.9	34.7	35.1
	Danville mine.					
19	Main slope 600 ft. from entrance. Ribs.	20	9.0	39.1	33.0	18.9
		100	8.6	33.5	38.5	19.4
		200	5.6	34.9	30.2	19.3
	Summit mine.					
20	Bug dust, 8th southwest.	20	18.0	21.0	54.1	6.9
		100	16.8	21.0	54.3	7.9
		200	..	..	..	..
	Somerset mine.					
21	Coarse, quite damp stuff from ribs.	20	7.8	26.8	49.3	16.1
		100	6.4	24.3	49.4	29.9
		200	..	..	..	..
	Vulcan mine.					
22	Main entry, 300 ft. in. Dust from ribs.	20	6.2	25.9	49.1	19.8
		100	6.0	27.9	47.0	19.1
		200	3.5	33.0	43.7	20.8
23	Main entry, opposite 8th B, upraise. Ribs.	20	11.5	25.8	54.2	9.5
		100	6.4	33.6	49.5	11.5
		200	1.6	32.9	43.6	12.9
	Rockvale mine.					
24	Dust from ribs of 5th south.	20	15.4	10.2	20.9	53.5
		100	12.2	12.8	19.6	56.4
		200	3.1	17.9	11.6	57.4
25	Dust from road in 5th south. Same place as No. 24.	20	9.8	13.4	19.1	49.7
		100	9.2	13.8	21.7	55.3
		200	5.0	17.3	19.0	58.7
26	Dust from timbers, main south entry, 1,500 ft. from shaft.	20	7.2	19.7	39.6	33.5
		100	5.7	21.2	39.0	34.1
		200	2.9	26.1	34.9	36.1

ANALYSES OF MINE-AIR SAMPLES.

	Standard mine.	CO_2.	O.	N.	CH_4.
1	Fifth northeast, Main intake[1] north side	0.25	17.4	82.35	....
2	Fifth northwest, room 8	....	20.8	79.2	....
3	Fifth southwest, 30 min. after shot	0.61	19.7	79.69	....
4	Ninth southwest, 100 ft. from main entry	....	20.5	79.04	0.46
5	Main south, 7th double parting	....	20.0	80.0	....
	Hastings mine.				
6	Main slope, 300 ft. from mouth	....	19.7	80.3	....
7	7th south double parting	....	20.4	78.5	1.1
8	1st dip off 7th south, shot night before	....	20.4	79.6	....
9	7th south at 7th crossing	....	20.4	79.6	....
10	Face of 7th south, pillar work		20.4	79.6	....
	Primero 1st east mine.				
11	Room 8, B-9, west	....	20.6	79.4	....
12	Intersection B-9 east and main-air course	0.4	20.6	79.0	....
13	Main return 1,000 ft. from fan	0.7	19.9	79.4	....
	Primero 1st north mine.				
14	Room 3, first blind A-12	....	20.6	79.2	0.2
15	Room 6, A-11	0.1	20.5	79.4	....
16	Main air course, 75 ft. outside A-7, overcast	....	20.2	79.8	....
	Cokedale mine.				
17	Room 10, 2nd B west, pillars	....	20.0	79.3	0.7
18	Face of 5th west C	....	19.8	79.4	0.8
19	Main return under 4th south undercast	....	20.0	79.6	0.4
	Pictou mine.				
20	Face of room 5, 4th cross off 8th south	....	19.7	80.3	....
21	Bottom of slope, face	....	20.5	78.4	1.1
22	Face of 10th north	....	19.7	79.9	0.4
23	Back entry, intermediate air course, 7th south	....	19.4	78.8	1.8
	Danville mine.				
24	Face of main slope	....	18.5	81.1	0.4
25	Main slope just above 7th south, above fire	0.3	20.5	79.2	....
	Summit mine.				
26	Main return, 100 ft. from shaft	....	19.9	80.1	....
27	Room 11 off 7th southwest	0.2	20.1	78.9	0.8
28	Face of 7th southwest	....	20.0	79.7	0.2
	Somerset mine.				
29	Room 40, 6th west	....	20.5	78.1	1.4
30	Room 2, 9th west	....	20.2	78.8	1.0
31	Main entry, 9th west	0.1	20.4	79.5	....
32	Face of main slope	....	20.1	78.7	1.2
33	Main return, 75 ft. from fan	0.2	20.6	78.8	0.4

ANALYSES OF MINE-AIR SAMPLES (*Continued*).

	Vulcan mine.	CO_2.	O.	N.	CH_4.
34	Face of workings, main entry, 600 ft. in.	....	20.5	78.9	0.6
35	No. 9-B upraise, 25 ft. from entry	0.6	20.1	78.7	0.6
36	Cross-cut between 8-B and 9-B upraises	0.4	20.5	78.5	0.6
	Rockvale mine.				
37	Room 28, C dip	0.2	20.0	78.6	1.2
38	1st dip, 5th south, off C dip	....	19.8	78.9	1.3
39	Main return in main south, 1,500 ft. from shaft	....	19.7	79.1	1.2

The dust samples from the Standard and the Summit mines, which are probably representative samples of dusts from the Boulder County field, show a fairly high percentage of moisture. This would tend to make these dusts safer than those of the southern fields, which are very dry. However, it would be dangerous to trust to this for safety from explosions, since we have not enough data on this question as yet. These dusts from the ribs and timbers and from the roadways usually contain considerable fire clay, but the results from experiments at the Pittsburg testing station on similar coal dusts containing a high percentage of fire clay have shown that even such dusts are dangerous.

The dusts in the mines in the southern part of the state are without doubt very dangerous. A similar dust having a composition, moisture 3.41, volatile matter 17.98, fixed carbon 47.22, ash 21.39, was tried in the explosion gallery of the Pittsburg testing station. The dust exploded from the effect of a blown-out shot of 500 grams of black powder, and propagated the flame through the entire length of the dusted gallery, and 27 feet beyond the dust zone.

Similarly, a road dust, rich in rock dust, giving the following analysis, moisture 2.75, volatile matter 15.45, fixed carbon 24.85, ash 56.95, exploded and propagated the explosion 20 feet beyond the dust zone. All the dusts in the tables except Nos. 12, 24 and 25 would be far more likely to explode than the samples experimented upon at Pittsburg, as may be seen by comparing the analyses.

An interesting dust is No 14, which was taken from a sheltered place on the ribs of the third north entry of the Delagua mine, and which had not been dislodged by the explosion. This may be taken as a fair sample of the Delagua mine dust, which, without doubt, contributed its share to the explosion of October 8th. This dust varies little in composition from the dust found in the other mines of that part of the state.

It is a pleasure to say that, in the Cokedale mine, there was very little dust; in fact, no suitable sample for analysis was found. In the Somerset mine there was practically no dust, though, after some trouble, a sample was obtained.

Of the mines visited, almost all were in danger from coal dust, and it is fair to assume that the great majority of the mines of the state are in the same condition. This matter should be remedied by proper legislation, requiring that the dust be rendered harmless by means of the addition of a large amount of moisture, and possibly by the removal of the resulting mud from the mine.

UNIVERSITY OF COLORADO.

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[1] The intake is contaminated by air from some old workings.

[CONTRIBUTION FROM DIVISION OF DRUGS, BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE.]

THE QUANTITATIVE DETERMINATION OF KETONES IN ESSENTIAL OILS.

By E. K. NELSON.

Received June 7, 1911.

While we have general methods for the estimation of alcohols, esters, phenols and aldehydes in oils, such a method seems to be wanting in the case of ketones. Some substances of this class, as for example, camphor, do not react with sodium bisulphite. Others, while they may react with bisulphite, can not be even approximately estimated by its use.

The methods of Sadtler[1] and Labbé,[2] while valuable in many cases could not be accepted as general methods because the reactions involved are not characteristic of all ketones.

All the ketones usually found in essential oils, however, do react with hydroxylamine to form oxims. The method of Walther[3] depending upon the transformation of the ketone into oxim on boiling with a standard alcoholic solution of hydroxylamine hydrochloride in the presence of alkali, and the determination of the amount of the reagent thus consumed by titration of the excess on completion of the reaction, seemed to offer advantages as a general method for the analysis of ketone-bearing oils. Walther experimented on the estimation of citral and carvone, but does not speak of having tried the method on other ketones, or aldehydes. The following work was undertaken to test the accuracy of Walther's method on ketones in general. The ketones used were prepared from the oils in which they occur, or were obtained in some cases on the market and purified. In every case the method was carried out the same way. The standard hydroxylamine solution was prepared by dissolving 20 grams hydroxylamine hydrochloride in 30 cc. water and adding 125 cc. aldehyde-free alcohol. One to two grams of the substance were boiled in a water bath under a reflux with 35 cc. of this reagent and 2 grams sodium bicarbonate, cooled, 6 cc. HCl added, through the condenser, followed by water and the mixture made up to 500 cc. The solution was filtered and in an aliquot part of the filtrate the free acid was neutralized by running in $N/2$ NaOH, using methyl orange. Phenolphthalein was then added and the hydroxylamine left in excess of that required to form oxim was titrated with $N/10$ NaOH. The results in the following table were obtained:

Considering the nature of the work and the difficulty of preparing absolutely pure materials to start with, these results may be considered as fairly satisfactory except in the case of fenchone. As this is a rather rare ketone, however, and as it is present in but few oils and in those only in small amount, a method for its estimation is not so necessary.

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[1] *Am. J. Pharm.*, 76–84; *J. Soc. Chem. Ind.*, **23**, 303.

[2] *Bull. Soc. Chim.*, **23**, 283.

[3] *Pharm. Centrh.*, 41–613.

Ketone or (aldehyde).	Wt. substance.	35 cc. reagent require *N*/10 NaOH.	Excess reagent require *N*/10 NaOH.	Time of boiling. Hrs.	Amount of substance returned. Per cent.
Carvone	2.3508	605.5	455.5	½	96.18
Carvone	2.3343	605.5	454.5	1	97.51
Carvone	2.2819	605.5	455.0	1	99.41
Carvone	1.9493	607.8	479.5	½	99.12
Pulegone	2.2852	605.5	452.5	½	101.77
Pulegone	2.3228	605.5	451.5	1	100.77
Camphor	1.025	.....	.....	½	92.3
Camphor	1.0626	.....	.....	1	97.13
Camphor	2.0509	.....	.....	2	99.08
Camphor	1.7177	.....	.....	2	101.5
Thujone	2.2793	604.6	459.0	½	97.1
Thujone	2.2903	604.6	458.0	1	97.3
Menthone	2.1416	.....	.....	1	97.5
Fenchone	0.9026	578.2	527.3	2	85.7
Fenchone	1.1823	578.2	540.6	1	50.6
Benzaldehyde	2.5447	606.7	375.0	½	96.5
Benzaldehyde	2.5278	606.7	376.0	1	96.7

In the case of spearmint oil the Walther method was tried in comparison with the estimation of the carvone by absorption in boiling sodium bisulphite solution as well as by the Labbé method.

RESULTS ON CARVONE; SPEARMINT OIL.

Sample.	Labbé method.	Walther method.	Absorption by boiling $NaHSO_3$.
1	54.7	58.4 53.1	55.0
2	61.3	65.5 66.4	67.5
3	....	61.43 60.7	61.5

A sample of tansy oil, assayed by the Walther method, gave thujone = 68.56 and 65.42 per cent. A sample of wormwood oil gave thujone = 33.15 per cent. and 31.24 per cent. Pennyroyal oil gave 81.87 per cent. ketone by this method calculated as $C_{10}H_{16}O$. A mixture of pulegone with at least two other ketones is present in pennyroyal oil. A sample of rosemary oil gave 30.33 and 30.24 per cent. ketone calculated as camphor.

The Walther method can not be recommended for the assay of any particular ketone-bearing oil until the influence on the reagent of other substances in the oil has been determined by working on known mixtures, and comparison, when that is possible, with other methods.

This work will require time. For the present it seems that the assay of oils in which carvone, camphor, pulegone or thujone is the main constituent can be carried out with fair accuracy by this method, at least affording a criterion of the purity of such oils.

THE MANUFACTURE OF AMMONIA IN BY-PRODUCT COKE OVENS.

By LOUIS CLEVELAND JONES.

Received March 9, 1911.

Nitrogen is to me the most intensely interesting element of all the eighty with which we chemists have to deal. It is present in only small quantities within the solid earth's crust but in tremendous quantities in the atmosphere, enough if condensed upon the earth's surface to submerge us all in a liquid layer only a little lighter than water and twenty feet deep. A sea of liquid nitrogen over all the surface of the earth gives you an idea of the abundance of this substance.

Uncombined, nitrogen is the most inactive and harmless material tha can be imagined. It can be mixed in all proportions with oxygen and hydrogen and yet retain its passive characteristics.

Combined, however, chemically with 2.5 parts of oxygen (another harmless even life-sustaining element) it forms fuming nitric acid which would consume the human body with almost explosive violence. Combined with three parts hydrogen it forms ammonia gas, a volatile alkali almost as dangerous a substance as its oxygenated cousin. In other compounds it forms the most sensitive explosives, set off by the gentlest breath of air, or if we wish, explosives the most powerful and at the same time the most useful.

Man cannot live without nitrogen in his food, yet combined in a particular manner with carbon (another harmless substance) it becomes one of the deadliest poisons known. Combined, however, with carbon in another way but in the same proportion it is physiologically harmless. In yet another way nitrogen combined with hydrogen, oxygen and carbon produces all that wonderful galaxy of colors of which aniline and nitro compounds are the base.

Uncombined, it requires the subtlest means (nitrifying bacteria) or else the most strenuous (the electric arc) to bring it into chemical union, but when once combined with other elements it forms the most stable of chemical compounds.

To illustrate the sources and uses of the particular nitrogen compound, ammonia, which we are discussing to-night, I have prepared two tables.

Table I shows some general sources of ammonia; II indicates some of the principal forms in which it is obtained and their general uses.

TABLE I.—SOURCES OF AMMONIA.

By-product coking of coal.
By-product of producer gas manufacture.
From distillation of peat.
From distillation of shale.
Blast-furnace gases.
Distillation of bones and leather.
Synthetically produced from $N_2 + H_2$ and osmium.
From nitrides of metals, titanium nitride.
From calcium cyanamide and steam.
Found in alkali lakes and waters from volcanic rocks.
Electric sparking of $N_2 + H_2$.
Sewage and urine.

In these two tables there is material for many days' discussion, but I propose to speak only of the production of ammonia in by-product ovens.

Production of Ammonia in By-Product Coking of Coal.—The yield of ammonia as sulphate in the actual coking operation varies from 18–28 lbs. per ton of dry coal. These look like rather small figures (about 5 lbs. NH_3) to be obtained from 2000 lbs. of coal, but the total annual production from by-product coke ovens in the United States alone amounts to the immense total as sulphate of ammonia, to about 75,000 tons; or at 25 tons to a car, 3,000 carloads, and at 50 cars each would equal 160 train loads, or a solid trainload 22 miles long. The total production

TABLE II.—AMMONIA BY-PRODUCT FROM COKING OF COAL.

	Sources.	Uses.
Weak liquor	From gas washers	Further manufacture
Crude liquor	From weak liquor	Manufacture of soda ash, felts, preserving timber
Partially refined liquor	From crude liquor	For explosives, ammonium nitrate
Liquor (partially purified liquid, free from sulphur)	From crude liquor	Synthetic cyanides, Ostwald process
Aqua	From crude liquor	Household and further mfg., refrigeration
Anhydrous	From crude liquor	Refrigeration
Ammonium sulphate	From crude (direct)	Fertilizers, further mfg.
Ammonium nitrate	From crude	For safety explosives
Ammonium chloride	From aqua (in S. A. process)	Electric batteries
Ammonium bicarbonate	From aqua and CO_2 gas	Baking and baking powders, smelling salts, dyeing
Ammonium picrate	From aqua and picric acid	Explosives
Ammonium chlorate		Explosives
Ammonium sulphide	From aqua	For chemical analysis and photographic work
Oxalate and other salts		
Ammonium phosphates		
Ammonium chromates		
$CaCl_2.8NH_3$		
"Dry ammonia"	$(NH_4)_2SO_4$–Na_2CO_3, etc.	Cleaning and laundry
Ammonium oleate	Aqua and red oil	Ammonia soap
NH_4CN		Ore extraction (Au, Cu, Ag)

of the world is probably more than 1,000,000 tons as sulphate. Thus does this little 5 lbs. of NH_3 (1/4 of 1 per cent. of the coal coked) make a great aggregate.

Nitrogen, of course, in the coal is the source of the ammonia produced from coal.

We have tested the nitrogen content in average samples of coal representing all the coal used during a month at several of the Semet-Solvay plants.

TABLE III.—NITROGEN IN COALS COKED DURING JUNE, 1907.

(Tests by Cole.)

Plant.	% Nitrogen in coal.			% Nitrogen in coke.	
A	1.104	1.214	1.104		
B	1.21	1.20			
C	1.29	1.32		1.104	1.11
D	1.38	1.39		1.518	1.49
E Boomer	1.24	1.16			
Smokeless	1.46	1.34			
F	1.21	1.22			
G	1.36	1.36			
H	1.33	1.35			
I	1.17	1.21		1.186	1.104
J	1.38	1.33		1.104	1.131
K	1.076	1.269	1.242	0.966	0.993
Coalite	1.20			1.29	1.331

Distribution of Nitrogen in the Coking Process.—It will be observed that the nitrogen in the coke produced at Plant D (on the basis of 76.7 per cent. coke yield) exceeds that in the coal—obviously an error, probably due to a non-representative or contaminated coke sample. As a general rule we have found that the nitrogen in the coke runs about 90 per cent. of that found in the coal.

From the above table the nitrogen in a ton of coal was distributed as follows:

TABLE IV.—NITROGEN BALANCE FOR OPERATION AT S. S. CO. PLANT C.

	lbs.	Calculated to $(NH_4)_2SO_4$. lbs.
Coal, 1.30 per cent. × 4.7 (× 2000)		122.6
Ammonia yield, actual	25	
Nitrogen in coke	78.2	
Gas 10,500 cu. ft. = 300 M^3 containing 5 per cent. N = 4.5 K	10.0	
Tar 90 lbs. 0.8 per cent. N = 0.72 lbs. × 4.7	3.5	
Pyridine 0.3 Gpl in 0.5 M^3 = 0.15 K × 0.83 × 22	0.3	
Simple cyanides	0.2	
Methyl cyanides	0.2	
		119.6
Loss		3.0

Using nitrogen in coke as 90 per cent. of that in coal.

TABLE V.—NITROGEN BALANCE FOR PLANT D.

	lbs.	lbs.
Coal, 1.385 per cent. × 4.7 = 6.5 × 2000		130.0
Actual ammonia yield	27	
Nitrogen in coke	90	
Nitrogen in gas	10	
Tar, pyridine and cyanides	5.9	132.9
Excess		2.9

Likewise making the nitrogen balance for the other plants we get the following figures:

TABLE VI.

Plant.	Total N in coal as sulphate. lbs.	Total N in products as sulphate.
A	114.0	113.2
B	113.2	114.3
E	121.2	124.4
F	114.3	115.1
G	127.8	127.0
H	126.0	126.2
I	111.8	112.4
J	127.5	126.2
K	118.0	116.7

Percentage Recovery.—It is evident thus that of the total nitrogen in coal only about 20–25 per cent. is recovered as ammonia in the by-product operation. If, however, we consider the nitrogen remaining in the coke to belong to the province of the blast-furnace man, we may state with greater satisfaction to the by-product operaton that only 8–10 per cent. of the total nitrogen of a coal is lost in the by-product operation. Stating the same in another way, of the total volatile nitrogen the by-product operation recovers 62 per cent. as ammonia, 14 per cent. as cyanides and other nitrogen compounds, 24 per cent. being lost as nitrogen gas.

Loss in Gas.—Since the presence of each percentum of nitrogen produced in illuminating gas represents a loss of sulphate of ammonia equal to two pounds per ton of coal, it would be of importance (though no method has been suggested) to decrease the amount of nitrogen evolved with the gas.

Loss in Coke.—The greatest portion of the nitrogen in a coking coal, *i. e.*, 60–70 per cent., escapes with the coke where it exists in an unknown combination until liberated by the burning of the coke in the cupola or blast furnace.

We have no information regarding the chemical compound which retains the nitrogen in coke so persistently, *i. e.*, when heated even to 1000–1100° C. Possibly it is there as an inorganic nitride formed with the ash of the coke or absorbed as cyanamides formed from some inorganic carbides derived from superheated carbon and ash. It is probable, however, that it may be held by the carbon alone since the coke made from oil residues or pitch, though free from ash, still contains nitrogen to the extent of about a per cent.

Nitrogen may be completely recovered from coke by heating with soda lime.[1]

Combined Nitrogen in the Blast Furnace.—When the coke goes to the blast furnace containing about 1.1 per cent. nitrogen, there is formed from this nitrogen, under certain conditions in the reducing blast-furnace gas, considerable ammonia which in Scotland is recovered by washing the gas in acid.

Ammonium chloride stalactites from the chlorides in the ore have been found hanging from some of the pipes carrying waste blast-furnace flue gases.

Likewise cyanogen is formed in blast-furnace gas near the bottom of the furnaces as high as 15.5 grams per M^3, equivalent to about 211 lbs. sulphate of ammonia per ton coke. About 71 lbs. are reported by Bell[2] in the exit blast-furnace gases. The first figure is far above theory for the total nitrogen. The evidence is therefore strong that there is at times at least an actual synthetic production of cyanogen from atmospheric nitrogen and carbon in the blast-furnace operation.

By-Product Operating Conditions.— In order to get high ammonia yields in the by-product coking operation we have to consider the following factors in the coal quality:

(1) The amount of nitrogen in the coal.

(2) The amount of volatile nitrogen, *i. e.*, the total nitrogen in the coal less that retained in the coke.

(3) The amount of volatile matter.

(4) The nature of the volatile matter.

  (*a*) As to oxygen content (water and oxygenated gases evolved).

  (*b*) As to calorific value.

(5) The amount and nature of the coal ash itself—CaO, Fe_2O_3.

I will discuss briefly these factors in the quality of a coal which affect its yield of ammonia.

First, the Amount of Total Nitrogen.—This varies greatly in various coals as given by the tests of the U. S. Fuel Testing Bureau.

Some Texas and N. Dakota lignites and a Morgan Co. Mo. coal contain as low as 0.71–0.75 per cent. nitrogen. On the other hand, coals from Straig Creek, Eastern Ky., from the Rock Island Coal Co., Indian Territory and a smokeless coal from Rush Run, West Va., contain 1.70–1.85 per cent. nitrogen. Natural asphalts contain 1.0–1.1 per cent. nitrogen. In by-product tar and pitch about 1 per cent. N has been found. In fact we have been able to obtain experimentally an ammonia yield as sulphate of 8–10 lbs. per ton from hard by-product pitch.

Second, Volatile Nitrogen.—No effort, as far as I know, has ever been made to determine the amount of volatile nitrogen in coals and its relation to ammonia yields. From this volatile nitrogen, of course, must come all the ammonia and other valuable nitrogen compounds. Unfortunately the nitrogen in the coke has rarely been determined, but the figures obtained by us show a definite relation between the amount of volatile nitrogen and ammonia yields. In practice the recovered ammonia with the other nitrogen compounds in the weak liquor plus the nitrogen in the gas would give the measure of the volatile nitrogen, but unfortunately the nitrogen in the gas commercially produced is seldom quite free from atmospheric nitrogen and flue gas nitrogen, due to leaks and the porosity of the coking chamber.

From experiments made in the bomb apparatus devised in our laboratory we have indications that the amount of uncombined nitrogen evolved in the gas is, for all the conditions of temperature commonly used in the production of illuminating or coke oven gas, practically a constant percentage. Samples of gas tested under conditions absolutely preventing contamination with flue gas or atmospheric nitrogen show the nitrogen content to be about constant all through the coking period, although it has been often stated that the gas evolved towards the end of the coking period consists largely of nitrogen.

Even under conditions of extremely low temperature, *i. e.*, producing coalite, considerable free nitrogen is evolved with the gas, while the unevolved nitrogen, *i. e.*, that in the coalite itself, is higher than in the original coal, since under these conditions a greater amount of nitrogen remains in the coke.

On account of the meager information at hand we are continuing the further investigation upon the volatile nitrogen in coal, and the conditions which increase its total as well as the proportion of the combined compared with the uncombined volatile nitrogen.

Third, Amount of Volatile Matter in a Coal.—In general the ammonia yield increases with the percentage of the volatile matter in the coal coked, though the nature of that volatile matter as regards volatile nitrogen, oxygen content and calorific value is influential.

Fourth, Nature of the Volatile Matter.—(*a*) In fact there are strong indications that the presence of oxygen in the volatile matter of a coal, though tending to produce poor coke structure, has a beneficial influence upon the yields of ammonia. It appears that the evolving moisture actually produced *in situ* at the carbonizing temperature either by dilution or other protecting influence tends toward a higher yield of ammonia.

(*b*) Early realizing the influence of oxygen in the volatile matter as determined by ultimate analysis, which as you know is a time-consuming and difficult

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[1] "Ammonia and Its Compounds," Camile Vincent, *Trans.*, **1901**, M. J. Salter, p. 44.

[2] Bell, "Principles of the Mfg. of Iron and Steel."

operation, and at best throws the combined errors upon the most influential constituent, oxygen, we have devised a simple method of calculation from the proximate analyses and calorific value to indicate the quality of the volatile matter in a coal; for, as you know, this is the factor that not only determines the character of the coke but also as well the amounts and quality of the by-products to be expected.

On the basis of this calculation we have been accustomed to classify coals according to the calorific value by per centum of volatile matter, as well as according to the total amount of volatile matter.

In the table following are arranged some typical coals in the order of their calorific value per unit of volatile matter. This order has also been found to be in accord in a measure with the behavior of these coals under the influence of heat.

TABLE VII.—CALORIFIC VALUE BY PER CENT. VOLATILE FOR SEVERAL TYPICAL COALS.

Coals.	H_2O. Per cent.	Volatile. Per cent.	F. Carbon. Per cent.	Ash. Per cent.	Sulphur. Per cent.	Phosphorus. Per cent.	Cal. val.	Cal. val. by per cent. vol.
A........	1.36	25.10	66.08	7.46	0.61	0.005	7907	105.5
B........	2.52	24.76	64.34	7.38	0.80	0.011	7787	105.0
C........	0.95	22.37	73.48	3.20	0.72	0.005	8242	103.9
D........	..	26.44	67.06	6.50	0.87	...	8107	103.7
E........	..	26.12	66.75	7.13	0.95	0.018	7960	102.9
F........	..	25.10	66.60	8.30	0.85	0.016	7888	100.6
G........	1.23	32.27	61.05	5.45	0.77	0.015	7901	92.4
H........	1.61	37.04	55.70	5.65	1.22	...	7856	91.5
I........	1.18	35.82	58.54	4.46	0.63	0.003	7972	90.8
J........	2.00	35.05	58.50	4.45	0.63	0.004	7817	88.5
K........	2.05	36.43	51.48	10.04	2.30	0.024	7291	87.0
L........	6.66	36.48	48.46	8.40	1.30	0.006	7036	86.6
M........	6.71	37.17	51.72	4.40	0.72	0.007	7158	80.0

Fifth, Ash.—Ash in a coking coal is in most cases only a diluent, an inactive impurity. When, however, consisting largely of iron oxide or calcium carbonate, it has an influence on the ammonia yields. Iron oxide in large amounts at high temperatures has a catalytic action upon ammonia gas and decreases its yield. Lime, on the other hand when present in considerable amounts, increases the expulsion of nitrogen from the coke.

GENERAL.

Operating Conditions which Affect the Yields of Ammonia, Cyanides, etc.—Since coals are generally, if not always, selected for coke- or gas-producing properties, cheapness and accessibility, and since the nitrogen, of course, in these given coals is the only source of ammonia, we strive to provide operating conditions which tend to keep as high as possible the amount of nitrogen volatilized (that remaining in the coke being of negative value); also we strive to have as great a percentage as possible of the volatilized nitrogen in the combined condition (principally ammonia).

Of course in those processes where the coke or coal is entirely consumed, *i. e.*, producers, it is possible to obtain a much higher yield of ammonia because all the nitrogen corresponding to that which in the by-product operation remains in the coke becomes available. Thus in the production of producer gas by the Mond process it is not unusual to obtain 80 lbs. ammonium sulphate per ton of coal. The actual yield in producers, however, when based upon the total nitrogen volatilized is not greater than in by-product ovens and the higher yield therefore from producers is not, as generally supposed, due to the lower temperatures.

The conditions in the coke ovens themselves which are under our control are:

Temperature.
Pressure.
Gas travel, height and fulness of ovens.
Introduction of foreign materials:
(*a*) Gas, steam, washed gas.
(*b*) Solids: iron oxide, lime.

LENGTH OF COKING PERIOD.

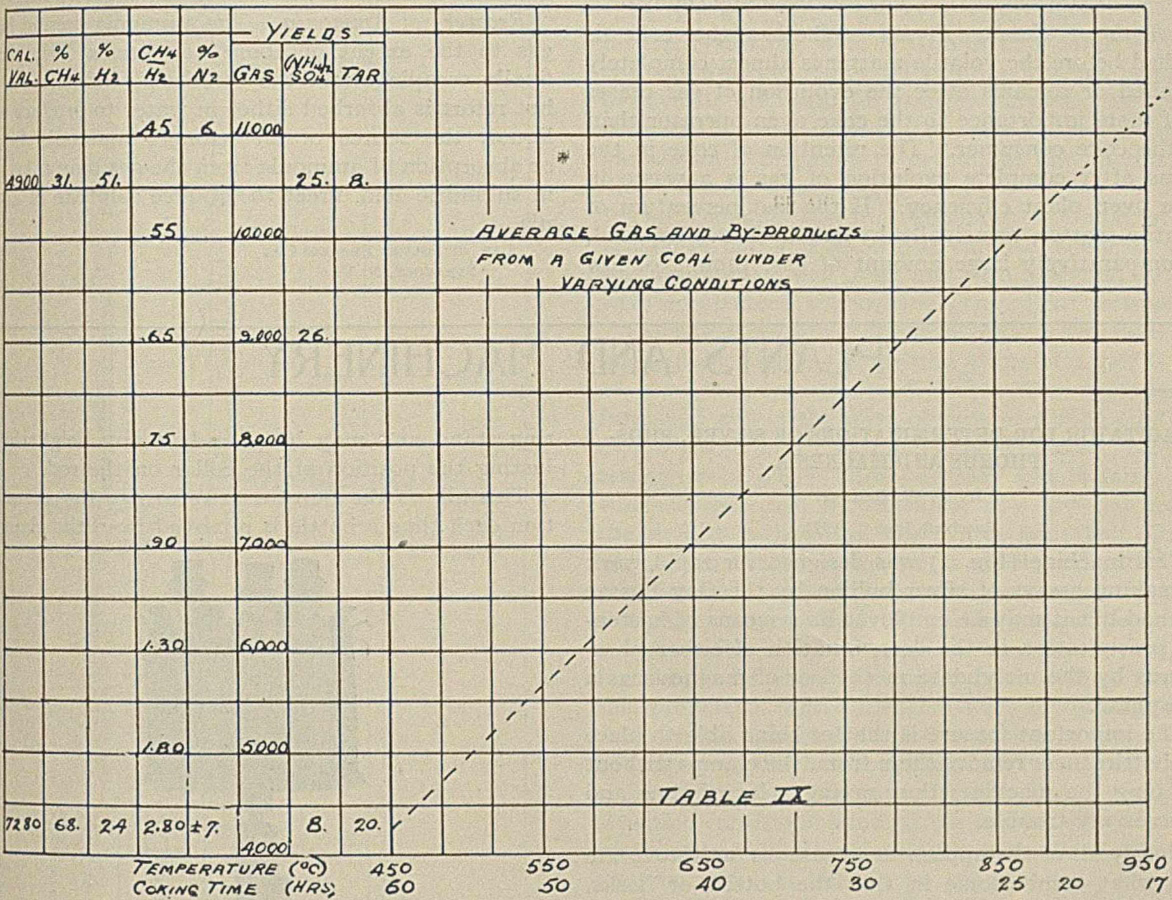
Temperatures.—Temperature is the chief factor in the by-product operation. Coal subjected to a gradually increasing temperature after drying at about 100° C. suffers practically no change until about 400° C., when it begins to decompose and give off gas and tarry matters. At about 430° C.—the temperature used to produce coalite—carbonizing takes place producing about 8 lbs. sulphate of ammonia, a coke still containing 4–5 per cent. volatile matter (largely hydrogen) and a high percentage of nitrogen, a rather high yield of exceedingly light tar, and four to four thousand five hundred feet of exceedingly high quality gas. The point which is of particular interest in this connection is that this gas seems to contain, as evolved, practically as much free nitrogen as if coked at higher temperatures. The ammonia yield being small and the other nitrogen compounds certainly not above normal, there remains of necessity in the coke a large portion of the nitrogen ordinarily volatilized. To speak of the temperature of coking is very misleading for the temperature in the retort during operation is different at almost every different point and at every different point of time. At the outside of the coking mass near the wall the temperature is perhaps 1100° C. while within the center of the coking mass not above 100–200° C. From the beginning of the coking period the isothermal lines converge upon the center of the coking mass until the coking is complete and the coke is withdrawn.

As a measure of average temperature conditions therefore I have, to a certain extent, abandoned thermometer or pyrometer and adopted other means, *i. e.*, gas analysis. This will appear from the following gas analyses from similar coals, one gas produced at low, the other at high temperatures.

TABLE VIII.

	P. G. coalite gas.	Ordinary coke oven gas.
Temperature....................	430° C.	1050° C.
Coking period..................	60 hrs.	17.7 hrs.
Volume of gas..................	4260 cu. ft.	10500 cu. ft.
CO_2..................	2.0%	1.7%
Illuminants..................	2.2	2.9
O_2..................	2.3	0.6
CO..................	3.0	4.8
H_2..................	21.2	51.6
CH_4..................	60.1	31.3
N_2..................	9.2	7.1
Calories per M^3..................	6397	4906
CH_4 to H_2..................	2.81	0.607
Combined O_2..................	3.50	3.25

With this gas data outlined on Table IX we have an interpretation of each by-product factor in terms of the other; the conditions represented are merely suggestive, and as it chiefly concerns gas manufacture details are reserved for a general discussion of the manufacture of illuminating gas in by-product ovens. It is of interest, however, in the consideration of the nitrogen balance of the by-product operation, since it seems to indicate that low temperatures as well as high produce free nitrogen and that there is an average condition of temperatures which produces maximum ammonia yields.



Pressure.—Pressure in a by-product coking retort is of particular importance for regulation of leakage of gas outward or of flue gas inward through the porous walls of the oven.

The variation of the few millimeters from the 760 one way or the other necessary to regulate leakage is practically without effect upon any composition or decomposition of the by-products sufficient to influence yields.

Gas Travel, Height and Fulness of Ovens.—The gas and all other by-products, including ammonia, travel from the coking coal to the hot walls and along them to the gas outlet. The hot oven walls and coke have therefore opportunity for catalytic action tending to decompose both ammonia and the hydrocarbons of the gas. This action is not all bad, for a portion of the tar oils is at the same time cracked to produce a greater gas volume, generally of more value than the corresponding amount of tar destroyed.

Foreign Materials. Effect upon Ammonia Yields.—In England the introduction of steam into the hot oven retort has been reported to give an increased ammonia yield. Further experiments in this direction have not been encouraging. Of course the presence of steam may, acting as a diluent, protect the ammonia from the oven walls, but I suspect the greater amount of the small increase of ammonia arises from the nitrogen in the coke, due to actual consumption of the coke by the steam to form water gas.

The introduction of ammonia-free gas through the retort during the coking process doubtless protects both the gases and the ammonia but has never been found commercially practicable.

Iron Oxide.—Fine iron oxide in the form of flue dust, a waste product from blast furnaces, has been introduced into coke to enable its recovery with the consumed coke. Our tests indicate that the catalytic effect of iron oxide in a coke oven is sufficient to decrease the ammonia recovery to such an extent that the saving in flue dust in this way would result in actual loss.

Basic Oxides.—As already suggested, the presence of lime in a coking coal has been shown in English gas practice to increase the ammonia yield, but the fluxing action of lime upon the oven walls has made the practice of doubtful value. At any rate the English retort gas makers who originally advocated the practice have abandoned it.

Whether the increased ammonia yield in this case is due to a greater expulsion of nascent nitrogen from the coke or to the prevention by the lime of the destructive catalytic effect of oxides of iron always present in the ash of coke has not been determined.

Length of Coking Period.—Whether the coke is pushed before the volatile matter is almost completely expelled or remains after the evolution of gas ceases is of more importance to the coke oven operator than to the coke consumer. The retention of coke in the ovens after complete evolution of gas is a waste in coke oven plant efficiency. If the last percentum of volatile matter, principally hydrogen, is not expelled, a comparatively large amount of gas, though of low quality, is lost. On the other hand, if coke containing an additional amount of unexpelled volatile matter, principally hydrogen, goes to the blast furnace, little harm is done except that of a diluent since all the hydrogen remains still uncombined in the blast-furnace exit gases where, of course, it is of value in case these gases are utilized for fuel or for gas engine power.

Recovery of Ammonia.—The ammonia present in the gas to the extent of about 100 grams NH_3 per M^3 finally escaping from the conflicting influences of the hot retort is absorbed either in water to produce weak liquor, the source of all stronger ammonia liquors, or absorption of ammonia from the gas may take place in sulphuric acid direct to produce sulphate of ammonia.

Lab. of Solvay Process Co.,
Syracuse, N. Y.

PLANTS AND MACHINERY

AGITATOR FOR DETERMINATIONS OF SILVER, PHOSPHORUS AND MAGNESIA.

By L. W. Bahney.

Received June 1, 1911.

This machine (Fig. 1) was designed for rapid work in making assays of silver bullion by the Gay-Lussac method but it may be employed as a means of hastening precipitation in the determination of either phosphorus by the molybdate method or of magnesia as a phosphate.

The important feature is that of being able to place the bottles in, or remove them from, the clamps without stopping the machine, thus saving a lot of time and unnecessary trouble.

Nearly all of the apparatus in use as agitators are somewhat cumbersome in that the bottles or flasks, in which the determinations are made, are either placed in a box that has a cover that must be clamped down each time or they are placed in some sort of a clamp that must be tightened and loosened each time, and always when the machine is at rest.

The clamps are made of spring brass mounted on a brass disk that is operated by an eccentric having a speed of 450 revolutions per minute, and a small electric or water motor is sufficient to do this.

At the bottom of the cups that constitute the base of the clamps is a piece of felt $^1/_4$ inch in thickness to prevent the bottles from being broken.

The machine is made in two sizes, for 3 and 12 bottles respectively, by the Denver Fire Clay Company, Denver, Colorado.

The burette attachment shown in Fig. 2 is used in the rapid determination of calcium oxid in lime[1] and consists of a 100 cc. burette (preferably glass cock) having a 5-inch length of $^1/_8$-inch glass tubing fastened to the tip by means of a piece of rubber tubing.

The burette is held, by two clamps, to a piece of brass tubing that will slide freely over the $^1/_4$-inch rod of a ring stand and may be placed at any height by adjusting the position of the collar on the rod.

This allows the burette to return to the same position each time a bottle is removed from the clamp.

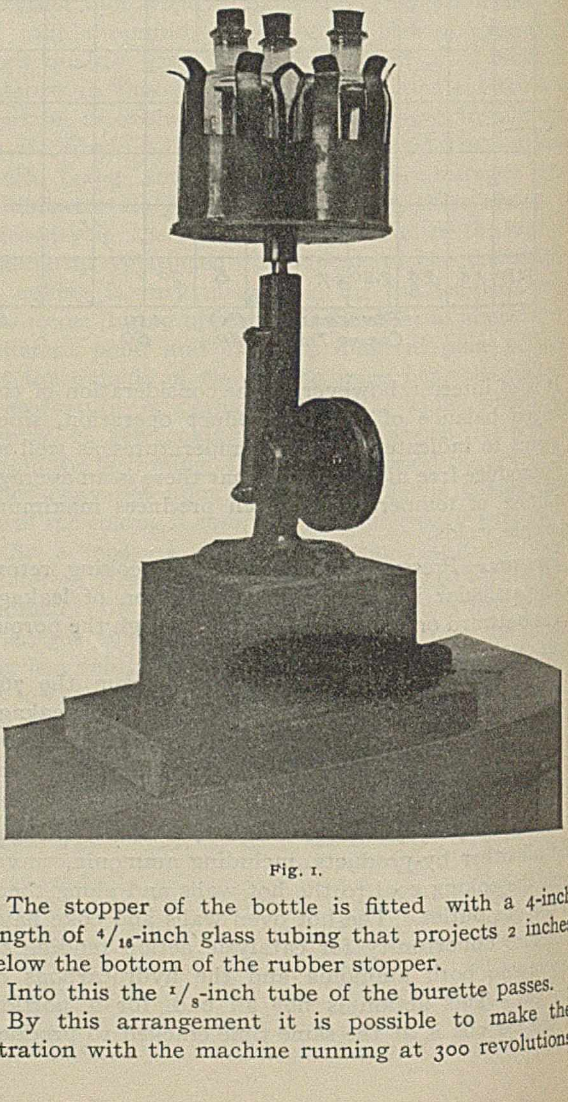


Fig. 1.

The stopper of the bottle is fitted with a 4-inch length of $^4/_{16}$-inch glass tubing that projects 2 inches below the bottom of the rubber stopper.

Into this the $^1/_8$-inch tube of the burette passes.

By this arrangement it is possible to make the titration with the machine running at 300 revolutions

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[1] This Journal, 2, 10 (1910).

per minute and have none of the solution splash out, at the same time having enough air passing into the bottle to allow the oxalic acid solution to drop freely into the bottle.

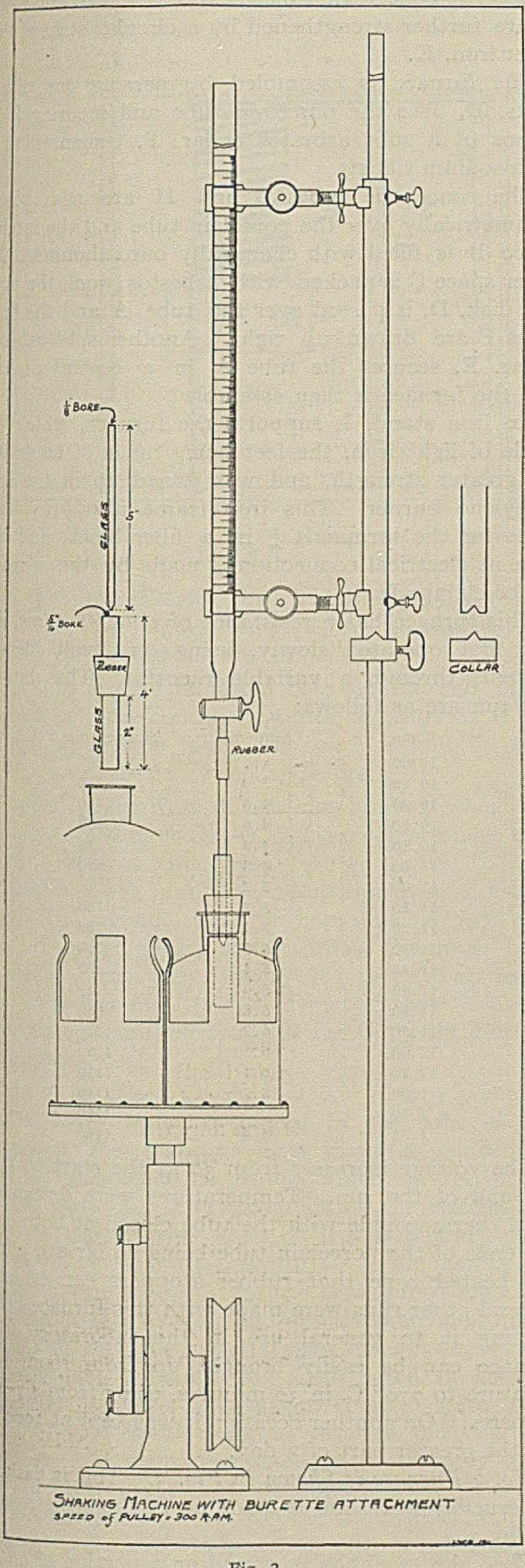

Fig. 2.

STANFORD UNIVERSITY,
May, 1911.

ELECTRIC TUBE FURNACES WITH CALORITE RESISTERS FOR THE LABORATORY.[1]

By Samuel A. Tucker.

Wire-wound resistance furnaces have now come into general use for electric furnaces in the laboratory and fill a place that perhaps no other heating appliance is capable of.

In our experience we have tried several types of resisters, starting with platinum and some types of chromium-nickel alloys. Platinum, besides being expensive, is not ideal for resister purposes, as the life is limited and repairs are by no means easy. Nichrome has shown a tendency to crystallize and in this condition breaks under slight strain.

The General Electric Company manufactures a resistance material known as calorite, some of which was kindly furnished to us, and with it several furnaces were constructed which have given great satisfaction.

Calorite is an alloy of nickel, iron, chromium, and manganese, and has a melting point of 1550° C. and a low temperature coefficient. The material as furnished was in the form of tape or ribbon 2.38 mm. (0.094") wide and 0.24 mm. (0.008") thick. It has a resistance of 0.878 ohm per foot and is fairly soft, which is increased by annealing at a low red heat in the air just as platinum wire can be annealed. Oxidation, when heated in the air, is merely superficial even at quite high temperatures, and there seems to be no tendency to crystallize. The alloy cannot be used in contact with silica at high temperatures, and the furnaces were therefore constructed with a view to this property. Three furnaces were made as follows:

No. 1 was designed for tube-heating having a short heating zone which will bring to an even temperature the average size combustion boat. The general construction consists in winding the resister on a porcelain combustion tube, surrounding it with chemically pure alumina which is held in an asbestos tube and then surrounding the whole with asbestos wool packed between the inside asbestos tube and the outside container which is also of asbestos.

Figs. 1 and 2 are drawings of No. 1 furnace.

A is the porcelain tube of Royal Meissen ware glazed inside, but not on the outside, 457 mm. (18") long with internal diameter of 25.5 mm. (1"), outside diameter 30.5 mm. ($1^3/_{16}$"). There were collars at

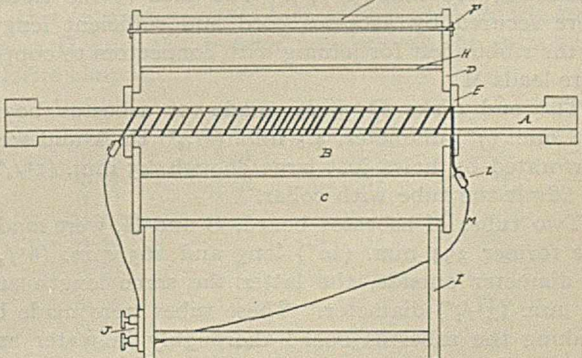

Fig. 1.

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[1] Read at the May meeting of the New York Section of the American Chemical Society.

each end of the tube which serve no purpose, but the tube would have been too short had they been removed. These collars had a diameter of 51 mm. (1$^1/_2$") and a length of 25.5 mm. (1"). The tube projected out of the furnace 95.5 mm. (3$^3/_4$") at each end, leaving an available winding space of 267 mm. (10$^1/_2$"). This was wound with the calorite ribbon taking 28 turns, distributed in 9 turns for the first 108 mm. (4.25"), 10 turns for the next 51 mm. (2") which is the central portion, and again 9 turns for the remaining 108 mm. (4$^1/_4$"). The ends of the ribbon were secured by asbestos cord and sufficient length of the ribbon left for joining with connectors to copper wire leads M.

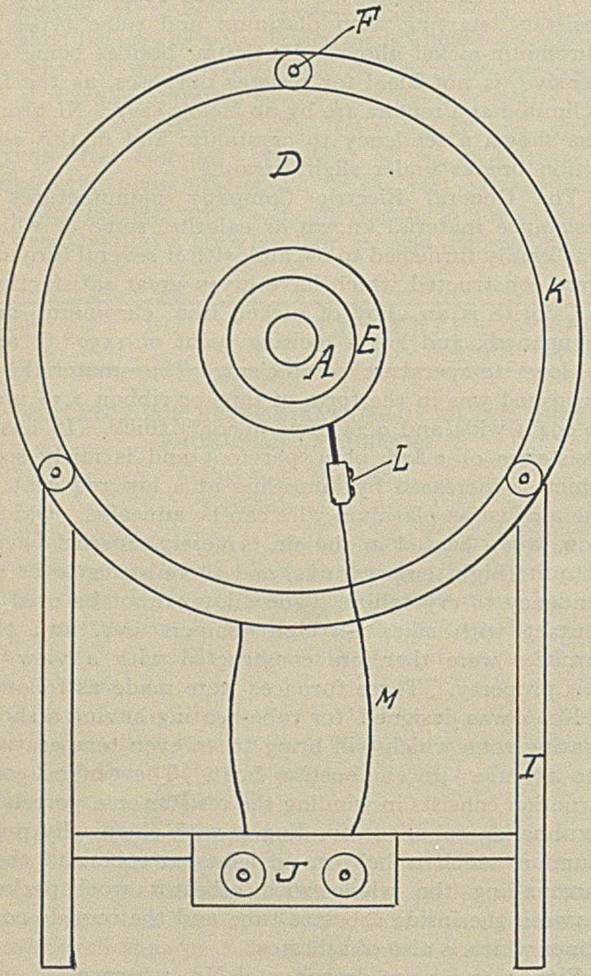

Fig. 2.

The end disks D were made of asbestos board 178 mm. (7") diameter, 4.5 mm. ($^3/_{16}$") thick and were perforated by holes just large enough, 45 mm. (1$^3/_4$"), to admit the tube with collar.

Two tubes of asbestos board, G and H, were made, the former 254 mm. (10") long and 165 mm. (6$^1/_2$") in diameter outside, the latter the same length and 89 mm. (3$^1/_2$") diameter. These tubes were made by soaking the asbestos board thoroughly in water and then rolling to the required shape over a bottle or roller and cementing the lapped joints with sodium silicate.

The end-piece D is bored through for the three long brass bolts F which hold the end disks tight to the two concentric tubes G and H. The end-pieces D are further strengthened by a circular strip of thin sheet iron, K.

The furnace is assembled by passing one of the disks, D, over the porcelain tube and securing it by means of a split asbestos collar, F, cemented to D with sodium silicate.

The concentric tubes G and H are next placed symmetrically over the porcelain tube and the interior space B is filled with chemically pure alumina. The outer space C is packed with asbestos wool, the other end disk, D, is passed over the tube A and the brass bolts F are drawn up tight. Another split asbestos collar, E, secures the tube A in a central position and the furnace is then assembled.

An iron stand, I, supports the furnace, which was made of light iron, the feet being made of angle iron for greater strength, and was joined up in the oxyacetylene burner. This iron frame also provides a place for the terminals J in a fiber block, and permanent electrical connection is made by the wires M to the clamps L.

This furnace has a resistance of about 8 ohms, and was first operated slowly, using 110 volt density current, through a variable rheostat. The data of this run are as follows:

Time.	Amperes.	Temperature ° C.
10.00	..	..
10.15	5.9	380
10.20	4.6	410
10.40	4.6	550
10.50	4.8	620
11.00	4.8	670
11.00	5.2	..
11.10	5.2	760
11.20	5.2	780
11.20	5.5	..
11.40	5.4	850
11.40	5.9	..
11.50	5.8	960
11.50	6.2	..
12.00	6.15	1030
12.20	6.1	1110
1.00	5.7	1140
1.10	..	1160
1.35	5.4	1140

The voltage increases from 30 at the start to 45 at the end of the run. Temperatures were determined by a thermocouple with the tube closed at both ends, the ends of the porcelain tube being so far away from the heated zone that rubber stoppers can be used. Several other runs were made with this furnace before putting it to general use in the laboratory. The furnace can be easily brought up from room temperature to 770° C. in 30 minutes, using from 4.7-4.95 amperes. On another occasion it was kept at 1000° C. for the greater part of a day.

No. 2 Furnace is Shown in Fig. 3.—This is designed for crucible work and is made up in the same manner as No. 1.

The calorite ribbon is wound on a portion of a large Meissen porcelain tube, A, which was cut from a large combustion tube, giving a length of 102 mm. (4"), including the collar. The inside diameter was 52.5 mm. (2$^1/_{16}$"), the outside diameter being 61 mm.

(2$^{3}/_{38}$"). Twenty turns of the calorite were wound on the 76.5 mm. (3") space and secured at each end by twisting a piece of the ribbon around the winding, as in this case asbestos cord was not permissible on account of the higher temperature to which these portions of the resister are subjected.

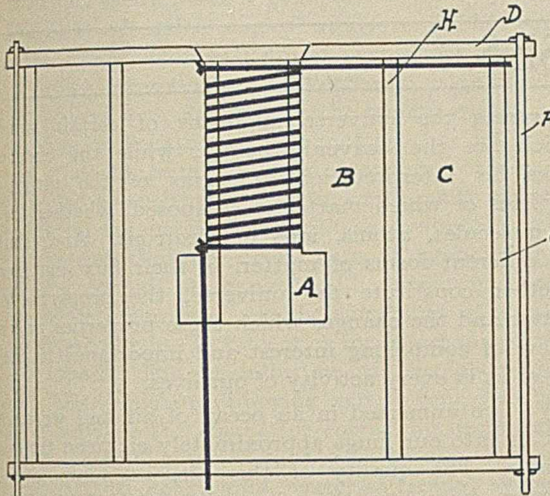

Fig. 3.

The tube is then mounted between the end plates D which hold the concentric tubes of asbestos G and H in position, the filling for space B and C being alumina and asbestos wood as before.

The end plates were of asbestos lumber, which can be easily turned in the lathe and is much stronger than ordinary asbestos mill board. These plates, D, have a diameter of 223 mm. (8$^{3}/_{4}$") and thickness of 6 mm. ($^{1}/_{4}$"). The outside tube or container is 197 mm. (7$^{3}/_{4}$") diameter, giving space to pass the brass bolts F which clamp the furnace together. The inside tube H is 115 mm. (4$^{1}/_{2}$") diameter, these measurements giving a suitable space, B and C, for the alumina and asbestos wool.

Tube A is closed at the bottom with a porcelain crucible cover which is placed in the tube at the bottom of the resister. This gives a convenient space for crucibles to be heated, which may be of any suitable material. The terminals of the resister are joined to copper wire which is led to binding posts in the end-piece D (not shown). A number of experiments were made in the use of different materials for the tube, such as winding the resister on an ordinary porous cup, but this material does not answer as well as porcelain. Difficulty was anticipated in keeping the resister in place, and various cements were tried. The most successful material for the purpose was found in a cement composed of chemically pure alumina with 10 per cent. phosphoric acid. The use of cement, however, is not to be recommended, and the resister can be kept in position with the aid of the binding clamps of calorite.

The furnace was used on 110 volt density current and gave the following results:

Time.	Amperes.	Volts.	Temperature ° C.
9.50	4.6	35.0	...
10.00	4.48	37.0	360
10.15	4.55	37.5	510
10.30	4.5	38.0	590
10.45	4.58	39.0	625
11.15	4.55	38.0	690
11.40	..	..	710
12.00	4.55	37.5	730
12.45	4.55	38.0	750
·3.15	4.3	37.0	730
4.00	4.4	38.0	700
4.30	4.6	39.0	700

The furnace was also run more quickly, in 2 hours using 5.3 amperes and 42 volts the temperature reached was 805° C. which could be kept nearly constant.

The furnace is not adapted to quite such high temperature work as the horizontal tube furnaces on account of the thickness of the wall of the porcelain tube and also because the temperatures as taken by the pyrometer are measured in the open space, thus the temperature of the resister must be very much higher than at the thermocouple junction, the difference being much greater than in the case of the horizontal furnace. 800° C. is about the maximum temperature that it is safe to use with this type of furnace.

Another horizontal tube furnace was built similar to No. 1 for heating a greater length of the porcelain tube. The inside diameter of the tube is 19 mm. ($^{3}/_{4}$") and the total length 610 mm. (24"). Allowing 153 mm. (6") to project at each end gives a winding space of 305 mm. (12").

This was wound as shown in Fig. 4 with 8 turns of the calorite in 38 mm. (1$^{1}/_{2}$"), 25 turns in the middle portions of 228 mm. (9") and 8 turns at the other end-space of 38 mm. (4$^{1}/_{2}$"). The object here is to heat the tubes as evenly as possible throughout a length of 305 mm. (12"), and this is accomplished by increasing the number of turns of the resister at the ends where the heat losses are greatest. The general dimensions of the furnace are nearly the same as for No. 1, except for the somewhat greater length of tube. In this furnace asbestos lumber was used for the end-pieces D and the resister was held at the ends with calorite clamps.

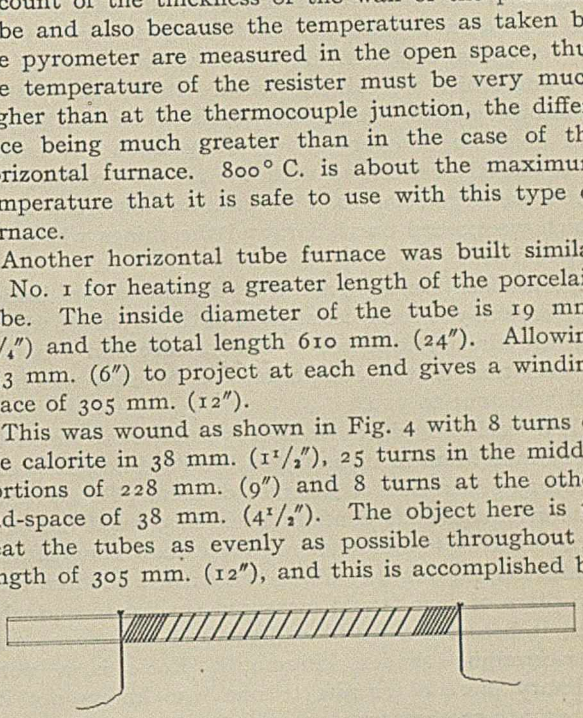

Fig. 4.

Time.	Amperes.	Volts.	Temperature ° C.
10.23	5.3	43.0	..
10.28	5.05	44.3	300
10.48	5.08	46.0	715
11.10	5.2	47.5	900
11.30	..	..	970
11.40	..	..	980
11.55	..	..	1010
11.55	4.75	46.0	..
12.03	4.72	45.0	1000
1.10	..	..	970
2.45	4.55	45.5	935
4.00	4.5	46.5	940
4.20	..	..	1050

The run with this furnace to try it out is given in the preceding data.

With care the temperature may be maintained constant at 1000° C. This has been done with No. 1 furnace in many experiments in which a boat was kept at a temperature of 925° C. for several hours.

Electrochemical Laboratory,
Columbia University.

ADDRESSES.

THE EARNING POWER OF CHEMISTRY.[1]

By Arthur D. Little.

Received July 11, 1911.

It may fairly be claimed for chemistry that it is at once the most fundamental and the most comprehensive of all the sciences. Its province, in the classical definition of Ostwald, is "The study of the different forms of matter, their properties, and the changes which they undergo." Thus defined, chemistry embraces the material universe, our solar system, the most distant stars and the flaming nebulae no less than the dust speck within the universe, on which we live and which we call the earth. It includes within its subject matter the physical basis of our own bodies and of those of every living thing upon the earth. It is directly concerned with the air we breathe, the water we drink, the food we eat, the materials upon which we expend our labor, and the things which we buy and sell.

To me has been assigned the pleasant task of bringing home to you some conception of the extent to which you are already indebted to this science and a better appreciation of the comprehensive benefits which it still holds out to you.

The world in which we live is a different world to every individual in it, as it has been a different world to every generation of the race of men. To no other generation have its confines been so opened out and broadened as to our own. To the man congenitally blind, tapping his way along the curb, a modern city is a place of sounds and measured spaces; to one who sees, it becomes a world of light and movement and ever-changing shades. Plymouth Rock is a very ordinary piece of granite to one who knows not its history; to the better informed it stands as the symbol of that adventurous spirit and uncompromising virtue on which the foundations of our country rest. To the world at large coal-tar is a black and evil-smelling nuisance; to the eye of the chemist it is replete with all the potentialities of the rainbow.

So it happens that the world as viewed by the chemist presents an aspect different in many ways from that in which it appears to the mind not chemically trained. As the astronomer perceives in the movements of the stars a relationship and coördination to which the average man is blind, and deduces from them generalizations by which both the intellectual and practical life of the community are profoundly influenced, so the chemist, who may be regarded as the astronomer of the infinitely minute, studies the movements and interchange of atoms and the structure of the molecular systems which result therefrom. In other words, the astronomer interprets the universe in terms of certain units, which are the heavenly bodies, while the chemist seeks his interpretation in terms of the ultimate particles of which matter is composed, whether they be molecules, atoms, ions or electrons. And, since the different forms of matter, in their flux and flow, together constitute the universe, the properties of matter and the changes which these properties undergo are of compelling interest and importance to each one of us in every activity of our lives.

We live immersed in an ocean of air and we draw this air into our lungs approximately eighteen times a minute. The quality of this air, its temperature, pressure, humidity, the minute impurities which may be present, affect our comfort and well-being in many ways. It supports the chemical processes of combustion by which our existence is maintained no less than those upon which we are chiefly dependent for light and heat and power. The nature of this all-enveloping atmosphere of air has always been a subject of speculation, though to little purpose before the advent of chemistry.

Modern chemistry had its birth in the eighteenth century study of the air and its relation to the processes of respiration and combustion. Prof. Ramsay has said that "To tell the story of the development of men's ideas regarding the nature of atmospheric air is in great part to write a history of chemistry and physics." The story is one which has reached its culminating interest in our own most recent times. For $35 you may now buy apparatus for reducing air to the liquid form and study the properties of matter at temperatures nearly as low as that of interstellar space.

Within the memory of the youngest undergraduate in chemistry the brilliant researches of Ramsay, Raleigh and other chemists have disclosed the presence in the air we breathe of five new gases of remarkable and in some respects unique properties. To one of these, neon, we now confidently attribute the long mysterious phenomena of the aurora borealis. Tubes containing highly rarefied neon may become as commonplace to our descendants as candles were to our forefathers. They glow with a rich, mellow, golden light on the passage through them of an electrical discharge.

The heavy toll of life in mine disasters would be unsupportably heavier were it not for the Davy lamp, the fire-damp indicators, the rescue outfits and the regulation of explosives, all of which have become possible only through the growth of chemical knowledge. Ventilating systems as applied to theatres, halls and dwellings are based on chemical studies of the rates and causes of increase in the carbonic acid

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[1] A public lecture to business men delivered June 29, 1911, under the auspices of the Indiana Section of the American Chemical Society.

content in the air of rooms. The proportion of sulphur permissible by law in illuminating gas finds its justification in similar studies on the air in rooms in which such sulphur-bearing gas is burned.

The chemical and biological study of public water supplies, which received its first systematic development little more than twenty years ago at the hands of Drown and Mrs. Richards in the laboratories of the Massachusetts Institute of Technology, has been the means of saving countless lives throughout the world and has led to such understanding and made possible such control of sources of pollution as to almost justify the statement that for every case of typhoid fever some one should be hanged. Chemistry can now determine in advance of use the suitability of a given water supply for use in boilers or for the requirements of any special line of industry, as paper-making, dyeing, cloth finishing, brewing and so on. Furthermore it supplies the means for correcting undesirable characteristics in a water supply as by use of filtration apparatus, coagulants, water-softening systems and the Moore method for the destruction of the algae which in many waters are the cause of unpleasant tastes and odors.

Nowhere is the practical value of chemistry in its relation to the affairs of every-day life more strikingly demonstrated than in connection with our food supply. Chemical fertilizers are in large and constantly increasing measure responsible for the enormous total of our agricultural products. The whole fertilizer business is under the strictest chemical control, and the farmer buys his fertilizer on the basis of a knowledge of its composition and effective value which puts the average purchasing agent of a manufacturing company or public service corporation to shame. The Association of Official Agricultural Chemists, and the laboratories of the agricultural colleges and experiment stations throughout the country are doing more to keep down the cost of living than all the lawmakers we send to state capitols and Washington.

One of the most insistent of the demands of growing plants is that for nitrogen in form available for plant food. A small proportion of the necessary supply of nitrogen in the assimilative form is derived from the manure of farm animals and from animal wastes of various kinds, but for many years the world has depended upon the nitrate beds of Chili as the chief source of this indispensable element of plant growth. It is bad enough to be tied in this way to a single faraway deposit, but the situation becomes alarming when we discover that this deposit can hardly meet the world's demand for nitrate for another twenty years. One may contemplate the Malthusian theory with indifference or even with disbelief, but here is a condition not to be gainsaid. The world must do something to meet it within twenty years or the world must make up its mind to starve. Fortunately for the world the chemists are already doing something. They have recognized that 33,800 tons of nitrogen are pressing down upon every acre of land and have boldly attacked the problem of rendering available such portion of this inexhaustible supply as the world may need. The methods employed have been daring and brilliant in the extreme.

In 1785 Cavendish in a paper before the Royal Society describes the production of nitric acid by the passage of an electric spark through air. A hundred years later Bradley and Lovejoy at Niagara Falls, by drawing air through an apparatus by which 400,000 arcs were made and broken each minute, demonstrated the possibility of the commercial manufacture of nitrates from atmospheric air. Birkeland and Eyde in Norway pass the air through furnaces in which it comes in contact with enormous flaming and rotating arcs. Rossi in Italy brings the air in contact with highly incandescent material of special composition. Although by these several processes nitrate has been produced by thousands of tons it is doubtful if the artificial product can yet compete with Chili niter. Even now, however, the margin is not a wide one and the results already accomplished amply prove that when our agriculture begins to feel the pinch of a failing nitrate supply the chemist may safely be relied on to meet the situation. This assurance is rendered doubly sure by the fact that a solution of the problem along altogether different lines is already nearly or quite within our hands. Dr. Frank has shown that by heating calcium carbide, itself a comparatively recent product of the laboratory, in a stream of nitrogen there is formed a new compound, calcium cyanamide. The practical interest in this compound depends upon the fact that when exposed to a current of steam it decomposes into ammonia and carbonate of lime and that the same reaction takes place slowly in the soil when the cyanamide is mixed therewith. Since the nitrogen in ammonia is directly assimilable by plants and since calcium carbide requires for its production only lime and coke and power we may view without serious concern the approaching failure of the Chilian nitrate beds.

But it is not only on the side of agriculture that chemistry touches our food supply. Chemistry pervades the packing industry, reducing the cost of food by utilization of by-products of the most varied character from oleomargarine to glycerine and soap and from soap to pepsin and adrenalin. To Atwater and his co-workers we owe our knowledge of the energy-producing value of different foods in the human economy and to Wiley and those other chemists behind him on the firing line we are indebted for the far-reaching benefits of the Pure Food Law.

Carbon disulphid made in the Taylor electric furnace has preserved the wine industry of France by destroying the phylloxera as it is ridding our own fields of prairie dogs and our elevators of rats and mice. Bread-making and brewing are coming each year more and more within the recognized domain of chemistry which is at the same time greatly enhancing the value of our staple crop by the increasing production of glucose, corn oil and gluten. Exactly one hundred years ago Kirchhof discovered the inversion of starch to glucose by dilute acids. To-day the United States alone is richer by $30,000,000 a year by reason of that discovery.

The relation of chemistry to the clothes we wear is perhaps less obvious but still of the first importance. More land is planted to cotton and cotton itself is cheaper because chemistry has taught the planter how to secure increased yields by proper fertilization and how to obtain increased profits by utilization of the cottonseed for oil and cattle feed. Chemistry is even now developing new sources of profit for the planter by adapting the short fiber adhering to the ginned cottonseed hull to the making of smokeless powder and the stalks of the cotton plant to paper-making.

The woolen industries are dependent upon chemistry for the processes of separating the pure fiber from the grease and dirt with which it is associated in the raw wool and for the methods of working up this wool waste into oleic acid, soap, lubricating oils and potash and ammonia salts, as well as for the process of carbonizing by which the wool is separated from the burrs and other vegetable material with which it is admixed in the fleece.

Many of the most brilliant achievements of chemistry have been directly concerned with the textile industries. A little touch of chemistry to cotton yarns and fabrics in the mercerizing process gave the world what is practically a new textile fiber—cotton with the beauty and luster of silk. A history of absorbing interest replete with struggle, the capture of positions of temporary advantage, the constant shifting of the fighting line, crushing defeats and signal victories might be written of the development of the bleach and alkali industry, upon the products of which the textile manufacturer depends for the finishing of his goods. We see the pathetic figure of Le Blanc dying in the poorhouse after enriching the world which Napoleon was devastating. No less interesting in its human and scientific aspects is the long story of the coal-tar colors in which chemists take so large a measure of justifiable pride. An investment of $750,000,000 follows Perkin's discovery of mauve.

Less notable, but nevertheless an industrial achievement of the highest order is the very modern development of artificial silk which, though made from wood pulp, far surpasses in brilliance and beauty the finest product of China and Japan. Closely related, thereto, is the artificial horsehair of which so large a proportion of women's hats are made and the still more recent artificial bristles of cellulose acetate with which you may have brushed your hair this morning.

A complex series of chemical reactions has its origin in the striking of every match, and civilization as we know it could hardly exist without the modern facilities for securing artificial light. For the extraordinary extension of these facilities during the past century the chemist has mainly been responsible. The immortal Faraday selected "The Chemistry of a Candle" as the subject matter of a classical series of lectures to audiences of children. From the rush candle and the tallow dip to the candles of stearin and paraffin is in itself a long journey, the milestones on which were set by Scheele, Chevreul, Heintz and Tilghman.

The refining of petroleum involved the solution of many difficult chemical problems. The Chicago fire is said to have been started by Mrs. O'Leary's cow which kicked over a kerosene lamp. In those days, however, it was not necessary to invoke the cow to start a conflagration with kerosene. Much of the lighting oil upon the market at that time would flash below 100° F. We owe our present safety in the use of kerosene largely to the work of Prof. Chandler.

The production of illuminating gas is wholly a chemical process. When coal gas was first employed for lighting the Houses of Parliament the members might be seen gingerly touching the pipes to discover if they were not indeed hot from carrying such flame. That gas is now so cheap is due in large part to the development by Lowe of the chemical process for making water gas by passing steam through a bed of glowing coals and to the chemical processes for gas enrichment. By the Blaugas system illuminating gas is now produced in liquid form and distributed in steel bottles to isolated consumers like so much kerosene.

The gas mantle by which the illuminating power of gas is raised from 16 to 60 candles on a consumption of $3^1/_2$ feet an hour constitutes one of the most signal triumphs of chemical research. Certain sands found in Brazil and known as monazite sands had long been a happy hunting ground for chemists by reason of the number of rare metallic elements to be found therein. They seemed to be a sort of chemical garret where everything not otherwise used up during the process of creation had been stowed. Dr. Carl von Welsbach was investigating the rare elements in these sands some thirty years ago and studying their spectra. It occurred to him that a better flame for his purpose or rather a better distribution of the metallic vapor in the ordinary Bunsen flame might be secured by distributing the metallic compound through the substance of a bit of cambric. He dipped the cambric in a solution of the salts, suspended it in the flame, burned off the cotton, and found that the fragile ash glowed with an amazing brilliance. So came into being the gas mantle which has revolutionized and saved the illuminating gas industry, though not until the initial discovery had been followed by years of the most painstaking and refined research.

In the development of electric lighting the chemist has played a part scarcely less important than that of the electrician.

The arc light was first shown by Davy between charcoal points and was maintained by the current developed by the action of chemicals in the enormous battery of the Royal Institution. To Faraday, whose achievements in electricity have overshadowed his renown as a chemist, we owe the discoveries upon which our modern methods of generating electricity are based. The early history of the incandescent lamp is a chronicle in equal measure of the difficulties of finding a proper material for the filament and those of producing the requisite degree of vacuum in the bulb. Both problems were solved by chemistry which first supplied the carbon filament made by dissolving cellulose, squirting the solution into a thread of the required diameter, drying and carbonizing the thread and thereafter flashing in an atmosphere of hydrocarbon vapor to deposit carbon on the filament precisely where and in exactly what proportion its original inequalities of resistance to the current made necessary. More recently Whitney and other chemists working in the same field first greatly raised the efficiency of the filament by the process of metallizing, so-called, and have since given us lamps of an altogether new order of usefulness by employing new materials, as tungsten, for the filament.

The second great problem, that of securing rapidly and cheaply the necessary high vacuum in the bulb, was solved in the most elegant manner by the extraordinary Malignani process. Malignani placed within the tubulature leading from the bulb and connecting the bulb and pump, a minute quantity of red phosphorus, started the pump and roughly exhausted to about 2 mm. of mercury. He then sent through the filament a current so heavy as to bring the filament to intensive incandescence and cause the gaseous residue within the bulb to faintly glow so that the bulb was filled with a luminous blue haze. He then sealed off the pump by fusion of the walls of the tubulature below the phosphorus and with the bulb still glowing touched the tip of the blowpipe flame to that portion of the tubulature wall against which the phosphorus rested. With the vaporization of the phosphorus the blue haze instantaneously disappeared and an almost perfect vacuum was secured within the bulb. The process is not one of oxygen combustion as might on first thought appear and its ultimate mechanism was not understood until many years subsequent to its discovery.

The improvements in incandescent lamps in the last ten years have resulted in the saving of $24,000,000 a year in the cost of lighting as compared with the cost of equal illumination by the older types of lamp.

To the art of illumination Wohler and Willson have contributed the calcium carbide and acetylene found on every automobile and in a hundred thousand isolated homes; Pintsch and Blau have developed separate systems permitting the transport of illuminating gases in steel tanks for the lighting of trains and houses; to Hewitt we owe the mercury lamp, to other inventors the flaming arc, to Nernst the high efficiency lamp which has his name, and, long before them all, to Bunsen the blue flame burner utilized by Welsbach and which constitutes the basic element in every gas stove.

I have endeavored in this cursory and most inadequate survey to indicate something of the extent to which chemistry contributes to the satisfaction of the demands and needs of every-day life. The earning power of the science becomes more directly apparent in its relation to general industry.

American manufacturing is in many respects the most intensive in the world. Nowhere is plant scrapped so quickly to be replaced by larger, faster and more efficient machines. Nowhere else is labor so speeded up by piece work, bonuses, motion studies, gang organization and the other devices of the efficiency engineer. In no country can new office systems, typewriters, adding machines, time recorders, memory ticklers, duplicating devices and all the paraphernalia of the follow-up be sold as quickly and in none are they utilized so thoroughly. Our manufacturers understand these things, and what they understand they want, and are quick to make the most of, provided always they can use it in their business. They do not understand chemistry, naturally they do not propose to have any chemist teach them their business. This is reflected in the attitude of their subordinates which is commonly one of militant skepticism. They, like their masters, cut themselves off from that great coördinated and organized body of knowledge brought together by thousands of highly trained minds through the incessant questioning of nature during a hundred years. They pay less regard to many of the laws of nature than they do to city ordinances. When under these circumstances they fail to make a satisfactory profit in competition with more enlightened Germany, they jack up the tariff. They ignore applied chemistry which offers them better protection than the highest schedules of the Aldrich bill.

Let us consider a few concrete examples of the earning power of chemistry. A large pulp mill found itself with over 100,000 cords of peeled wood piled in its yard and this wood was beginning to rot. A few thousand gallons of sulphite liquor sprayed over the pile from a garden hose killed the fungus and saved the pile. The same mill was losing 23 per cent. of its wood as barker waste. Laboratory trials proved that an excellent quality of paper could be made from this waste, all of which in this mill is now profitably worked up. Other mills still throw 20 per cent. or more of their initial raw material away. The mill was cooking in 16 hours. Laboratory cooks were made in $7^1/_2$ hours and the time of the mill cook reduced to 10. Finally, by a proper spacing of the digesters, the production of the plant was brought from 97 tons a day to 149 tons.

Cylinder oils generally cost about what you are accustomed to pay. Plants which employ a chemist pay from 19–27 cents. Manufacturers who do not need a chemist commonly pay 45 cents, 65 cents or even, if they know their own business very well, $1.50 a gallon. There is probably not a large plant in the country in which, if it is not already under chemical control, the lubrication account cannot be cut in two. In the engine room of one large cement plant the average monthly cost for lubricants had been $337. It is now $30. A concern paying 37 cents a pound for a special grease which the superintendent needed to run the mill now buys on specification for $5^1/_2$ and the mill still runs. Another company within our knowledge saves $12,000 a year on cutting oils alone.

In a plant near Boston using two tons a week of special steel rolled very thin, their chemist was able in about two years to reduce the cost of the material from 80–40 cents a pound while at the same time standardizing and greatly improving the quality of the steel. We recall savings of $2,100 a year on wrapping paper, $3,600 on boiler compounds, $6,800 on a minor article of supply, $100,000 a year on a single raw material. Prof. Duncan in his fascinating and suggestive book, "The Chemistry of Commerce," says: "On three separate occasions the writer has visited the same glass house to see the workmen bailing out a lake of violet spoiled glass from the same immense tank, and all because it was deemed by the foreman 'theoretical' to have the manganese analyzed in order that its quality might be adjusted to its oxidizing value. Thousands of dollars were thus wasted and thousands more lost through failure of the firm to fulfil its contracts on time, and all of it could have been saved at the cost of, say, $10 for a simple analysis."

Chemistry points out the only proper way to buy supplies which is on the basis of their industrial efficiency by means of specifications defining the quality desired and rigid tests to make sure that quality is secured. Independent estimates by those in exceptional positions to know place the efficiency value of supplies as purchased and used by American manufacturers at 60 per cent. of what it should be.

Comparatively few American manufacturers light their cigars with $20 bills. It is too slow a method of burning money. They prefer to burn it by shovelfuls, so they burn it in the boiler room. They forget that in ostensibly buying coal they are really buying heat and they pay good money for slate and sulphur balls with no knowledge of the actual number of British thermal units they are receiving for a dollar. Perhaps they depend upon a trade name ignoring the fact that coals from different mines in the same district vary greatly as does also coal from the same mine. Moreover coal, like some other things, is not always true to name. A few years ago the Boston School Committee decided to buy its coal on specification. It had previously bought "New River coal of the best quality" and that definition of its desires was included in the specification which, however, also included a chemical definition of what coal bearing this name should be. When deliveries were made by the same dealer who had previously supplied school coal they proved to be an inferior grade of Pennsylvania coal with sulphur in some samples running up to 6 per cent. When the contractor was called to account, he admitted that he did not know the state in which New River coal originates nor the transportation route by which only it could come to Boston. His comment to the committee was, "I don't see what you are fussing about, it's the same coal you've always had." Later when the temperature in the piles in a certain school ran up 90° in one day he was called upon to remove all coal delivered by him to schools in that district and substitute therefor New River coal, which he did at heavy loss to himself and corresponding gain to the city.

Important as are the losses in the initial purchase of coal, they are small compared with those which attend its burning. Many a mill owner looks out of the window and sees, without knowing, his dividends go up the chimney. Under well regulated conditions of combustion the flue gases should contain not less than 12 per cent. of carbonic acid gas. They frequently contain no more than 3 per cent. This means that for every ton of coal burned under the latter conditions more than 52 tons of excess air are heated to the high temperature of the flue gases. Chemistry meets these conditions by analyzing the flue gases and regulating the draft as indicated by the percentage of carbonic acid found. At $2.25 a ton, which is much below the average price, the fuel bill of the United States was over $1,000,000,000 in 1910. Of that amount chemistry could easily have saved $100,000,000.

Chemistry aids the manufacturer who will listen to her teachings in countless other ways. It substitutes a rigid control of processes for the guesswork and uncertainty of the rule of thumb. It increases the productivity of labor by supplying more efficient processes.

In the sulphur mines of Sicily young boys called *carusi* climb with groans and curses for four hundred feet bearing in a stifling atmosphere 40 pound loads of sulphur ore upon their backs. In Louisiana, thanks to Frash, two concentric pipes are driven to the ore, a hot solution of calcium chloride is forced through one pipe to melt the sulphur which is then pumped to the surface through the other, at a trivial fraction of the cost of raising the ore in Sicily.

In the old days of making paper the rags were piled in a heap, moistened and allowed to stand for weeks until fermentation had proceeded far enough to soften them. Now they are boiled with lime for a few hours. They used to be bleached by the slow action of the sun and dew as they were spread upon the grass. They are brought to better color now over night by bleaching-powder. Cutting tools made from high-speed steels multiply the output of the lathe and planer. The addition of 1 per cent. of calcium chloride to the electrolyzing bath doubles the yield of potassium chlorate.

Chemistry aids the manufacturer by standardizing his product and reducing seconds and rejections. It costs just as much to tan goat skins into seconds as into firsts though seconds bring a third as much. Chemistry even comes to the front bearing ammunition during an advertising campaign. You may remember the offer of a blowpipe and a bit of charcoal coupled with the information that if your paint was a lead paint as the advertiser believed it should be you could quickly prove its quality in the laboratory of your kitchen by reducing from the paint a little pellet of metallic lead. You do not see that advertisement now. It disappeared about the time that some one else informed the world that zinc paints are "unalterable even under the blowpipe."

Nowhere, however, does chemistry render such efficient service to the manufacturer as in turning to profit waste and nuisance. To this phase of its service we shall return again.

To quote once more Prof. Duncan:

"During the next five years the small manufacturer who is swept out of existence will often wonder why. He will ascribe it to the economy of large scale operations, or business intrigues or what not, never knowing that his disaster was due to the application of pure science that the trust organizations and large manufacturers are already beginning to appreciate."

A few of us have been surprised, and none more than the railway managers themselves, by the well supported statement before the Interstate Commerce Commission that the railroads of the country could save $300,000,000 a year by the application of scientific management to the operation of their properties. Every chemist who has studied the problem is well aware that the entire amount in question could be saved through utilization of the proved results of chemistry alone.

Abraham S. Hewitt is authority for the statement that the Bessemer process has added $2,000,000,000 yearly to the world's wealth. By far the greatest portion of this increment has come through the economies which this process of steel-making has rendered possible in transportation.

Our own study of car painting practice on 21 electric roads has developed the fact that 50 per cent. of the cost of materials and labor is wasted and more than 50 per cent. of the time spent by the cars in the shops is unnecessary.

The classic work of Dr. Dudley as the head of the laboratories of the Pennsylvania system has gone far to standardize railroad practice throughout the country. Few even among railroad men realize how greatly the whole community is in his debt. His specifications cover rails, soaps, disinfectants, oils for signals and for lubricating, paints, steel in special forms for every use, car wheels, cement, signal cord and every detail of equipment. He has made the transportation of life and property cheaper, safer and more expeditious by reason of his application of chemistry to the problems of railroad management.

In a recent address Dr. Frankforter, voicing the opinion of every thoughtful chemist, said: "The United States is the most wasteful nation in the world; wasteful in living, wasteful in manufacturing, and wasteful in conserving its natural resources." So heedless and appalling is this waste that the mind trained in chemistry stands aghast. I have lately visited a southern lumber mill which burns 1,900 cords of wood a day in its incinerator. There are two hundred such burners in the country limited in destructiveness only by the amount of material sent to them. From such wood chemistry is prepared to extract three gallons of turpentine a cord, 10 gallons of ethyl alcohol, or paper pulp to the value of $20. We waste each year 500,000,000 tons of coal and each day a billion feet of natural gas. With peat deposits fringing our entire eastern coast we pay $4 a ton for coal delivered on the bog. Beehive coke ovens flame for miles in Pennsylvania and excite no comment while the burning of a $1,000 house would draw a mob. We fill the Merrimac River with wool grease making it a stench, while the towns along its course buy soap and fertilizer and lubricants from Chicago, Chili and Pennsylvania. We burn coal-tar in Massachusetts and import coal-tar colors at high prices from Germany. Over the great northwest we burn each year 5,000,000 tons of flax straw while we pay $40 a ton for imported paper stock from Norway. In the South 300,000 tons of paper fiber of the highest grade are burned with the cottonseed hulls to which it is attached or used with them to adulterate cattle feed. Corn-stalks to an incalculable tonnage rot or are burned each year while chemistry stands ready to convert them into feed containing 30 per cent. of sugars on the dry basis, or into alcohol for light and power. Waste molasses is sold for three cents a gallon or dumped into the stream while alcohol sells for 40 cents a gallon. Skim milk is fed to hogs or thrown away because no one has the enterprise to extract its casein which is worth more than beefsteak for food.

In the face of such conditions we still meet young men who would inform us that the day of opportunity is past. The truth is that opportunity is knocking not once but insistently and long at every entrance to the chemist's laboratory.

Nowhere is the earning power of chemistry better shown than in its ability to transform cheap raw materials into products of exceptional value. A cord of wood is worth perhaps $10 with a dry weight of a little over a ton. Its value, therefore, is about a half a cent a pound. In the form of chemical fiber for paper-making half the weight is lost but the remainder is worth $2^{1}/_{4}$ cents a pound. As paper it finds a market at 4 cents. Made into artificial silk by more refined chemical processes it commands $2.00 a pound, while as cellulose acetate bristles it is worth $4.00.

Many of our great industries are founded on minute chemical facts. Goodyear drops a bit of gum mixed with sulphur on a hot stove and the rubber industry results. The fact that silver salts happen to blacken when exposed to light is responsible for a corporation with $35,000,000 capital on which the earnings are over 20 per cent. a year. The dipping of cotton yarn in caustic soda while tightly stretched has revolutionized the manufacture of the better grades of cotton textiles. Because the chemist learns that glycerine treated with nitric acid becomes explosive our army engineers are able to separate two continents. Becquerel, having placed a bit of uranium upon a photographic plate in a black paper wrapper, finds on development that the plate has blurred. The observation leads Prof. and Madame Curie to study similar actions by uranium ores and presently the thought of the world is enriched by altogether new conceptions of the constitution of matter, and our minds are awed by the magnitude of forces previously unrecognized.

Two classes of securities find a ready sale in Massachusetts—$3^{1}/_{2}$ per cent. bonds and gold bricks. It is not an easy matter to raise money for a sound chemical proposition which promises 20 per cent. Much the same conditions undoubtedly prevail throughout the country. Boston, which invested largely in sea water gold, the Hickman machine for converting starch to cane sugar, and the electrical process by which spruce wood was transformed into Australian wool with the grease in and the burrs attached, is just now figuring its losses on synthetic rubber. It left to other communities the formula of the Altoona cobbler for burning ashes, the process for converting water into kerosene, and the Lamoine diamonds. Men who turn a box of strawberries upside down and require a pastor's certificate of character from the office boy, rush into misapplied chemistry with never a thought of expert investigation or advice. The pity is the greater when one realizes, as every chemist does, the generous scale by which are measured the rewards of chemistry properly applied and wisely administered. Ten years ago a Massachusetts company with a capital of $20,000 was organized to conduct a manufacture based on chemistry; two years ago it charged off $700,000 on real estate and equipment; to-day it has a surplus of over $1,000,000. The great Badische Anilin und Soda Fabrik, the Elberfeld Co., Brunner, Mond & Co., the E. I. duPont de Nemours Powder Co., Meister, Lucius & Bruning, the Solvay Process Co., and many others well-known to every chemist are among the most profitable industrial organizations in the world. The one thing lacking for an enormous development in this country of equally profitable enterprises based on chemistry is a reasonable appreciation by our business men of the earning power of chemistry.

The ordinary investor who may safely trust his own judgment in matters involving cotton, wheat, mortgages, railroad shares or telephones is not equipped by training or experience to decide upon the validity of propositions involving chemistry. He must, if he would avoid disaster, rely upon the opinion of disinterested experts. Such opinion should cover the soundness of the chemistry involved, the state of the art relating to the manufacture, the patent situation, the available market, the nature and extent of competition, the supply of raw material, the stage of development of the process, the cost of plant and the costs of production. These last should be itemized and the basis for conclusions regarding every item should be fully stated. Large allowances should invariably be made for depreciation and in most cases equally liberal allowances for contingencies. Secret processes should be left to the fool and his money.

In this environment and on this occasion I cannot forbear making a brief concluding reference to that organization of chemists which now enjoys your hospitality. At Northumberland, Pa., there lies the body of an obscure English dissenting clergyman who went through life on a salary of £30 a year, although he had enriched the world by the discovery of oxygen. It was around the grave of Priestley on July 31, 1874, that the idea of the American Chemical Society first took form in the minds, and may I add the hearts, of a few American chemists met to do honor to his memory. Subsequent meetings were held in New York at the home of that Nestor among American chemists, Prof. Charles F. Chandler until on April 20, 1876, the Society was formally organized. From a feeble organization of distinctly local character, with only 200 members in 1887 it has through the service and self-sacrifice of a long series of devoted officers become the largest chemical society in the world, with 5,500 members, and is to-day the most powerful influence in America for the advancement of chemical science. Its claim upon the loyalty and support of every American chemist can no longer be denied or set aside. With equal justification it may appeal to the whole community for recognition and encouragement.

There are in the country at least 100,000 doctors and nearly 125,000 lawyers. There are only 10,000 chemists to carry on a work incomparably more important than litigation and no less beneficial than medicine to the life of the community if that life is to be worth living. Some measure of the mere material benefits which chemistry can offer may be found in the fact that the annual production of the chemical industries of the United States is already nearly equal in value to our agricultural products. Let us, however, not forget that these benefits have come, as many more will follow, because chemists have never faltered in pursuing truth for years through the labyrinth of difficult researches with no better guide than the slender and often broken thread of an hypothesis. Turgot has said: "What I admire in Christopher Columbus is not that he discovered the new world but that he went to look for it on the faith of an idea."

THE UTILIZATION OF THE WASTES OF A BLAST FURNACE.[1]

By Edward M. Hagar, President, Universal Portland Cement Co., Chicago.

Received May 22, 1911.

Until the last decade, practically the only utilization of the wastes or by-products of a blast furnace was the use of a portion of the waste gases to raise the temperature of the incoming blast through heating the brick work in so-called hot stoves, and in some cases a small portion of the power value of the gases was obtained by burning them under boilers to generate steam for driving the blowing engines.

At the present time the calorific value of the waste gases is being utilized directly in gas engines for blowing purposes and for generation of electric power, a considerable portion of the slag is used in the manufacture of Portland cement, and the flue dust, consisting of the finest ore and coke particles, is being collected and converted so as to be rechargeable into the furnaces.

The aggregate saving or profits resulting from these three developments is a matter of millions of dollars per annum, and in a modern blast furnace plant, it would almost seem that pig iron was the by-product; and, indeed, the investment in the equipment to utilize these former wastes exceeds that of the blast furnace itself.

The writer, in his work, has come in contact with

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[1] Presented before the Congress of Technology at the Fiftieth Anniversary of the granting of the charter of the Massachusetts Institute of Technology.

these evolutions, with plants in operation, or under construction, of a capacity to produce twelve million barrels of Portland cement per annum from slag and limestone, using over one million three hundred thousand tons of slag in a year, these plants being driven entirely by electric current generated by gas engines directly from the waste blast-furnace gases, the power requirements being forty thousand horse power for twenty-four hours every working day. In one of the cement plants the first commercial method for reclaiming flue dust was discovered.

By using the blast-furnace gases directly in combustion engines, after suitable washing to remove the grit, the power obtained from a given amount of gas is equal to at least two and one-half times that obtainable by burning the gas under boilers for generating in steam engines.

A modern blast furnace of the usual size, with gas blowing engines, and gas engines driving electric generators, will provide sufficient gas to furnish seven thousand kilowatts electric power, in addition to driving its own blowing engines.

This permits the most modern steel works, such as those at Gary, Indiana, to practically do away with the use of coal for power purposes, operating the rolling mills by electric power from the surplus gases.

The United States Steel Corporation, of which the Universal Portland Cement Co. is a subsidiary, has already installed two hundred and fifty thousand horse power gas blowing and gas electric units, which, it can easily be figured, displaces or saves the consumption of approximately a million tons of coal per annum as compared to the old-fashioned method.

With the modern high blast pressures, and the use of fine Mesaba ore, the finest of the particles, together with the coke dust, are blown out through the top of the furnaces and are caught in the flues, dust catchers and gas washers.

The iron ore in this dust amounts to fully 3 per cent. of the total ore charged, which aggregates the large amount of approximately a million and a quarter tons per annum in this country. Until within a few years, this dust has been thrown away or used as filling, although containing about 40 per cent. metallic iron.

For many years efforts were made to use this material by compressing it into briquettes, but the cost of the operation, together with the fact that the briquettes disintegrated and the dust was again blown out, led to an abandonment of the briquetting plants.

The first commercially successful method of utilizing the dust was discovered by passing the material through the cement kilns at South Chicago. Experiments showed that with the proper heat treatment the coke dust could be burned off and the iron ore conglomerated into nodules or nuggets averaging over 60 per cent. iron content. These nodules, when fed to the blast furnace, were easily and completely reduced. The fact that the sinter of the flue dust contains such a high percentage of iron and that all of the sinter is reduced, together with its physical shape assisting the steady movement of the charge downward in the blast furnace, thereby preventing so-called slips, makes the sinter more valuable per ton than any ore.

It was necessary to derive mechanical means for preventing the accumulation of the sinter on the walls of the kiln. Plants have been in operation for some years using this process, with endless chains carrying scrapers constantly passing forward through the kiln, and cooled in water on their return outside of the kiln.

Recently other methods of utilizing dust have been devised which may prove successful commercially, and the indications are that within a short time the greater portion of this former waste will be prevented.

The development of the Portland cement industry in this country and the extension of its uses have been marvelous, and the following table shows a remarkable increase in the production of Portland cement in the United States every year since 1895, when this country first reached the production of approximately one million barrels:

Year.	Production of Portland cement of United States Barrels.	Production of Universal Portland cement. Barrels.	Percentage of Universal to total American production of Portland cement.
1895	990,324	.....	..
1896	1,543,023	.....	..
1897	2,677,775	.....	..
1898	3,692,284	.....	..
1899	5,652,266	.....	..
1900	8,482,020	32,443	0.39
1901	12,711,225	164,316	1.29
1902	17,230,644	318,710	1.85
1903	22,342,973	462,930	2.08
1904	26,505,881	473,294	1.78
1905	35,264,812	1,735,343	4.92
1906	46,463,424	2,076,000	4.55
1907	48,785,390	2,129,000	4.36
1908	51,072,612	4,535,000	8.89
1909	62,508,461	5,786,000	9.27
1910	73,500,000—Gov. est.	7,001,500	9.52

It may be of interest to note the increasing percentage of the total American production shown by universal Portland cement, which is the only Portland cement manufactured in this country using slag as one of the raw materials. With the new plant now approaching completion the aggregate production of Universal Portland cement in the Chicago and Pittsburg districts will amount to over one-eighth of the country's total. Expressed in weight, the output of the finished product will be over two million gross tons per annum. Our plants in the Chicago district will consume all the available slag that is suitable for the purpose from an aggregate of nineteen blast furnaces in the South Chicago works of the Illinois Steel Company and in the Gary Works of the Indiana Steel Company.

Comparing the pig iron production and Portland cement production of this country in figures of long tons, the percentage of Portland cement to pig iron in 1890 was six-tenths of 1 per cent., in 1900 $10^{3}/_{10}$ per cent., and in 1910 47 per cent. The continuation of any such relative growth would mean that before 1920 the tonnage of Portland cement would considerably exceed that of pig iron. I would hesitate, however, to predict that such would be the case.

Portland cement is defined by the United States Government as the product obtained from the heating or calcining up to incipient fusion of intimate mixtures, either natural or artificial, of argillaceous with calcareous substances, the calcined product to contain at least one and seven-tenths times as much of lime, by weight, as of the materials which give the lime its hydraulic properties, and to be finely pulverized after said calcination, and thereafter additions or substitutions for the purpose only of regulating certain properties of technical importance to be allowable to not exceeding 2 per cent. of the calcined product.

From this definition it will be seen that the raw material for Portland cement is not limited to any particular form of material, it may be made from any combination of materials that together furnish the proper elements. In this country Portland cement is manufactured from a number of raw materials, which, with a few exceptions, may be classed under four heads:

First.—Argillaceous limestone (cement rock) and pure limestone.

Second.—Clay and shale and limestone.

Third.—Clay or shale and marl.

Fourth.—Slag and limestone.

In all cases the raw mixture is a combination of some form of clay and some form of lime, and in the first and fourth classifications the clay materials contain some lime. This simply reduces the proportion of lime material necessary for a proper mixture.

In the manufacture of Portland cement from slag and limestone the molten slag flowing from the furnaces is granulated by a stream of water, loaded into cars and transported to the cement plants, where it is dried in rotary driers, and receives the first grinding; it is then mixed in automatic weighing machines, with the proper proportion of ground and dried calcite limestone. These are then ground together and burnt to a hard clinker at a temperature of nearly 3000° F. in rotary kilns, using pulverized coal for fuel.

This clinker, after seasoning, is crushed and ground and mixed with a small percentage of gypsum to regulate the setting time. The cement is ground to such fineness that 96 per cent. passes through a sieve having ten thousand meshes, and 80 per cent. passes a sieve with forty thousand meshes to the square inch. It is then conveyed to the stock house for storage prior to shipment.

It is necessary to use a flux in furnaces supplying slag for cement manufacture, a pure calcite limestone. The limestone burnt with the slag must also be a pure calcite stone. It is also essential that the ores be of a uniform and proper character.

Inasmuch as Lake Superior ores are noted for their remarkable uniformity of analysis, the resultant slag obtained from the use of these ores and a pure calcite limestone is more uniform in its analysis than any form of natural clay deposits used in the manufacture of Portland cement, and the variation in the proportions of the two raw materials used in the manufacture of Portland cement from slag is less than those of any other materials mentioned above.

In addition, the opportunity for analysis and selection of the proper ingredients through the use of an artificial material is a great advantage as compared to the necessitous use of natural materials just as they are found with their variations in analysis at different depths.

In the intense heat of the kiln, under the influence of the oxidizing flame, any sulphides in the slag are completely burned out.

The rotary kiln commonly used ten years ago was sixty feet long and six feet in diameter. This has gradually been increased in length and diameter until the modern kiln is one hundred and forty to one hundred and fifty feet long and eight to ten feet in diameter, and there are a few even larger kilns in use. Kilns are usually set at an incline of three-quarters of an inch to the foot. With the lining and contents the modern kiln weighs one hundred and fifty tons, and in revolving upon two bearings presents interesting constructional features.

In the case of the plant at Buffington, Indiana, using twenty-six thousand horse power, situated between South Chicago and Gary, Indiana, electric power is supplied at twenty-two thousand volts from the steel works at these points. Each piece of machinery is driven by its individual motor, supplied with alternating current at four hundred and forty volts. The high tension line is connected through the cement plants, and the gas engines at these two steel works, fourteen miles apart, operate continually in parallel. This enables the cement plant to draw its power from either source, or from both sources at the same time, as may be desirable. It has happened that one of these works has supplied power to operate the cement plant and furnished additional power at the same time to the steel works at the other end of the line.

The method of manufacture above described is the standard method of manufacturing Portland cement from natural deposits, and the finished product differs in no way from other Portland cements in chemical analysis, fineness, specific gravity, color, nor in the operation in practical work. It has no peculiarities whatever and has no limitations as to its applications. There is no difference, from the chemist's point of view, between the manufacture of Portland cement from natural deposits, such as limestone and clay or shale, and its manufacture from limestone and slag. Slag is really a mixture of the clay from the ore with the lime content of the stone used as a flux in the furnace.

Our method of manufacture of Universal Portland cement does not embody any real invention, nor is it based on any patents. It is simply an adaptation to an artificial raw material of the regular Portland cement process formerly applied only to natural deposits.

True Portland cement in which slag is used as one of the raw materials should not be confused with puzzolan or so-called "slag cements" which are simply mechanical mixtures of slag and slaked lime ground together without burning. Such cements are suitable only for use under ground and in moist locations.

The manufacture of Puzzolan cements in this country has practically been abandoned.

The remarkable growth of the Portland cement industry is not equalled by any other manufactured article. This is due to the economy, durability, and plasticity of cement and concrete work. While large engineering work, such as dams, bridges, and heavy reinforced concrete buildings, consume large quantities of cement, the bulk of consumption at the present day is in a multitude of small uses. It takes an average shipment of only five barrels a day to take care of the average customer of a large cement company.

For example, there is a steady increase in the application of cement to new uses on the farm, such as silos, fence posts barn floors, feeding floors, watering troughs, corn cribs, etc. There, as elsewhere, concrete is rapidly displacing all forms of wood construction, this process being hastened by the continually advancing cost of lumber.

Beautiful effects are now being obtained in concrete surface finishes and its use in decorative work is advancing rapidly.

The use of Portland cement will continue to increase until the campaign of education of the small user has reached its finality. In this direction a great work is being done to educate the general public in the proper use of cement by individual manufacturers by the Association of American Cement Manufacturers, and by the cement shows which are given in several of the largest cities every year.

In conclusion, it will be seen from the foregoing that most of the problems of utilization of wastes or by-products of the blast furnace have been solved, and that these solutions, in addition to being highly profitable, are powerful factors towards the conservation of our natural resources.

Portland cement manufactured from slag, to a large extent, replaces wood; the waste gases displace coal, and reclamation of the flue dust conserves the deposits of iron ore.

THE TECHNICS OF IRON AND STEEL.[1]

By Theodore W. Robinson, Vice-President, Illinois Steel Co., Chicago, Ill.

Received May 22, 1911.

The basis of modern civilization is the increased productiveness of labor and the accumulated wealth that has resulted from the universal use of iron and steel. The manufacture of iron and steel represents a comprehensive application of scientific research and discovery, and the indebtedness of society to our institutions of technical learning is exemplified in no more forceful way than by their influence upon our most important industry. Human progress since medieval times has been closely allied with iron's progress. The essential elements of existence have ever been food, raiment, habitation and transportation, and the difference between our modern conditions and the conditions of the past is fundamentally the difference of the labor efficiency with which these necessities are produced. Closely analyze all the fields of human endeavor and, whether it be in the essentials of existence or the luxuries of life, somewhere the world's greatest metal will be found playing a vital part. The political demarcation of nations has been wrought and maintained by the war products of the foundry and the forge, but it is in the realm of industry that there has been found that potency of iron which has caused the progress of the last century to surpass the accomplishments of twenty centuries. Let him who questions this statement compare the average conditions of living within these periods, and let him recall that the revolutionary inventions of modern civilization are directly due to or have been permitted by the use of our most precious metal.

It is manifestly impossible in a brief address to trace the evolution of the iron and steel industry, much less to attempt a detailed description of its manufacture. We may, however, briefly discuss some of the salient changes and economies that have taken place within the past fifty years. The underlying principles of the manufacture of iron and steel are the same to-day as they were half a century ago. The mining of ore, of coal, and of limestone; the manufacture of coke; the smelting of these raw materials into pig iron; the refining of pig iron into wrought iron or steel, and its rolling or forging into the finished product—all these steps are essentially the same as they were before; and the blast furnace, converter, open-hearth furnace and rolling mill are still the agents of reduction and conversion. No industry has been more ready to recognize the merits of discovery and invention, or quicker to reap the benefits, and a well equipped iron and steel plant is to-day the very embodiment of applied science. To this is due the fact that as measured by quality, quantity, cost, and diversity of product, the efficiency of former operations has been revolutionized.

It is of interest to briefly record the progress made in this country in the manufacture of iron prior to 1860, partially that we may have a better conception of the remarkable development that has followed. The first pig iron made in America was manufactured in 1644 at Lynn, about ten miles from Boston, and there, too, was refined the first bar iron made in this country. The capitalization of this pioneer enterprise was $5,000, and a skilled workman commanded a wage of about 55 cents a day. Referring to this industry, Governor Winthrop said that, "the iron work goes on with more hope, it yields now about seven tons per week." Such was the inception of the American iron and steel industry, and with the little plant at Lynn as a nucleus, Massachusetts for a hundred years after the settlement at Plymouth was the chief seat of this country's activity. To the Boston iron works the credit is due of rolling in 1846 some of the first iron T rails ever produced in America, and fifty years ago Massachusetts was still one of the most

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[1] Presented before the Congress of Technology at the Fiftieth Anniversary of the granting of the charter of the Massachusetts Institute of Technology.

important centers of our nail industry. Even at this later period our iron plants consisted of small units of mine and mill located throughout the country with special reference to the proximity of local ores, fuel and water power facilities.

But the industry was expanding, and the year before the Massachusetts Institute of Technology was founded America produced a little over 900,000 tons of pig iron. An index of the accomplishment of fifty years prior and subsequent to 1860 is had in the 1810 production of 54,000 tons of pig iron, as against over 27,000,000 tons of pig iron produced in 1910. Such a phenomenal growth has, of course, been made possible by our wealth of natural resource; but raw material is of but potential value until won by the arts of industry, and even when converted is largely valueless until transported to its point of consumption. Cheap conveyance is a vital factor and the beneficent influence of iron and steel upon the progress of prosperity of this nation and of the world finds no more striking exemplification than its use in the art of transportation. Without the steel rail our prairies, forest and mines would still largely lie in their pristine glory and the interior fastnesses of the continents would be inviolate. Fifty years ago this country had but 30,000 miles of railroad. Transportation was expensive, slow and served little more than the important centers. The Pacific Coast was many weeks distant from the Atlantic Seaboard and the stage-coach and the pony express were essential elements of communication. The maximum capacity of the freight cars on the Pennsylvania Railroad was 9 tons, and our waterways largely dominated our commerce and industry. To-day our country is served by 240,000 miles of railroad; our freight cars are of fifty and even 100 tons capacity and the cost of transportation has been so lowered that the average renumeration of at least one of our large systems is less than five mills per ton mile. The effect of these changes is partially indicated by the 23,000,000 immigrants who have come to this country since 1860, by the increase of 60,000,000 in our inhabitants, and by the rapid movement westward of the center of our population.

But how comes it that in the short span of less than a generation such strides could be made in an industry which has basicly changed but little? The application of scientific research is alone responsible and it is primarily responsible because it made possible the economic development of the Bessemer and open-hearth processes, which were given to the world a few years prior to 1860. The Bessemer process was a metallurgical failure until Mushet's discovery of the efficacy of carbon and manganese addition, and it could not have been a commercial success without the mechanical improvements of many later workers in the field. The success of the open hearth was even slower. The development of the steel industry accentuated the necessity of exact methods. The comparatively rough-and-ready way of producing wrought iron would not answer for the more difficult accomplishment of high-grade steel. As it became recognized that the price of success was the scientific vigilance of technical men, the chemist, the metallurgist, the mechanical engineer, the steam engineer and the electrical engineer—all became essential factors. In the early stages, tonnage, as an essential element of cost, was a main consideration. Now quality stands first, and while tonnage has gone on apace, the strict inspection that commands production to-day subordinates volume to character. Under our superlative wealth of natural resource and under the insistent demand for maximum output, the questions of waste and conservation were secondary questions, and the time and money involved in the utilization of by-products were not thought commensurate with the return. But scientific management has brought about a new order of things: the selection and use of the raw materials entering into the manufacture are all subject to the analysis and control of the chemical laboratory. Chemistry is the monitor of the various steps in the transformation of ore to the finished product and with the physical laboratory stands sponsor for both the twelve-inch gun and the almost invisible wire that is drawn through the diamond die. Nearly every domain of science is called upon. The knowledge and control of heat is fundamental in the development of power and in the reduction of fabrication of steel. The essence of economic production lies in an intelligent application of the laws of hydraulics, hydrostatics, thermodynamics, and strength of materials. Electricity and magnetism play a prominent part in the transmission of power and illumination, and the refining of steel by electric energy is a departure destined to have an important future.

A modern steel plant is indeed a complex but wonderfully efficient machine. The remarkable influence that steel has exerted in the last century has been made possible by the radical reduction in its cost of manufacture. The price of steel rails affords a measure of what has been accomplished in this regard. Less than fifty years ago steel rails made their advent in this country at an equivalent of approximately 8 cents per pound. To-day rails sell for $1^1/_4$ cents per pound, or less than one-sixth of their former cost. While the reduction in cost during the last decade is naturally proportionately less than in the few decades that preceded, it is significant that in spite of the general increase in the prices of commodities the relative price of steel in this country, as shown by the commodity index, has continued to decrease in recent years. It is an eloquent testimonial to the efficiency of modern methods and to the conservatism of our iron masters that this has been accomplished in spite of the decreasing richness of our ores and a substantial increase in the cost of both labor and material.

In studying the causes of our cost reductions, two prominent factors appear. First, the fuel required to convert ore into a finished product has been largely reduced; second, the intensity of production, which roughly measures the increased efficiency of labor, has been enormously increased. At the mine in transportation, at the furnace and in the mill, machinery has taken the place of men, and a man in the steel industry to-day accomplishes from ten to fifty times as much work as did his predecessor fifty years ago.

In 1860 a thousand tons of pig iron per month was an extraordinary production for a blast furnace, and one and a half gross tons of coke was required for each gross ton of pig iron produced. To-day an output of 18,000 tons per month from a single furnace excites little comment, and the average coke consumption of the modern American furnace is a gross ton of coke for each ton of pig iron. This increase in tonnage, and decrease in fuel is the result of the uniformity and enlargement that has followed scientific management and not because of any radical departure in blast-furnace practice. In the refining of pig iron the gas producer, the regenerative furnace, the hot metal mixer, and the improvement in our prime movers have been important elements in the reduction of fuel; but it is mainly due to the substitution of the open hearth and the Bessemer converter for the puddle furnace that we are able to produce steel with nearly one-fourth less coal than was formerly required to produce iron. Our prime movers fifty years ago consisted essentially of slide valve steam engines in conjunction with low-pressure flue boilers, having an over-all efficiency of but 4-5 per cent. of the total heat in the fuel realized as work in the engine. To-day high-pressure water tube boilers and compound condensing engines with efficient valve gear have more than doubled the thermal efficiency, and the combination low-pressure steam turbine and non-condensing compound steam engine gives us a thermal efficiency of even 16 per cent. In other words, one ton of fuel with such an installation is able to do as much work as four tons of coal was formerly able to do.

The introduction of the gas engine marks another epoch in power production. With a thermal efficiency of 25 per cent., a given quantity of blast-furnace gas produces in the gas engine at least twice the amount of power obtainable with the modern boiler and steam engine. The gas engine when combined with the electric generator permits the highest development in plant concentration and in the production and transmission of power. With modern equipment the blast furnace produces a surplus amount of gas over and above its own heat and power requirements equivalent to at least 500 pounds of coal for each ten of iron produced. A notable example of the efficient use of blast-furnace gas as a by-product is presented in the new Gary, Indiana, plant of the United States Steel Corporation. There has been erected or is in process of installation over 100,000 horse power in gas engine units varying from 2,500 horse power to 4,000 horse power each, and the contemplated plant when finished will have more than 200,000 horse power in gas engines using blast-furnace gas. These, when aided by the surplus gas from the connected by-product coke ovens, will not only furnish all the heat, light and power required for all the mill departments, practically without the aid of coal, but will afford, as well, a substantial surplus available for neighboring industries.

It can be readily appreciated, therefore, that the aggregate saving of fuel in the iron and steel industry must be enormous, and one whose effect upon the conservation of the nation's coal supply must be important. The following figures based upon actual practice give an approximation of what this annual saving amounts to. Last year the United States produced 27,298,545 tons of pig iron and 25,917,281 tons of Bessemer and open-hearth steel. Had the same coke ratio been required to smelt this pig iron as that required in 1860 we should have used 23,000,000 net tons of coal more than we actually did use. Moreover, had the pig iron which was converted into steel last year been converted into wrought iron, we should have consumed 33,000,000 tons more coal than that which was actually burned. The measure, then, of last year's fuel economy in our iron and steel industry was approximately 56,000,000 tons of coal. But this is not all. The production of coke in the United States last year was about 41,000,000 net tons, made mostly in the bee-hive oven. Had this same tonnage of coke been produced in by-product coke ovens, 10,000,000 tons less coal would have been required and there would have been an additional saving of by-products in surplus, gas, tar and ammonia of a value of $39,000,000. Basing our calculations on 1910 production and giving coal an arbitrary value of a dollar a ton, these savings in the iron and steel and coke industries amount to $107,000,000 per year, as the sum of what we have done and what we will shortly do toward the conservation of our coal supply.

Such are some of the savings that have permitted our manufactured products to successfully enter the markets of the world. The United States has been one of the world's great granaries. The United States is now one of the world's great workshops. Fifty years ago our exported foodstuffs surpassed in value the exports of all our manufactured products. To-day the value of our manufactured products sold abroad largely exceeds the value of the shipments from our farms. In 1860 we exported iron and steel to the value of $6,000,000. Last year we contributed $179,000,000 in iron and steel to the markets of the world.

While we are largely indebted to the development of the natural sciences for such results, the technics of iron and steel embrace a wider field. The science of modern organization and the ethics of management represent in themselves as marked a departure as we find in the actual operations of our works.

Half a century ago the ownership and control of our iron works lay largely in the individual, by actual ownership or through small organizations. Plants were small and comparatively numerous. There was close contact between employer and employee and the workmen were few and their duties correspondingly varied. The economies of specialization, intensity and concentration were largely unknown or impractical.

To-day our mines and mills are principally controlled by large corporations. Ownership stands in thousands of small and widely scattered stockholders, and policy and operation are guided by their representatives. Plants are large and intensified production is commanded by armies of skilled men working with specialized machinery.

In achieving high efficiency and resultant low costs, the large corporation is an economic necessity. Its effectiveness in the elimination of waste is the power of large financial resource and concentrated direction. There is no better exemplification of the composite force of many owners than the plant at Gary. This, our latest extensive plant, has arisen in four years from the unbroken sand dunes of lower Lake Michigan, and is a striking illustration of the possibility of $55,000,000 when expended by a highly developed organization.

But the change that has come with our modern system is more than in the material improvement of plant and machinery. There has followed a clearer conception of the relationship of the public, the wage earner and the investor. Industrial success means loyalty and team work, and intelligent management appreciates that profits if they are to be sustained must not be preferential to justice and humane treatment. Coöperation with one's competitors, pension funds for the superannuated, systematic endeavor for the prevention of accidents, voluntary compensation for the injured, recognition of faithful service, elimination of Sunday work, profit-sharing, sanitary surroundings, the club, the hospital—all these are manifestations of a humane and efficient policy.

Business administration in our complex industrial life embodies many elements beside the natural sciences. There is the science of men as well as the science of machines, and both are necessary for the broadest type of industrial efficiency.

A training that is either too cultural or too specialized does not harmonize with present requirements and the Massachusetts Institute of Technology, in recognizing the commercial as well as the technical needs of the times, is but maintaining her tradition for progressive thought and leadership in method.

SCIENTIFIC SOCIETIES.

INDIANAPOLIS MEETING, AMERICAN CHEMICAL SOCIETY.

Four hundred and thirty-two members and guests attended the summer meeting at Indianapolis, which was the largest summer meeting of the American Chemical Society ever held. The meeting was an unusually successful one, both from the standpoint of work accomplished and the general enjoyment of those present.

Those members who appeared a day early were treated to an automobile ride around the famous Indianapolis Speedway, followed by a dinner at the University Club.

The general meeting itself opened on Wednesday morning, June 28th, with an address by Charles Baskerville, on "The Chemistry of Anesthetics," and by W. Lash Miller, on "The Chemical Philosophy of High School Textbooks." At the close of this session Dr. W. F. Hillebrand presented a preliminary report for the Committee on the Quality of Platinum Laboratory Utensils, which was afterwards discussed in the sessions of the Industrial Division.

The hospitality of the local members knew no bounds and a complimentary luncheon was served each day. Also an unusually attractive complimentary "smoker" was held at the German Club House on Wednesday night, at which mementoes were distributed, consisting of bakelite cigar holders, watch fobs bearing the Society's emblem, and steins, also stamped with the Society's pin in blue and gold. On Thursday evening a public lecture by A. D. Little on "The Earning Power of Chemistry" was delivered at the German House, followed by a concert in the German House gardens. Visits to manufacturing plants were a feature of the meeting, among which should be especially mentioned Eli Lilly & Co., the Van Camp Packing Co., Kingan & Co., E. C. Atkins & Co., Encaustic Tile Co., Nordyke & Marmon Automobile Co., Fairmount Glass Works, the Indianapolis Water Works, and the Polk Sanitary Milk Co. An especially interesting program was also arranged for the visiting ladies, all of whom expressed themselves as thoroughly pleased with the entertainment given.

On Friday evening nearly two hundred members and guests gathered at the Columbia Club for the usual midsummer banquet. The banquet was a great success. The tables were decorated with flags and flowers, the menu offered was of the best and the speeches were greatly enjoyed. Dr. H. W. Wiley acted as toastmaster and introduced as the special speakers of the evening Governor Marshall, of Indiana, and ex-Vice-President Fairbanks. Many ladies attended the banquet, which was also graced by the presence of Mrs. Marshall. One of the best orchestras in the West furnished music during the evening.

A transcript of the minutes of the meetings of the Industrial, Fertilizer, Agricultural and Food, and Pharmaceutical Divisions follows, as well as an account of the meeting of the Rubber Section. The record of papers in the Organic, Physical and Inorganic Divisions and the Biological Section will appear in the regular proceedings of the Society.

Division of Industrial Chemists and Chemical Engineers.

George D. Rosengarten, *Chairman.*

Dr. Rosengarten thanked the Division for his election and requested the earnest coöperation of its members in order to secure papers of value and further the work of the Division.

The reading of the minutes was dispensed with.

The report of the secretary was read and accepted, of which the following is an extract:

"The secretary has to report for the Executive Committee that since the last meeting they have elected as Chairman of the Division in the place of George C.

Stone, resigned, George D. Rosengarten, of Philadelphia. They have also approved of the proposal made by the Committee on Methods of Analysis of Glycerine, which is a sub-committee of the Industrial Division Committee on Analysis of Soap and Soap Products, that they coöperate with the International Committee on Glycerine Analysis and unite with the International Committee in the preparation of a joint report if it appears to the said committee advisable to do so.

"There has been a slight increase in the membership of the Division since the last meeting, the number of registered members now being about 1,050."

The secretary further presented a financial statement and reported on the present status of the technical directory, which can be published as soon as sufficient funds are available.

The Report of the Committee on Soap Products and Glycerine, read by Professor Langmuir, was discussed and accepted.

The Report of the Committee on Official Specifications was read in part, and the committee continued.

No report was made by the following committees:

Definition of Trade Terms,
Research Problems,
Standard Methods of Analysis,
Descriptive Bibliographies,
Publicity,
Special Compounds.

The Report presented by Dr. Hillebrand on the "Quality of Platinum Laboratory Utensils" was discussed by Professor Langmuir, William Brady, F. C. Phillips, and John White.

The Report of the committee appointed to draft resolutions regarding the retiring Chairman, Arthur D. Little, was made, and it was

VOTED: To adopt these resolutions and to spread them on the minutes to become a part of the permanent records of the Division.

The following papers were read:

"Hop Standards: Considered from the Chemical Standpoint," by H. V. Tartar, showing the different results obtained by the different methods of analysis, compared with results from the author's own methods.

"Losses in the Storage of Coal," by Horace C. Porter and F. K. Ovitz, showing that under usual conditions and not piling too high, coal is not changed in storing, wet or dry.

"Refractories and Laboratory Appliances made from Alundum," by P. A. Boeck. Exhibition of samples and statement as to its usefulness, discussion by White and Hillebrand.

"Determination of Vanadium in Vanadium and Chrome-Vanadium Steels," by John R. Cain; read by Dr. Hillebrand.

"Need of Professional Code of Ethics among Chemists," read by Lucius P. Brown, substitute for Francis L. Parker; discussed by Charles C. Kawin, A. D. Little, Edward A. Barrier, Bronzius, H. V. Farr, in favor of certification, public and technical. McCormack favored such plan.

On motion of Mr. Bryan, seconded by Mr. Handy, it was

VOTED: That the chairman of the Division appoint a committee to consider the question of the need of a professional code of ethics among chemists.

On motion of James O. Handy it was

VOTED: That the Division of Industrial Chemists and Chemical Engineers recommend to the attention of the Directors of the American Chemical Society the advance publication and circulation of certain papers, in order to bring out discussion.

That we further suggest the desirability of having the discussions at our meetings reported accurately.

"The Examination of Fir Oil Obtained by Steam Distillation of Douglas Fir," by Henry K. Benson and Marc Darrin; read by Horace G. Byers.

"The Wood Distillation Industry of the Pacific Northwest," by Henry K. Benson; read by Horace G. Byers.

"Ratfish Oil as a Paint Material," by Henry K. Benson and Wallace Eshleman; read by Horace G. Byers.

"Analysis of Commercial Nitrous Oxide," by W. R. Smith and E. D. Leman; read by secretary.

"A Differential Test for Sulfur-chloride and Sulfur-dioxide Substitutes," by Charles P. Fox; read by secretary.

"Marine Fiber," by Charles P. Fox; read by chairman.

"A Method of Analysis of Lead Ores," by John Waddell; read by secretary.

"A Method of Analyzing Some Commercial Gold Alloys," by James O. Handy.

"Concentration and Purification of Iron Ore, High in Sulfur, by Roasting in a Rotary Kiln," by James O. Handy. Temperature and speed in the desulfurization of iron ores seemed to be the theme of the paper, which called forth quite a little discussion on methods and apparatus.

The following papers were read by title:

"The Rapid Analysis of Alloys," by Guillermo Patterson, Jr.

"The Testing of Inks, Typewriter Ribbons and Carbon Papers," by Percy H. Walker.

"Storage Battery Efficiency," by J. S. Staudt.

"A New Modification of Gas Analysis Apparatus," by B. G. Klugh.

"Determination of Dust in Blast-Furnace Gas," by L. A. Touzalin.

Dr. Rosengarten adjourned meeting.

GEO. P. ADAMSON,
Acting Secretary.

Division of Fertilizer Chemistry.

The meeting of the Fertilizer Division was called to order by the chairman, Mr. P. Rudnick.

The minutes of the last meeting were read and approved.

The following was the program:

"Note on the Permanganate Methods for Availability of Organic Nitrogen," by John Phillips Street.

"The Use of Fused Silica Dishes for Potash Determination in Fertilizers," by W. D. Richardson.

"The Availability of the Insoluble Nitrogen in Certain Commercial Fertilizers," by B. L. Hartwell and F. R. Pember.

"The Use of Alundum Crucibles for Total Phosphoric Acid and Potash Determinations in Fertilizers," by W. D. Richardson.

"The Availability of Nitrogen in Complete Fertilizers," by Jacob G. Lipman.

"Notes on Estimation and Valuation of Potash," by P. F. Trowbridge.

Report of committees:

Paul Rudnick, for the Committee on Nitrogen.

G. A. Farnham, for the Committee on Phosphoric Acid.

J. E. Breckenridge, for the Committee on Potash.

C. F. Hagedorn, for the Committee on Phosphate Rock.

F. B. Carpenter, for the Committee on Fertilizer Legislation.

On motion regularly made and seconded it was decided that the publishing of the Nitrogen Committee Report in full be referred by the Executive Committee to the Council, and then, if favorably received, members of the Fertilizer Division be asked for contributions to cover cost of publishing.

On motion meeting adjourned.

J. E. Breckenridge,
Secretary.

The Division of Agricultural and Food Chemistry.

The meeting was called to order by the chairman, Mr. H. E. Barnard.

The following papers were read:

"Composition of the Drainage Water of a Soil with and without Vegetation," by T. L. Lyon and J. A. Bizzell.

"The Cryabiotic Point," by W. D. Richardson.

"The Analysis of Canned Tomatoes," by E. H. S. Bailey and H. L. Jackson.

"The Chemical Changes which Take Place during the Spoilage of Tomatoes, with Methods for Detecting this Spoilage in Tomato Products," by R. F. Bacon and P. B. Dunbar.

"The Action of Non-Acid Foods on Tin Containers with Special Reference to Canned Shrimp," by R. F. Bacon and W. D. Bigelow.

"Determination of Tin in Food Products," by Edward Gudeman.

"A Chemical Study of Certain 'Sand-Hill' Soils of South Carolina," by T. E. Keitt.

"A Short Method for the Determination of Soluble Arsenic in Commercial Lead Arsenates," by T. O. Smith and B. E. Curry.

"Methods of Estimating Fat in Tissues," by Waldemar Koch.

"The Effect of Phosphorus Manuring on the Amount of Inorganic Phosphorus in Slat Turnip Roots," by Burt L. Hartwell and Frederick S. Sammet.

"The Detection and Determination of Small Quantities of Ethyl Alcohol, Methyl Alcohol and Formic Acid," by R. F. Bacon.

"The Determination of Malic Acid," by P. B. Dunbar and R. F. Bacon.

"Detection of Benzoic Acid in Coffee Extract," by H. C. Lythgoe and C. E. Marsh.

"Composition of Tincture of Ginger Made with Varying Strengths of Alcohol," by H. C. Lythgoe and L. I. Nurenberg.

"Akron (Ohio) Water: Home Treatment for Bath and Laundry," by Charles P. Fox.

The following papers were read by title:

"Two New Pieces of Apparatus. (*a*) Apparatus for the Continuous Extraction of Liquids with Immiscible Solvents Lighter than Water. (*b*) A Compact Apparatus for Quantitative Determinations Based on the Measurement of an Evolved Gas," by R. F. Bacon and P. B. Dunbar.

"The Influence of the Reaction of Solution on the Development of Wheat Seedlings," by J. F. Breazeale and J. A. LeClerc.

"The Distribution of Organic Constituents in Soils," by Oswald Schreiner and Elbert C. Lathrop.

"Dihydroxystearic Acid in Good and Poor Soils," by Oswald Schreiner and Elbert C. Lathrop.

"Studies on Organic Soil Nitrogen," by Elbert C. Lathrop and Bailey E. Brown.

"The Composition of the Timothy Plant at Different Stages of Growth," by L. D. Haigh and P. F. Trowbridge.

"The Volatile Acids of Corn Silage," by Arthur W. Dox and R. E. Neidig.

"The Arsenic Content of Shellac and the Arsenical Contamination of Food Products from that Source," by H. B. Smith.

"The Solubility of Lime in Contact with Clay and Water," by B. E. Curry.

The Division considered the advisability of adopting by-laws to govern its meetings and referred the matter to the Executive Committee with power to draft a set of by-laws and present them at the next meeting for action.

It was pointed out that the expenses incidental to the meeting such as typewriting and postage had heretofore been borne by the President and Secretary of the Section and the Division voted that the bills incurred n this manner regarding the present meeting be referred to the Finance Committee with the recommendation that they be paid from the treasury of the American Chemical Society.

It was also voted that the Council be requested to assign to the Division of Agricultural and Food Chemistry papers on Sanitary Water Analysis and Supplies.

Respectfully,
W. D. Bigelow,
Secretary pro tem.

Division of Pharmaceutical Chemistry.

The first session was called to order by the chairman, Mr. B. L. Murray, eighteen members being present.

The chairman stated that he had no address to read, but spoke of the progress which the Division had made, commenting especially upon the increase in membership from 66 at the beginning of the year to 150 at the present time.

The secretary presented a report telling of the work done to increase the membership and, as treasurer, reported collections amounting to $66.50, expenses amounting to $39.00 and a balance of $27.50.

Methods of promoting the growth and activity of the Division were then discussed and it was agreed that the work of the Committee on Quantitative Methods offered the best means of interesting the members in the work of the Division; and that the work of this committee should be extended. No action, however, was taken at this session.

The following motion by A. D. Thorburn was adopted:

That the Division expresses its approval of the secretary's action in trying to secure new members, and of the expenses thus incurred, and directs that the campaign for members be continued as far as the time of the secretary and the funds available will allow.

The following papers were read by the secretary and were discussed by several members:

"The Determination of Camphor in Spirits of Camphor," by L. D. Havenhill.

"Rapid Determination of Beeswax and Honey," by Fred Klein.

The following papers were read by title:

"The Volatile Acidity of Tragacanth and Other Gums," by W. O. Emery.

"Acetate Collodion," by E. C. Worden.

C. H. Briggs then read a paper on "The Estimation of Minute Quantities of Nitroglycerin," by W. L. Scoville.

After a brief discussion the meeting adjourned.

SECOND SESSION.

After the reading of the minutes of the previous session, W. A. Pearson gave an illustrated lecture on "The Manufacture and Testing of Drugs."

C. E. Caspari then read a paper on "Pharmacopoeial Revision," by Joseph P. Remington.

The reading of this paper was followed by an extended general discussion of pharmacopoeial matters.

THIRD SESSION.

The reading of the minutes of the previous session was dispensed with and after a brief report by the secretary, for the benefit of those not present at the first session, the Report of the Committee on Quantitative Methods was presented by F. O. Taylor, the chairman of the committee.

On motion by C. T. P. Fennel the report was received and on motion of C. E. Caspari a copy of the report was ordered to be sent to the chairman of the Pharmacopoeial Revision Committee.

Mortimer Bye presented the following motion:

That the present Committee on Quantitative Methods be retained; but that the number of members be increased at the discretion of the chairman of the Division, and that the scope of the work be enlarged by the committee.

This motion was duly seconded and after discussion by Messrs. Caspari, Rosengarten, Taylor, Fennel, Eldred, and Murray was carried.

L. A. Brown then presented his paper on "Aromatic Spirits of Ammonia."

The following papers by Edw. Kremers were read by title:

"Precipitated Sulphur, a Study of a Dermatological Prescription."

"The Moisture Content of Drugs."

C. M. Pence then presented his paper on "A Study of the Bromine and Iodometric Methods for the Determination of Resorcinol."

C. E. Caspari suggested that a copy of this paper be sent to the chairman of the Pharmacopoeial Revision Committee.

A. D. Thorburn presented a paper on the "Estimation of Morphine by Extraction with Phenyl-Ethyl Alcohol."

The following papers were read by title:

"The Relation of the Alkaloids of Gelsemium to One Another," by L. E. Sayre.

"Notes on the Iodometric Determination of Strength of Formaldehyde Solutions," by J. S. Chamberlain.

"The Pharmacopoeial Standard for Desiccated Thyroid Glands," by Reid Hunt and Atherton Seidell.

E. G. Eberhardt presented two papers on "A Modified Form of Repercolation" and "Tincture of Cantharides."

H. T. Graber read a paper on "Some Observations upon the Assay of Digestive Ferments."

C. H. Briggs presented a paper by C. F. Ramsay on "A New and Accurate Method for Determining the Tryptic Value of Pancreatin," also a paper by A. Zimmerman on "The Accelerating Action of Hydrochloric Acid upon the Starch Converting Properties of Pancreatin and Malt."

H. T. Graber presented another paper by Mr. Zimmerman on "Laboratory Studies of Pepsin, Pancreatin, and Combinations of These Ferments."

The secretary read two papers:

"A Few Results Obtained from Pepsin Assay," by O. P. Eyre, and "Investigations made with Dry Egg Albumin in View of Replacing the Albumin Coagulated in the Egg, for Greater Accuracy in the U. S. Pharmacopoeia Pepsin Assay," by A. Zimmerman.

All of the papers on digestive enzymes were discussed collectively and it was suggested by A. H. Clark that, as a number of new facts had been brought out, copies of these papers should be sent to the Pharmacopoeial Revision Committee. The meeting then adjourned.

FRANK R. ELDRED, *Secretary.*

Meeting of the Rubber Section.

A preliminary meeting of the Rubber Section was held at 10 o'clock on June 30th at the German House, where a general consultation was held on the question of the continuance of the Rubber Section and also regarding means of increasing the activities of the members. The meeting was adjourned to 4 P.M.

The adjourned meeting was called to order at 4 P.M. at the Claypool Hotel by the secretary in the absence of the chairman with sixteen members present.

Dr. George Oenslager was elected temporary chairman and the minutes of the previous meeting, held in Boston, December 30, 1909, were read and approved.

Prof. Charles Knight submitted a report on progress from the Committee on Methods of Analysis. The report was accepted and the secretary directed to send mimeographed copies to all members of the Section.

The Committee on Specifications rendered a written report and the committee was discharged with thanks.

It was voted that the Section recommend to the Council of the Society that it appoint a Committee on Specifications, of the Rubber Section, to act in conjunction with a similar committee from the Division of Industrial Chemists.

It was voted that the Committee on Abstracts be discontinued.

It was voted that all members of the Section be asked to furnish the Committee on Methods of Analysis with their methods for the determination of acetone extract, free sulfur, total sulfur and ash in rubber; also that samples of rubber when sent out be sent to all the members of the Section who expressed a willingness to make coöperative analyses for purposes of comparison.

The meeting then adjourned.

Frederick J. Maywald, *Secretary.*

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES.

On April 25, 1911, there was called together in Paris a preliminary meeting of delegates of the Chemical Society of London, the German Chemical Society and the Chemical Society of France, for the purpose of organizing an international association. The Chemical Society of London was represented by Messrs. Frankland, Meldola and Ramsay; the German Chemical Society was represented by Messrs. Jacobson, Ostwald, and Wichelhaus; the Chemical Society of France, by Messrs. Béhal, Haller and Hanriot. As a result of their deliberations the following by-laws for an international association were adopted.

Article I. An International Association of Chemical Societies is hereby founded.

Article II. The object of the Association is to form a bond between the chemical societies of the world in order to consider chemical problems of general and international interest.

Article III. All chemical societies can take part in the Association.

Article IV. The Association is directed by a Council formed from a certain number of members. Each country can be represented in the Council only by a single chemical society, which shall designate three representatives.

Article V. The existing Council consists of the delegates of the charter societies; namely, the German Chemical Society (Deutsche Chemische Gesellschaft), the English Chemical Society (Chemical Society of London) and the French Chemical Society (Société chimique de France). Representation of any society in the Council will be decided by the Council itself and by a majority of two-thirds of the members voting. Correspondence vote will be permitted in this case.

Article VI. The Council will fix at each reunion the time and place of the next session.

Article VII. The Council names at the beginning of each session a President, who is at the same time President of the Association and who presides at all functions until the end of the session.

Article VIII. The Bureau consists of the President, the Vice-President and the Secretary General, comprising the delegates from the same country.

Article IX. The President is charged to convoke the Bureau; he will carry out the decisions of the Council, fix the order of the day for meetings of the Council, and formulate the relations between the different societies. The President will have approved the minutes of the meetings. However, the minutes of the last meeting can be approved by correspondence.

Article X. The work of the Association will consist of nomination of commissions in charge of studying questions submitted to them by the Council; publication in the journal of the affiliated societies or by any other method of publication which the Council may determine; conferences or congresses.

Article XI. The general expenses will be borne by the affiliated societies in proportion to the number of their members. All expenses other than general expenses will be charged to the different societies only under the individual agreement of the particular society. The Secretary-General shall submit at each session for the approval of the Council a financial statement for the interim.

Article XII. Modification of the present by-laws can be brought about only by a majority of two-thirds of the members of the Council. Correspondence vote is also permitted in this case.

During the session it was voted to invite the American Chemical Society, the Chemical and Physical Society of Russia, and the Union of Italian Chemical Societies to be represented in the Council and to name each three delegates. This invitation was duly presented to the Council of the American Chemical Society at their Indianapolis meeting and after careful consideration, on motion of Past President John H. Long, the following vote was passed.

The American Chemical Society views with favor the proposal to join with the chemical societies of London, France and Germany in the formation of an international association on the lines suggested in the provisional program forwarded by Professor Ostwald, and the President of the American Chemical Society is hereby empowered to enter into correspondence on the details of the proposed organization.

CHICAGO MEETING OF AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, JUNE 21-24.

The third semi-annual meeting of the American Institute of Chemical Engineers was an important and successful event in the history of that society.

The chemical engineers were welcomed to Chicago by Mr. Wade, who represented the Mayor of Chicago, and by Dr. T. B. Wagner, representing the local committee.

Among the interesting papers presented was a very able address by the President, Dr. F. W. Frerichs, on

"Methods of Attacking Chemical Industrial Problems," which was accompanied by complete detailed drawings and models of an installation for the manufacture of soda by the Solvay Process Company; also the great difference in both conditions and prices between this country and Germany was demonstrated by estimates on a process, which though successful in Germany, would prove a failure in the United States.

The report of the Committee on Chemical Engineering Education was read by Dr. Samuel P. Sadtler, chairman of that committee, and a paper discussing the "Four-Year Course in Chemical Engineering" was read by Professor J. H. James, of the Carnegie Technical School of Pittsburgh. A paper giving a summary of the work of the "Committee on Five-Year Engineering Courses of the University of Ohio" was presented by Professor J. R. Withrow.

Other papers presented were: "Industrial Chemical Calculations," by Professor J. W. Richards; "Rapid Determination of Tin in Food Products," by Dr. Edward Gudeman; "Distillation on the Continuous System," by Dr. C. L. Campbell; "The Institute and the United States Patent System," by Dr. William Grosvenor; "Practical Value of Calorific Tests on Anthracite Coal," followed by another on "Two Methods of Testing Asphalt," by Dr. S. F. Peckham.

A number of industrial excursions were made to plants among which was a visit to the plant of Messrs. Swift & Company.

The Toronto meeting of the American Electrochemical Society will be held September 21–23, 1911. There will be many interesting papers presented at this meeting.

EDUCATIONAL

The University of Maine recently conferred its Doctorate of Science upon Prof. Charles L. Parsons, of New Hampshire College, Secretary of the American Chemical Society.

Dr. K. Polstorff, Associate Professor of Pharmacological Chemistry at the University of Goettingen, Germany, died on June 20th at the age of 66 years.

Dr. P. Walden, Professor of Chemistry at the Polytechnic School of Riga, Russia, has been elected a member of the St. Petersburg Academy of Sciences.

On June 26th Dr. Julian W. Baird, Professor of Chemistry and Dean of the Massachusetts College of Pharmacy, died at the age of 53 years.

Dr. Wm. C. Rose has been appointed Assistant Instructor in Physiological Chemistry at the University of Pennsylvania.

NOTES AND CORRESPONDENCE.

To the Editor of the "Journal of Industrial and Engineering Chemistry."

SIR:

In the July issue of your Journal, there is a communication from Dr. Leo H. Baekeland in which he discusses my Belgian patent relating to new condensation products, a brief notice of which appeared in your June number of this year. In reply to the same, I desire to explain that I have been too busy in commercially exploiting and developing these products and on other technical researches and enterprises to find time to produce any matter for publication other than patent applications, of which I have about forty now pending in the United States relating to this subject.

By invitation from the editor of THIS JOURNAL, I had previously promised to write an article on this subject, which will, I hope, follow this communication in the near future, as soon as the condition of pending applications for patents and my other work connected with the commercial development and exploitation of my inventions will permit.

It goes without saying and as a matter of course that if my Belgian patent gives my invention no approved standing as to novelty of subject matter and the proper restriction of my claims, neither do the Belgian nor French bakelite patents confer any such approved standing on bakelite.

But it should be clearly understood that from the beginning of my work, and at all times during and since, I knew that my products and my processes were each and all of them totally different, physically, chemically and patentably, from any, each and all of the products or processes described before or during the time any or all of my work was in progress, inclusive of any or all publications by Dr. Baekeland.

I will, however, briefly describe the substance called condensite which is now being manufactured and sold in the United States by the Condensite Company of America at Glen Ridge, N. J., under my patent applications pending in this country, among which is one corresponding to the Belgian patent referred to in the July number of THIS JOURNAL.

Condensite is a high-grade plastic which may be rapidly molded in its uncured state and can be hardened with or without pressure, in from one minute, more or less, to one hour, more or less, depending on the particular composition, its mass and the care with which it has been manufactured. The products, which are now being manufactured and marketed and used in the United States for more than six months last past, are each respectively of constant composition and absolutely reliable products in their molding properties.

It is adapted for molding in either open or closed molds without the necessity, as for instance in the rubber industry, or in the manufacture of bakelite, of a vulcanizer or equivalent apparatus, in a very simple and rapid manner and the strength is so great and the contraction so small that beautifully molded objects are made and metal parts can be molded within it and without any difficulty from cracking.

Present experience shows that for practical purposes and under certain conditions, condensite is oil-proof and is acid-proof, except in the cases of nitric acid, concentrated sulphuric acid, and the strongest hydrofluoric acid. Cold or hot, dilute or strong solutions of caustic soda or caustic potash do have an action on it, and the statement on page 439 of the June issue of This Journal should be read and understood in the light of the foregoing. Unfortunately, I did not have an opportunity of editing that note.

Condensite is harder and is stronger than hard rubber in tensile strength. It differs from other phenolic condensation products in several features which are of vital importance, among which the following may be mentioned: freedom from stresses due to excessive shrinkage and other causes, such as the retention of vapors due to the reaction under a compensating pressure; for all practical purposes it is non-odorous in the cured state, and nearly so in the uncured state; uniformity and reliability of manufacture; extremely high dielectric strength even when small per cents. (say 2 per cent.) of lampblack are compounded with it and the molded object is not specifically made for high tension insulation; when specifically so made, its dielectric strength is enormous.

The expression "quantitative synthesis" should be intelligible to Dr. Baekeland, but, assuming that his questioning is in good faith, I will explain that that expression is a descriptive statement of a synthetic operation in which the fate of all materials used at the beginning of the operation is accounted for at the end of the operation in contradistinction to the ordinary and usual synthetic operation in which only selected parts of the initial materials are accounted for at the end of the operation.

As to Dr. Baekeland's comment on what I have offered in my Belgian patent as to the molecular weight of one of my new products, I say that at the time I made those determinations I was fully aware of all the disturbing or possibly disturbing conditions referred to by Dr. Baekeland, but I believed then and I believe now that within the limits indicated in that patent I succeeded in overcoming those experimental obstacles. By reference to the Belgian patent it will be seen that, at the best, my statement as to molecular weight is merely a surmise and is not made as a hard and fast and rigidly proven fact.

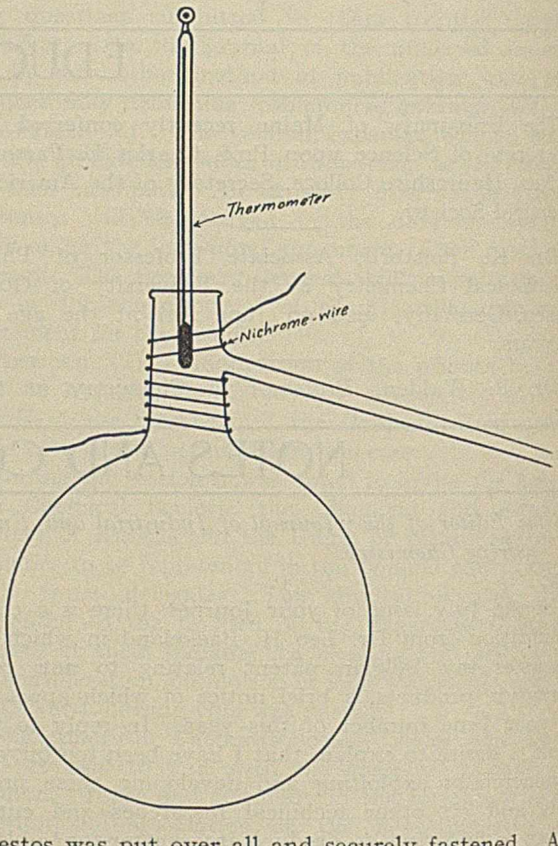
In answering Dr. Baekeland's communication, I trust I may be pardoned for confining myself to some of the technical matters discussed therein and leaving for some other occasion those points which have their interest only from a legal or commercial point of view and which while of paramount importance to Dr. Baekeland because of his financial interest in bakelite, of which he is the inventor, are doubtless of minor, if of any interest to the readers of This Journal.

J. W. Aylsworth.

Glen Ridge, N. J., July 5, 1911.

FLASK FOR DISTILLATION OF TARS.

In This Journal, 3, 110, is a "Note on the Distillation of Tars Containing Water." The object of this method was to provide a means for the prevention of "bumping." Previous to the article, a method had been in use in the Laboratory of Industrial Chemistry in the University of Washington, which effectually accomplished this result. A thin sheet of asbestos paper was wrapped once around the neck of the distilling flask, and this in turn wound with a few turns of No. 30 Nichrome resistance wire. A thick covering of asbestos was put over all and securely fastened. An electromotive force of 15–30 volts impressed on the terminals of this wire will furnish enough heat to keep the neck of the flask up to the required temperature, and in this way end any condensation which would have gone on in the neck. As a practical laboratory method, this has been tried and proved satisfactory in preventing "bumping" in the distillation of wood tar.



C. E. Brown,
G. B. Shadinger.

University of Washington,
Seattle, Wash.

NOTE ON THE TWITCHELL PROCESS OF DECOMPOSING FATS.

In the decomposition of fats and oils by the Twitchell process the progress of the decomposition is followed by titrating the free fatty acids at any stage of the operations. The percentage of free fatty acids found does not necessarily represent the percentage of decomposition of the neutral fat in the original mixture, though it is often quite close to this figure even with considerable free fatty acids present at the start. As the decomposition of the neutral fat is the object sought it is important to be able to figure its decomposition correctly.

To this end we must know:

The total fatty acids obtainable from 100 parts of neutral fat.

The true combining weight of these fatty acids.

The true per cent. of free fatty acids at the start (titrated, using true combining weight).

The true per cent. of free fatty acids in the product (titrated, using true combining weight).

With this data we can derive an expression giving us the true per cent. of decomposition of the neutral part of the mixture taken at the start.

Let x = percentage of decomposition expressed decimally, as 90 per cent. decomposition would be expressed as 0.90.

Let y = per cent. of free fatty acids in the product, also expressed decimally, as 95 per cent. would be expressed as 0.95.

F = a factor that varies with the per cent. of free fatty acids originally present.

Then x =

$$\frac{100y - \text{per cent. of free fatty acids originally present, expressed as a whole number}}{\text{Total fatty acids in neutral part of mixture at start} + \text{F}\,y.}$$

In this expression y is found by titration, using correct combining weight of fatty acids. Original free fatty acids are found by titration.

Total fatty acids are neutral fat by multiplying the per cent. of neutral fat in the mixture by the per cent. of total fatty acids obtainable from such neutral fat.

F is found as follows:

100 — the free fatty acids gives the neutral fat.

The neutral fat — the fatty acids obtainable from it gives F.

An example will make the matter clearer.

Let the free fatty acids originally present be 3.84 per cent.

Let the final free fatty acids (as expressed on the final product) = 0.8996 = y.

Let the neutral fat give 0.9511 of its weight of total fatty acids.

100.00 = Neutral fat + fatty acids (free).
3.84 = Free fatty acids.

96.16 = Neutral fat.
91.46 = 96.16 × 0.9511.

4.70 = F = factor for y.

Then for our example, $x = \dfrac{100(0.8996) - 3.84}{91.46 + 4.7(0.8996)}$

solving, $x = 0.90$

Decomposition = 90 per cent. of neutral fat.

It will be noticed that the decomposition is almost the same as the amount of free fatty acids found in the final product, and for the higher percentages of decomposition this will be the case with either neutral fat to start with or a mixture containing several per cents. of free fatty acids. That it is not the case under all circumstances may be seen if we consider the original mixture to contain free fatty acids without any decomposition of neutral fat.

Where the original mixture or final product contains moisture or other substances besides the fat and fatty acids, the two latter should be considered as making up 100 per cent. of fatty matter and figured accordingly.

W. H. Low.

SUMMARY OF CEMENT INDUSTRY IN 1910.

The statistics of cement production in 1910, as reported by Ernest F. Burchard, of the United States Geological Survey, indicate that the cement industry ranks within the first eight extractive industries in the United States, the value of the cement produced being exceeded only by the value of the coal, pig iron, petroleum and gas, clay products, copper, gold, and stone.

The total quantity of Portland, natural, and puzzolan cements produced during 1910 was 76,934,675 barrels, valued at $68,052,771. This was an increase of 10,244,960 barrels, or 15.3 per cent., in quantity, and of $14,442,208, or 26.9 per cent., in value, over the figures for 1909. The increase in quantity is one of the largest ever recorded, and the fact that the increase in value was proportionately higher indicates that trade conditions were slightly more satisfactory than during 1909.

Portland cement constituted the main item in this output, the total for the year being 75,699,485 barrels, valued at $67,506,479. This quantity is equivalent to 12,841,430 long tons, valued at $5.26 a ton. It approximates 47 per cent. of the quantity of pig iron produced in 1910. The average price per barrel in 1910, according to the figures reported to the Survey, was a trifle less than 89.2 cents. This represents the value of the cement in bulk at the mills, including the labor cost of packing, but not the value of the sacks or barrels. The prices ranged generally between 72.7 cents a barrel in the Lehigh district and $1.38 on the Pacific coast. While the average price for the whole country increased from 81.3 cents in 1909 to nearly 89.2 cents in 1910, with corresponding increase in the eastern, central, southern and western districts, the average price in the Pacific coast States dropped from $1.52 to $1.38, a decrease of 14 cents a barrel, due, no doubt, to the advent of new mills in California, the Rock Mountain States, and Western Texas, and to the increased capacity of other plants supplying the coast territory, where attractive prices have hitherto prevailed.

The number of producing plants increased from 108 in 1909 to 110 in 1910, but the total number of rotary kilns in operation decreased from 930 to 900. The figures indicate, however, that the proportion of large kilns is increasing, 471 kilns 100 feet or more in length being reported in 1910.

The Portland cement plants in the East, including plants in Pennsylvania, New Jersey, New York, and Massachusetts, produced 33,306,560 barrels in 1910, at an average price of 75 cents a barrel. The plants in the Central States—Ohio, Indiana, Michigan, Illinois, Iowa, and Missouri—produced 22,617,009 barrels, at 91 cents. The plants in Kansas, Colorado, South Dakota, Utah, Arizona, and Montana, included under "Western States," produced 7,672,369 barrels, at $1.03. The Pacific coast plants, in California and Washington, produced 6,385,588 barrels, at $1.38. The plants in the South, located in Maryland, Virginia, West Virginia, Kentucky, Tennessee, Georgia, Alabama, Oklahoma, and Texas, produced 5,717,959 barrels at 94 cents.

The Barbar Asphalt Company has engaged Dr. Albert Sommer to take charge of a new department which will embrace recently developed Trinidad liquid asphalt products. Dr. Sommer until lately was in charge of the scientific development work of the Texas Company.

The next meeting of the International Association of Chemical Societies will be held on April 13th, 1912, in Berlin under the presidency of Prof. Wilhelm Ostwald.

Dr. H. E. Sawyer, formerly of the Bureau of Chemistry of the U. S. Department of Agriculture, died on July 5th at the age of 43 years.

CONSULAR AND TRADE NOTES.

THE COBALT SILVER MINES.

Since the inception of the camp in 1904, the silver mines of the cobalt district have shipped ore containing 93,275,077 ounces of silver, valued at $48,265,236, after freight and smelting charges were deducted. During 1910 there were 33,519 tons of ore shipped by the mines, having a silver content of 29,856,069 ounces, worth $15,375,000.

By calendar years, the production of the cobalt district was:

Year.	Ore shipments, in tons.	Silver content, in ounces.	Value.
1904	158	206,875	$ 111,887
1905	2,144	2,451,356	1,360,503
1906	5,335	5,401,766	3,667,551
1907	14,788	10,023,311	6,155,341
1908	25,624	19,437,875	9,133,378
1909	30,677	25,897,825	12,461,576
1910	33,519	29,856,009	15,375,000

This camp has in seven years produced ore of a gross value of a little over $50,000,000. Of this sum $30,000,000 was net profit, and there is now in sight an ore reserve conservatively estimated at $30,000,000. The average value of the total tonnage shipped was approximately $500 per ton, and each ton netted a profit of $266.

KAURI-GUM INDUSTRY OF NEW ZEALAND.

In 1910, for the first time in the history of the kauri-gum industry of New Zealand, except in 1893 (a year of panic and depression in the United States), exports to the United States have been exceeded by shipments to Europe, the United States taking only 3,839 tons, as against 4,150 tons purchased by Europe. During the preceding year 5,127 tons were exported to the United States, as against 3,123 tons to Europe. As a general average, the United States in recent years has taken about two-thirds of the annual output of kauri-gum in New Zealand. Over one-half of New Zealand's total exports to the United States still consists of this gum, the exports invoiced during 1910 through the American consulate-general and agencies being valued at $1,271,891 out of total exports from New Zealand to the United States valued at $3,409,468. During the preceding year the value of kauri-gum exported to the United States was $1,891,497, so that there was a decrease for 1910 of $619,606.

SWEDISH WOOD-PULP TRADE.

The proposal of the Swedish and Norwegian wood-pulp associations to limit the production was fully approved by the members to go into effect on June 1, 1911, continuing until January 1, 1913. It is stated that the agreement calls for a reduction of at least 150,000 tons in the production of mechanical pulp for the period stated. The limitation does not apply to chemical pulp at all. Prices for both chemical and mechanical pulp are said to be on the rise. Shipments of mechanical pulp to the United States are increasing.

Declared exports of all kinds of pulp from Gothenburg to the United States for the first quarter of 1911 aggregated $322,282 in value, as compared to $263,855 for the corresponding period in 1910 and $259,066 in 1909. The following figures show the values declared for export from Gothenburg to the United States annually for the past six years:

1905	287,677
1906	269,931
1907	734,655
1908	809,736
1909	964,822
1910	1,232,474

This was chiefly dry chemical pulp, with occasional shipments of wet chemical and wet and dry mechanical pulp.

MUSSEL MUD AS FERTILIZER.

In most of the bays indenting the shores of Prince Edward Island are found extensive deposits of mussel mud, so-called locally, being organic remains of countless generations of oysters, mussels, clams, and other bivalves of the ocean and of crustaceous animals generally. The shells, usually more or less intact, are found embedded in dense deposits of mudlike substance and this combination is a fertilizer of high value and potency. It supplies lime and organic matter, besides small quantities of phosphates and alkalies. An ordinary dressing of it secures fertility in a striking manner to the poorest of most exhausted soils. The shells decay slowly, year by year throwing off a film of fertilizing stuffs. The deposits around Prince Edward Island vary from 5 to 25 feet in depth. They are taken up by dredging machines worked from rafts in summer or from the ice in winter.

SODA IN BRITISH EAST AFRICA.

The Magadi Soda Co. (Ltd.) has been formed with a capital of $6,387,281, to acquire a 99 years' lease of and to develop the important deposit of natural soda covering an area of some 30 square miles, known as Lake Magadi, in the British East Africa Protectorate, to connect the same with the Uganda Railway by the construction of a branch line, about 100 miles long, and to build a pier and approaches thereto at or near Kilindini. The Uganda Railway administration has undertaken, on a year's notice and at its own expense, to provide all necessary rolling stock sufficient to carry 160,000 tons of soda or soda products per annum.

THE RUSSIAN PLATINUM INDUSTRY.

The Ministry of Commerce at St. Petersburg has placed before the Council of Ministers a project for regularizing the platinum industry. It is proposed to prohibit the export of plattiniferous ores from a date when Russian laboratories can take over the whole Siberian output for refining, and steps are being taken to subsidize out of treasury funds such private laboratories as require more modern equipment. Special regulations are also being drawn up by which State control of the extraction and price of the metal will be established.

COTTONSEED-OIL REFINERY IN CANADA.

The first refinery of cottonseed-oil products in Canada is that of Gunn's (Ltd.), in Toronto. The plant is equipped to manufacture a complete line of salad oils, cooking oils, and shortening composed of compounds of vegetable and animal fats and oils. The capacity is 20,000,000 pounds per annum. The company has a line of tank cars engaged in carrying cottonseed-oil in its crude state from the mills of the Southern States.

IODINE FROM CHILE.

The Domeyko iodine works in the north of Chile are said to be the largest in the world, with an annual capacity of 400,000 pounds. The total production of iodine in Chile for 1910 amounted to 1,279,150 pounds.

TIN MINING IN BOLIVIA.

The Pulacayo tin mines in Bolivia have reached the depth of 2,304 feet, and the richness of the ore increases as the mine descends. This mine has been worked for more than 300 years.

BOOK REVIEWS.

Applied Electrochemistry. By M. DE KAY THOMPSON, PH.D. 329 pp. The Macmillan Company. Price, $2.10 net.

This is a work which is the result of the studies of applied electrochemistry by one who is well equipped with the knowledge of the theoretical side of the subject. It is intended as an introduction to applied electrochemistry for students who are already fairly well equipped with a knowledge of theoretical chemistry and electrochemistry.

Electrochemical measuring instruments are first described and sufficient detail given to permit one to make and operate the different types with a knowledge of the probable accuracy to be obtained. Frequent references to the literature are made in the case of most of the subjects taken up and these enormously increase the value of the book. Under electrochemical methods of analysis a number of interesting processes are given for determining concentration of various salts or ions through direct reading electrical measuring instruments. These are interesting as suggesting such applications to untried fields, but are admittedly not intended as representing electrochemistry now usefully applied in analysis. Such applications are still quite rare, but their comprehension by the student insures an understanding of some of the important quantitative principles of electrochemistry.

The ordinary processes of electroplating are briefly considered. Apparently in each case the best known formulae for the baths have been selected from the literature.

In the 25 pages devoted to electrolytic winning and refining of metals, a general review of the well-known processes is given, together with brief descriptions of some commercially unsuccessful processes. This scheme of discussing processes which have been only "near processes" seems a good one, as it must show the student how help may be gained from carefully considered failures.

The book makes no claim of presenting new material, but rather of forming a collection from the literature of what one would naturally call applied electrochemistry, and to this is added the most recent conceptions of theoretical electrochemistry in connection with the subject. It certainly covers a broad field in a clear and concise manner, and the choice of processes and methods is apparently wisely made. Separate chapters are devoted, in addition, to those subjects mentioned below:

Electrolysis of Alkali Chlorides, 56 pp.
Primary Cells.
Storage Batteries.
Electric Furnaces.
Metallurgy of Iron and Steel.
The Fixation of Atmospheric Nitrogen.
Ozone.

The general impression made by the book is a good one and is what might be expected from a well trained student and teacher of the principles of electrochemistry. The illustrations are well selected and up to date.

While the application of the science is advancing so rapidly that the strictly applied portions ought to be frequently rewritten, yet the principles and the historical accounts, which are the more useful portions for the student and teacher, will remain prominent and permanent. W. R. WHITNEY.

Drying Machinery and Practice. By THOMAS G. MARLOW. 326 pp.; 174 illustrations; 22 tables. New York: D. Van Nostrand Co. Price, $5.00 net.

The press work and general make-up are good. It is written in a clear, concise, and logical style that can be readily understood by the ordinary reader. It is an English book and consequently deals with English practice and machinery but the fundamental principles are, of course, universal in application.

At the outset the author clearly states the reasons for drying materials, as well as the different degrees of dryness as found in practice. A brief outline of each division of the subject is taken up in a general way, followed by a detailed description of the machinery and manner of using the same, giving the results of practice, such as the power required, the amount of, and the condition of, the resultant product, so that the reader can form a correct opinion of what may be expected in practical work.

In discussing the subject of drying by evaporation, the author shows how to determine the amount of air required to produce certain results under given conditions by the use of tables which give considerable data, yet it would perhaps have been a wise addition to have added some formulas for the complete thermodynamic analysis of mixed gases as applied to drying. Attention is called to the methods of generating and applying heat to various forms of drying apparatus, also the dangers arising from the resulting gases due to evaporation; the methods of handling the material to be dried, the action of heat upon the substance, with results obtained from practice, yet no general rule to assist in the solution of some specific problem.

The appendices containing the "Bibliography of Drying and Desiccating" and the "Glossary of Terms" are both very useful; for any one who wishes to go thoroughly into the subject of drying or to those who desire to investigate some special line, the former will be of considerable help.

In general, the information contained in the work is evidently the result of practical experience; consequently, it is of a practical nature and from that standpoint covers the ground very well, but by the addition of some national or empiric formulas the field of its usefulness would no doubt be enlarged.

C. W. THOMAS.

Practice of Copper Smelting. By EDWARD DYER PETERS. 693 pages. McGraw-Hill Book Company. 1911. Price, $5.00 net.

The arrangement Dr. Peters has chosen for his otherwise excellent book is a very unfortunate one. In his first work, "Modern Copper Smelting," he produced one of the best books on metallurgy ever written. His two later volumes, the "Principles of Copper Smelting," and the present "Practice of Copper Smelting," are intended as parts of a whole, but the division is unfortunate, and if one is using either it is constantly necessary to refer to the other.

In the present work Dr. Peters has found it necessary to explain the theories of the different processes, but these explanations are seldom complete and the reader is referred to the "Principles." In a note on page 410 he says: "A simple, direct statement—not absolutely correct, and to be amended later when it has sunk in—may or may not make some useful impression on the average student; but an absolutely correct statement, buried in exceptions and complications, will certainly not be of any use to him." He has carried this to an extreme and frequently makes his statements so simple that they are misleading. He then repeats them, sometimes several times, in each case qualifying and getting nearer to completeness, and ends by referring the reader to the "Principles." This continual repetition has made the book as bulky as if the principles had been given fully and completely at once and does not appear to have any marked advantage over the method followed in his first work.

Aside from this defect, if it is one, the book is admirable. It starts with an account of the ores of copper and methods of sampling. This is short but sufficient for the purpose. The next two chapters are a very condensed description of the general methods of extraction and of the behavior of ores at high temperatures. Next comes roasting; first the principles, then mechanical furnaces and heap roasting. He then takes up the blast furnace, its construction, variations, accessories and management, followed by illustrations of present practice under different conditions. Reverberatory furnaces are treated in the same manner. Then a chapter on the blast furnace *versus* the reverberatory, defining the limitations of each and showing that they are supplemental to each other rather than actual rivals. The next chapter deals with fines and the very troublesome question of how to deal with them. This chapter is particularly good and is of much value to others than copper smelters. The two following chapters deal with the converter and refining: they are treated in the same complete manner as the blast furnace and the reverberatory. Next is a short chapter on flue dust and smoke, giving a review of the recent methods of dealing with these substances. The chapter on slags is perhaps the least satisfactory of any in the book. While it contains much useful information it is too elaborate to be elementary and yet is far from complete. The concluding chapter includes such various subjects as furnace construction, reverberatories, arrangement and details of plant, hot blast stoves, smelter tariffs, costs and tables. It contains much good advice and many useful hints. The hot blast stove shown, however, is the only archaic piece of apparatus described in the book, but with such a stove it is not to be wondered at that heated blast is not popular with copper smelters.

In the preface Dr. Peters says: "Owing to the great development—I have, therefore, believed it best to introduce comparatively few illustrations of processes, but to select those from the best modern practice, and to study them in detail." This he has followed consistently, not loading the book with descriptions of obsolete methods and processes, but all his examples are from the most successful practice of the present day or are descriptions of methods that have proved satisfactory, under conditions that are unusual but still likely to be encountered at widely separated points.

He has wisely not gone at any length into the question of costs, that being so much influenced by local conditions, but gives sufficient information about quantities and kinds of materials, labor and repairs to enable any experienced metallurgist to make his own estimates.

He has confined himself entirely to the dry methods and describes these completely and well. It is a pity that the limitations of space prevented him from taking up electrolytic refining and thus completing the subject in one book. On the whole, the book is an excellent one and should be in the library of every metallurgist.

G. C. STONE.

NEW PUBLICATIONS.

By D. D. Berolzheimer, Librarian American Chemical Society.

The Manufacture of Starch, Dextrin and Starch Sugar. By F. Rehwald. 8vo., 309 pages. $0.75. Vienna. 1911. (German.)

Yearbook of Electrochemistry and Applied Physical Chemistry. By H. Danneel and J. Meyer. Vol. XIII. L. 8vo., 497 pages. $5.00. Halle. 1911. (German.)

Grinding Appliances and Plants. By Carl Naske. $3.75. Leipzig: Otto Spamer. (German.)

Zinc, Cadmium, Copper and Mercury. By A. Bouchonnet. 8vo., 402 pages. $1.25. Paris. O. Doin & Fils (French.)

Systematic Handbook of Volumetric Analysis. By Francis Sutton. 10th edition. 8vo., 613 pages. $5.25. London: J. and A. Churchill.

Sampling of the Coal in the Mine. By Joseph A. Holmes. *Bureau of Mines, Technical Paper 1.*

The Escape of Gas from Coal. By Horace C. Porter and F. K. Ovitz. *Bureau of Mines, Technical Paper 2.*

Action of Dilute Acids and Salt Solutions upon Gelatin. By Henry R. Proctor. *Journal of the American Leather Chemists' Association*, June, 1911. pp. 270-308.

Estimation of Sulfides in Alkali Cyanid. By E. C. Rossiter. *Journal of the Society of Chemical Industry.* May 31, 1911. pp. 583-588.

Testing of Creosote. By C. Edward Sage. *Journal of the Society of Chemical Industry*, May 31, 1911. pp. 588-594.

Modification of Raschig's Theory of the Lead-Chamber Process. By Edward Dwers. *Journal of the Society of Chemical Industry.* May 31, 1911. pp. 594-603.

Recent Progress in Calorimetry. By Walter P. White. *Metallurgical and Chemical Engineering*, June, 1911. pp. 296-298.

Methods of the United States Steel Corporation for the Technical Sampling and Analysis of Gases. By J. M. Camp. *Metallurgical and Chemical Engineering*, June, 1911. pp. 302-306.

New Studies in Geochemistry and Geophysics. By A. Brun. 4o. $6 00. Paris, 1911. (French.)

Manufacture of Cement. By J. Fritsch. 8vo., 503 pages. $5.00. Paris, 1911. (French).

Official Ethical Oils and Balsams of Fourteen Pharmacopeias. By C. Rohden. 8vo., $2.00. Berlin: Julius Springer. (German.)

Qualitative Chemical Analysis. By Wilfred W. Scott. 8vo., 176 pages. $1.50. New York: D. Van Nostrand Co.

Alcoholic Fermentation. By Arthur Harden. P. 8vo., 102 pages. $1.25. New York: Longmans Green & Co.

Workshop Receipts. Spon's, 4 Vols., 12 mo., 2100 pages. $6.00. New York: Spon & Chamberlain.

Methods for the Examination of Milk and Dairy Products. By C. Barthel. Second edition. L. 8vo., 309 pages. $1.75. Leipzig, 1911. (German.)

Sulfur-tars. By W. Scheithauer. L. 8vo., 200 pages. $2.50. Leipzig, 1911. (German.)

Petroleum, its Physics, Chemistry, Geology, Technology and Production. By C. Engler and H. Hoefer. Vol. III. L. 8vo., 192 pages. $14.00. Leipzig, 1911. (German.)

The Phase Rule and its Applications. By A. Findlay. 8vo., 372 pages. $1.50. London, 1911.

Textbook of Inorganic Chemistry. By A. F. Hollemann. Ninth edition. L. 8vo., 468 pages. $2.50. Leipzig, 1911. (German.)

Biological and Biochemical Studies on Milk. By C. J. Konig. L. 8vo., 193 pages. $2.00. Leipzig, 1911. (German).

The Preparation of Malt and the Brewing of Beer. By E. Leyser. 3 Vols., L. 8vo., 193 pages. $8.75. Leipzig, 1911. (German.)

Metallurgy of Tungsten, with Special Reference to the Electrometallurgy, the Compounds and the Alloys of Tungsten. By H. Memicke. L. 8vo., 194 pages. $3.75. Berlin, 1911. (German.)

Handbook of Chemico-metallurgical Analysis. By J. Hognon. 8vo., 155 pages. $1.00. Paris: Gauthier-Villars. (French.)

The Corpuscular Theory of Electricity; The Electrons and Ions. By Paul Drumaux. 8vo., 168 pages. $0.75. Paris: Gauthier-Villars. (French.)

Metallurgy. By W. Borchers. Translated. 8vo., 271 pages. $3.00. New York: John Wiley & Sons.

Laboratory Manual of Inorganic Chemistry. By E. C. Bingham and Geo. F. White. 12mo., 147 pages. $1.00. New York: John Wiley & Sons.

How to Enamel. By Howard M. Chapin. 12mo., 70 pages. $1.00. New York: John Wiley & Sons.

Essentials of Volumetric Analysis. By Henry W. Schimpf. Second edition. L. 12mo., 358 pages. $1.50. New York: John Wiley & Sons.

Introduction to Chemistry. By Willhelm Ostwald. Translated. L. 12mo., 368 pages. $1.50. New York: John Wiley & Sons.

Technical Methods of Ore Analysis. By Albert H. Low. Fifth edition. 8vo., 362 pages. $3.00. New York: John Wiley & Sons.

Pumping Machinery. By Arthur M. Greene. 8vo., 703 pages. $4.00. New York: John Wiley & Sons.

Laboratory Manual for Food Chemists. By A. Bujard and E. Baier. 8vo., 730 pages. $3.00. Berlin, 1911. (German.)

Yearbook of the Sugar Industry of the Russian Empire for the Year 1909-10. By M. A. Tolpygin. 8vo., 365 pages. $3.75. Kiew, 1911. (Russian.)

Course in Organic Chemistry. By W. Ipatjew. 8vo., 373 pages. $1.50. St. Petersburg, 1911. (Russian.)

The Manufacture of Ceresin. By B. Sach. L. 8vo., 217 pages. $2.25. Halle, 1911. (German.)

Laboratory Manual for the Fat and Oil Industries. By J. Marcusson. L. 8vo., 159 pages. $1.50. Halle, 1911. (German.)

Treatise on Analytical Chemistry. By C. Blas. Vol. III. Quantitative Analysis. 8vo., 497 pages. $4.50. Louvain, 1911. (French.)

Handbook of Mineral Chemistry. By C. Doelter. Vol. I, Part 1. L. 8vo., 160 pages. $1.50. Dresden, 1911. (German.)

The Technology of Metals. By M. G. Jemangulow. Part I. Alloys. 8vo., 321 pages. Price, $1.22. St. Petersburg, 1911. (Russian.)

Experimental Introduction to Inorganic Chemistry. By H. Blitz. Fourth edition. $1.00. Leipzig: Veit & Co. (German.)

Citric Acid and its Derivatives. By W. Hallerbach. $1.25. Berlin: J. Springer. (German.)

Apparatus and Methods for the Sampling and Analysis of Furnace Gases. By J. C. W. Frazer and E. J. Hoffman. *Bureau of Mines, Bulletin 12.*

Briquetting Tests of Lignite. By Charles L. Wright. *Bureau of Mines, Bulletin 14.*

Progress in the Colloid Chemistry of the Albuminoids. By Hans Handovsky. 8vo., 56 pages. Dresden, Th. Steinkopff. $0.50.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

Quantitative Determination of Cantharidine in Cantharides and Tincture of Cantharides. By A. Kneip, N. Ney and F. Reimers. Archiv. der Pharmazie. Vol. 249, Heft, 4, pp. 259-258. (German.)

Treatment of Tannery Effluents. By J. A. S. Morrison. *Journal of the American Leather Chemists' Association.* Vol. VI., No. 7, pp. 326-342.

Grinding Wheels, their Production and Use. By W. Herminghausen. Stahl und Eisen. Vol. XXXI, No. 21, pp. 830-847.

Preparation of Coal for the Market. By Henry Louis. *Journal of the Society of Chemical Industry.* Vol. XXX, No. 11, pp. 662-672.

Valuation of Crude Rubber. By Fritz Frank. *India Rubber World,* Vol. XLIV, No. 4, pp. 364-366.

Experimental Study of Flame Standards. By E. C. Crittenden. *Transactions of the Illuminating Engineering Society,* VI., No. 5, pp. 417-436.

Desiccation of Air by Calcium Chlorid. By Felix A. Daubine and Eugene V. Ray. *Metallurgical and Chemical Engineering,* Vol. IX., No. 7, pp. 343-347.

The Rare Earths with Special Reference to the Thorium Industrie. By C. Richard Boehm. *Zeitschrift fuer angewandte Chemie,* Vol. XIV., Heft 26, June 30, 1911, pp. 1203-1209.

The Principles and Practice of Cider Making. By B. T. P. Barker. *Journal of the Institute of Brewing,* 1911, No. 5, pp. 425-451.

The Chemical Behavior and Preservative Action of Sulfites in Beer. By Julian C. Baker and F. E. Day. *Journal of the Institute of Brewing,* 1911, No. 5, pp. 465-479.

Crude Rubber and its Valuation. By Clayton Beadle and H. P. Stevens. *India Rubber Journal,* 1911, No. 25, pp. 1399-1406 of Supplement.

Measurement of High Temperatures. By C. T. Heycock. *Journal of the Society of Chemical Industry,* 1911, No. 12, pp. 724-727.

RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

993,331. Process for the Manufacture of Formates.

This process consists in subjecting caustic alkali in lump form to the action of carbon monoxid under pressure at an initial temperature of about 100–120° C., thereby converting the outer surface of said lumps into formate, progressively separating the formate from the outer surfaces of the lumps by agitation so as to give the carbon monoxid access to the portions within, and, after about two-thirds of the lumps of caustic alkali have been converted into formates agglomerating the formed formates by adding about 2 per cent. of water, thereafter subjecting the mass to the further action of the carbon monoxid, and maintaining the temperature below the decomposition temperature of the formed formate during the progress of the reaction.

Fig. 1.

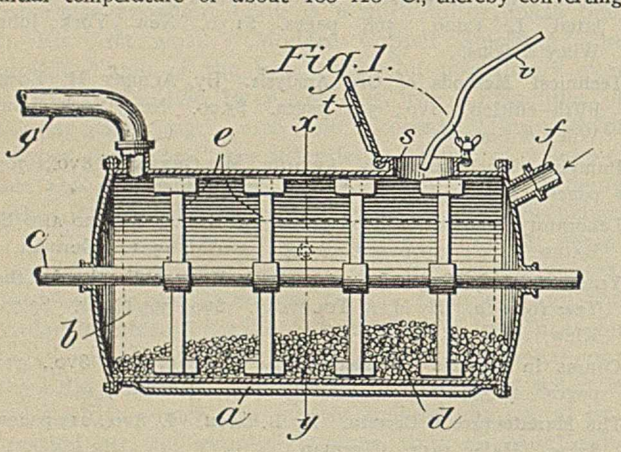
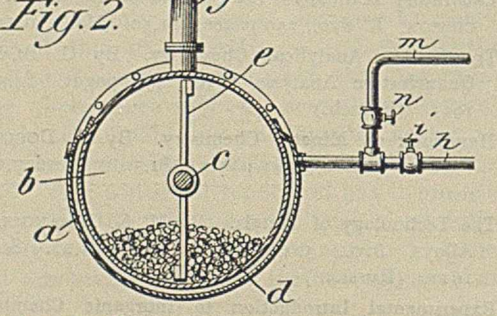


Fig. 2.



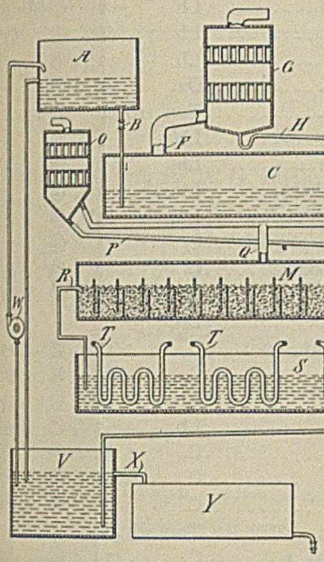
The accompanying illustration shows the patentee's apparatus in which he carries out the process.

The inventor is Arnold Wiens, of Bitterfield, Germany

992,551. Process of Producing Carbon Tetrachlorid.

In practicing this process a mixture of disulfur dichlorid and carbon tetrachlorid containing about 53 per cent. carbon tetrachlorid and 47 per cent. sulfur chlorid, at about atmospheric temperature, is allowed to flow by way of a pipe into a chlorinator C, the rate of the flow being controlled by a cock B. In the chlorinator it flows slowly from one end to the other finally overflowing at the overflow pipe D. During its passage through the chlorinator it meets and absorbs a current of chlorin, entering at E, said chlorin flowing in the opposite direction toward the outlet F. The chlorin solution overflowing at D passes into a mixer J, wherein carbon disulfid is admixed. The rate of carbon disulfid supply is controlled by a cock K. It is admitted in about the proportion of one molecule of carbon disulfid to six atoms of dissolved chlorin. The mixture now containing admixed carbon disulfid overflows continuously from the mixer by way of the overflow pipe L into the converter M. Any vapor formed in the mixer J passes by a pipe N to a condenser O, where the vapors are condensed and flows back by the pipe P into the converter M. The converter M consists of a series of compartments loosely filled with pieces of iron, for instance, sheet metal clippings, and so arranged that the liquid enters at the bottom of each compartment and overflows at the top to the bottom of the next. During its passage the iron acts catalytically and the carbon disulfid is converted to carbon tetrachlorid and sulfur chlorid. Considerable heat is evolved in the converter; with the mixture entering at 15° C. the temperature rises to around 40° C. at the exit. Any vapor formed in M passes by way of the pipes Q and N to the condenser O where it is condensed and flows back into the converter M.

The liquid after passing through the various compartments of the converter M finally overflows through the pipe R to the cooler S where it is cooled by contact with the cooling coils T, through which cold water, brine, or cold carbon tetrachlorid or other cooling liquid is circulated. The temperature of the cooling liquid, rate of flow, and surface of the coils is so regulated that the mixture finally overflows by the overflow pipe U at about atmospheric temperature. From U the liquid flows into the receiver V, whence it is pumped by the pump W to the reservoir A to begin its round anew.

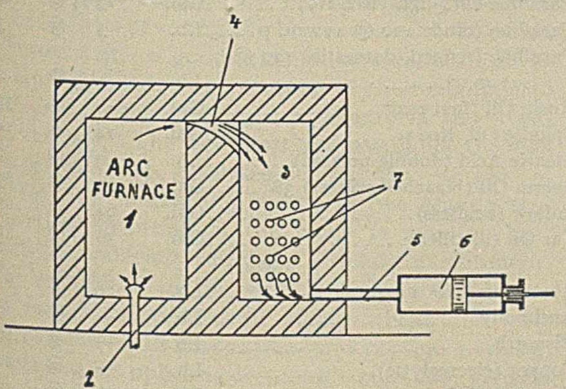


As the mount of carbon tetrachlorid and sulfur chlorid accumulates, a portion overflows by the overflow pipe X into a stock tank Y. Carbon tetrachlorid of a very pure form is readily separated from the stock tank mixture. The sulfur chlorid after separation is marketed as such or otherwise utilized.

The inventor is William F. Doerflinger, of New York, New York.

991,357. Process of Producing Nitric Oxid from Mixtures of Nitrogen and Oxygen and Apparatus Therefor.

This invention comprises a process wherein a mixture comprising nitrogen and oxygen, is heated to a reacting temperature, is thereafter permitted to expand without material reduction in temperature, additional heat being supplied during such expansion, and is finally cooled; and it also comprises apparatus suitable for carrying out the process comprising a reaction furnace, an expansion chamber in communication with said furnace, means for permitting expansion of hot gases from said furnace into said reaction chamber without cooling during such expansion, special heating means being provided if desired, and means for cooling the hot expanded gases.



In applying the process to the manufacture of nitrogen oxids where gaseous mixtures containing nitrogen and oxygen are subjected to the action of an electric arc, an arc is formed and the gases introduced into it at approximately normal pressure. After treatment in the arc, the intensely hot gases are permitted to expand into a chamber in which a partial vacuum is maintained, without material reduction in their temperature. Reduction in the temperature of the hot gases may be prevented either by supplying additional heat to the gases during the expansion, or by throttling their flow into the expansion chamber. The pressure in the expansion chamber should be relatively low, and for the best results should not be over 400 mm. of mercury.

The inventor is Harry Pauling, of Gelsenkirchen, Germany, assignor to Salpetersaure-Industrie-Gesellschaft, Gesellschaft Mit Beschrankter Haftung, of Gelsenkirchen, Germany.

993,017. Apparatus for Obtaining Nitrogen from Air.

This apparatus is defined in the patent as comprising a furnace of considerable area in proportion to its height and having a top and bottom both sloping downward from the inlet to the outlet of the furnace, means for supplying sulfur and air to the inlet end of said furnace, a conduit at the outlet end of said furnace for the resulting gases, means for removing from said gases the excess of sulfur and the sulfurous acid, a suction pump at the advance end of the conduit for drawing the air into the furnace and the gases from said furnace, and means for confining the nitrogen, substantially as described.

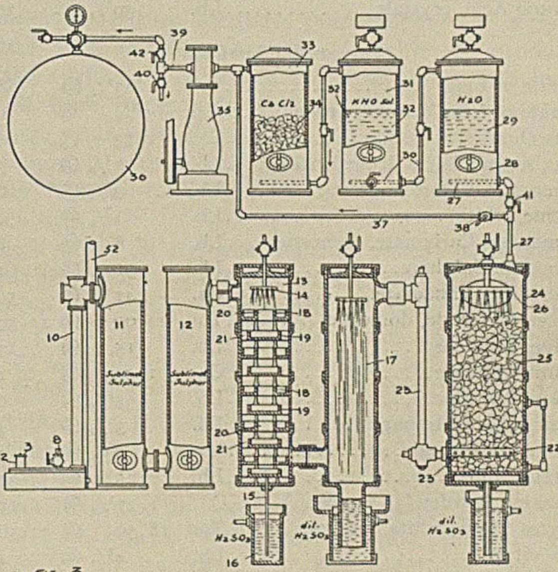


FIG 3

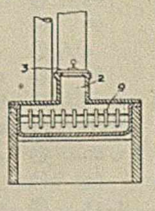
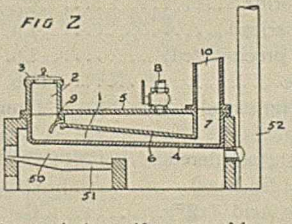


FIG 2



The inventor is Charles Blagburn, of San Francisco, California, assignor to himself, trustee.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JULY.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	14½	@	16
Alcohol, grain (188 proof)	Gal.	2.50	@	2.54
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof)	Gal.	40	@	42
Amyl Acetate	Gal.	2.53	@	2.56
Acetic Acid	C.	1.66⅓	@	1.86⅔
Aniline Oil	Lb.	11½	@	11¾
Benzoic Acid	Oz.	11¼	@	12
Carbon Tetrachloride (in drums)	Lb.	8	@	12
Carbon Bisulphide	Lb.	5	@	7
Chloroform	Lb.	27	@	35
Carbolic Acid (in drums)	Lb.	11⅓	@	12⅔
Citric Acid (domestic)	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	46½		
Dextrine (imported potato)	Lb.	5½	@	7
Dextrine (domestic corn)	C.	2.53⅔	@	2.73
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	21½	@	22½
Iodoform	Lb.	2.95	@	3.00
Oxalic Acid	C.	7⅛	@	7¾
Pyrogallic Acid (bulk)	Lb.	1.25	@	1.55
Salicylic Acid	Lb.	31	@	33
Starch (corn)	C.	1.77⅓	@	1.93⅓
Starch (potato)	Lb.	4¼	@	4⅝
Starch (rice)	Lb.	7	@	8
Starch (wheat)	Lb.	4⅞	@	5¾
Tannic Acid (regular in bulk)	Lb.	48	@	50
Tartaric Acid, crystals	Lb.	30¼	@	30¾

Inorganic Chemicals.

Acetate of Lime (gray)	C.	1.83⅓	@	1.88⅓
Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Aqua Ammonia (in drums) 16°	Lb.	2¾	@	3
Ammonium Chloride, gray	Lb.	5¾	@	6
Arsenic, white	Lb.	1⅞	@	2⅜
Ammonium Carbonate, domestic	Lb.	8	@	8⅜
Aluminum Sulphate	Lb.	90	@	1¾
Ammonium Vanadiate	Oz.	41	@	50
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chlorate	Lb.	15	@	17
Barium Chloride	C.	1.90	@	2¼
Barium Nitrate	Lb.	5½	@	6½
Borax, crystals in bags	Lb.	3½	@	4
Boric Acid, crystals	Lb	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.17½	@	1.25
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	4½	@	4¾
Calcium Chloride	C.	65	@	90
Calomel, American	Lb.	90	@	92
Chalk (light precipitated)	Lb.	4½	@	6
Cobalt Oxide	Lb.	80	@	1.00
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (in bags)	C.	60	@	85
Hydrochloric Acid (18°)	C.	1.15	@	1.75
Hydrochloric Acid (22°)	C.	1.45	@	1.75
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8	@	8½
Lithium Carbonate	Lb.	57	@	60
Magnesite (raw)	Ton	10.00	@	11.00
Mercuric Chloride	Lb.	81	@	84
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Nitric Acid, 42°	Lb.	4⅞	@	5½
Phosphorus	Lb.	45	@	1.00
Phosphoric Acid, s. g. 1.75	Lb.	21	@	25
Plaster of Paris	C.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9⅜	@	11
Potassium Cyanide (bulk)	Lb.	20	@	24
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals,	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4½	@	4¾
Potassium Bichromate, 50°	Lb.	7⅜	@	7¾
Pumice Stone	Lb.	2	@	4
Quicksilver	Lb.	66	@	67½
Salt Cake (glass-makers)	Lb.	62½	@	77½
Silver Nitrate	Oz.	34	@	36
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5⅝	@	5¾
Sodium Bisulfite (not incl. pkg.)	C.	75	@	1.37½
Sodium Hydroxide, 60 per cent	C.	1.80	@	1.85
Sodium Hyposulfite	C.	1.30	@	1.50
Sodium Nitrate	Lb.			7¼
Sodium Nitrate, 95 per cent., spot	C.	2.12½	@	2.15
Sodium Silicate (liquid)	C.	65	@	1.50
Sodium Stannate	Lb.	9¾	@	10
Strontium Nitrate	Lb.	7¼	@	8
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13¼	@	13½
Tin Oxide	Lb.	50	@	52
Tin Chloride (36°)	Lb.	11	@	11½
Zinc Chloride (granulated)	Lb.	4½	@	4¾
Zinc Sulphate	Lb.	2¼	@	2½

Oils, Waxes, Etc.

Beeswax (pure white)	Lb.	40	@	45
Black Mineral Oil, 29 Gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	10	@	11
Ceresin (yellow)	Lb.	9	@	20
Corn Oil	C.	5.90	@	5.95
Cottonseed Oil (crude), f. o. b. mill	Gal.	38	@	40
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9	@	9¼
Lard Oil (prime winter)	Gal.	78⅓	@	85
Linseed Oil (raw, city)	Gal.	83	@	84
Linseed Oil (double-boiled)	Gal.	90	@	91
Paraffine Oil (high viscosity)	Gal.	23½	@	24
Paraffine (crude 120 @ 122 m. p.	Lb.	3	@	3¼
Paraffine (refined, domestic) 120 @ 122 m. p.	Lb.	4½	@	4¾
Rosin Oil (first run)	Gal.	—	@	37
Spindle Oil, No. 1	Gal.	14	@	14½
Stearic Acid (double-pressed)	Lb.	9½	@	9¾
Sperm Oil (bleached winter) 38°	Gal.	82	@	85
Tallow (acidless)	Gal.	64	@	66
Tar Oil (distilled)	Gal.	30	@	31

Metals.

Aluminum [No. 1 ingots]	Lb.	20	@	21¼
Antimony	Lb.	—	@	9
Bismuth	Lb.	—	@	1.80
Copper (electrolytic)	Lb.	—	@	12½
Copper (lake)	Lb.	12⅝	@	12⅞
Lead	Lb.	4.46	@	4.50
Mercury	Lb.	61.3	@	61.5
Nickel	Lb.	40	@	50
Platinum (refined)	Oz.	42.50	@	43.00
Silver	Oz.	52¾	@	53
Tin	Lb.	—	@	43¼
Zinc	Lb.	5.45	@	5.50