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EDITORIALS

RESEARCH

Much progress has been made in recent years in the establishment of research laboratories in the more progressive manufacturing plants in this country; yet a canvass of the situation will show that a comparatively small percentage of industrial managers is even now convinced that a careful scientific study of processes and products will pay, and these managers do not look with favor upon the suggestion that a very small portion of their earnings might with profit be invested in a reserve of knowledge of their industry.

The American manufacturer has found the development of his business so easy and rapid, either on account of favorable raw material conditions, or a greedy demand for his products that it has not been necessary for him to devote attention to the study of more efficient processes, in order to reap enormous profits. In other cases the time and energy of many managers has been so taken up with the problems of keeping up with the natural demands, due to the growth of the country, that a scientific study of the industry has been, and will continue to be, deferred until profits begin to fail.

Probably the greatest factor in retarding the development of scientific research among our industries has been high tariff. This high tariff has caused many of our industries to prosper and pay enormous profits in spite of their short-sighted management. Political research, with a view to exploiting the consumer, is well understood by such managers and it is a regrettable fact that many of them have spent thousands of dollars on the lobby and not one cent for placing their business on a sound scientific footing.

Perhaps the managers who have specialized in this form of political research are the victims of certain economic conditions and should not be held responsible for the selection of this method of building up their business. They are employed to produce a product at a profit and it is not always stipulated by the stockholders or directors how that profit shall be produced. No stockholder has yet been discovered who raises any question as to the source of profits so long as they are large. The relations between the amount of real money invested and the profits accruing therefrom have long since been submerged in water—the universal solvent for excessive profits. The position of the manager under such conditions is truly distressing and blame attaches more to the people and practices which have made it necessary for him to follow the chances for the greatest profits regardless of all ethical considerations.

The recent reductions in the tariff on many products and the removal of that seductive prospect from the field of probability for increasing profits will undoubtedly result in stimulating interest in the scientific study of processes and products as the most likely means of maintaining earnings. The loss of this tariff protection will, in the end, exert a great stabilizing influence on our industrial development. The protection of industry by flimsy artificial regulations is sooner or later bound to collapse, and the wiser course would be to build upon stronger foundations. It may take some time for manufacturers who have enjoyed tariff protection to realize that relief from their present predicament may come through a more systematic application of research methods but ultimately, after the hope of increasing profits by the political route has been entirely eliminated, they will turn to the scientific method.

The control and use of the immutable laws of nature obviously offer a more stable basis upon which to build and a more uniform source of profit than any structure built upon artificial conditions created by legislation.

The quality of many of our manufactured products is not up to the highest standard, but the demand has been so pressing that the goods have been accepted in spite of their defects. Many concerns spend almost as much time and money in making their goods stay sold as they spend on their manufacture. We all know that it is an occasion for comment and often congratulation when a piece of machinery is delivered which is capable of being put into use without disclosing fundamental defects in design, arrangement, construction or materials. A delivery of supplies which does not occasion complaints, endless correspondence or probably adjustments is a curiosity in some industrial work.

The quality problem is by no means settled in our industries and before we reach the saturation point of our domestic markets and attempt to branch out into foreign trade in competition with the skill and workmanship of other nations, we shall have to solve it. Cut-and-try methods for the design of equipment, which result in such monstrosities as a ten-foot vacuum pan with a four-inch vapor outlet, a machine where the same sized shaft is used throughout regardless of the fact that the working load ratio in different parts of the machine is 45 to 1, and other misfits too numerous and well known to mention, will have to be replaced by scientific methods. The superlative claims of advertising managers and the "talking points" of salesmen, which they often admit are not necessarily points of merit, will avail for a time but the buyer is slowly awakening to the fact that he is buying value and that there is a definite relation between *value* and *price*.

The quality and value of a product are based upon the application of correct principles in its conception, preparation and use, and these correct principles can be established only by scientific investigation. It is difficult to see how substantial progress can be made in this direction without such study.

Many managers take the position that they will not install research laboratories for the purpose of developing their industry because they can purchase from abroad or elsewhere ready-made improvements and developments without taking the risk of the experimental expenses. This policy is practiced by a number of well-known corporations. Its wisdom may never be determined because it will be impossible to decide, when successful, whether its success depends upon the method or upon superior advantage from other causes. It seems fair to assume, however, that the chances are against successful business administration on this policy. The risk of not finding new developments or of not having an opportunity to purchase them, may result in losses many times greater than the expense of maintaining research departments.

There are problems in industrial work which are common to all industries in a certain field or to a large group of industries in the same field in which coöperation in research would benefit all alike. I refer particularly to such problems as the disposition of wastes from dye-houses, paper mills, gas works, the smoke nuisance problem which is important to all steam power using industries, flue dust from smelter stacks, flue dust from pyrites burners, cement dust from cement mills, etc.

It is easily conceivable that a number of concerns in similar or identical fields might coöperate for the investigation and the development of common problems for the equal benefit of all concerned and probably the salvation of the industry itself. Such coöperation is now being brought about in a measure by the scientific societies and organizations represented in different industries. For example, the Michigan Gas Association supplies funds for the investigation of problems in gas manufacture common to the constituent members of that organization. The American Tanners' Association is conducting investigations common to the tanning industry, and other societies are showing a disposition to coöperate on research problems. Substantial progress on coöperative research will not be made by the technical societies, however, on account of the limited means at their disposal and the comparatively large number and magnitude of the problems.

If industrial concerns were to combine for the support of specific investigations on problems of common interest, great progress might be made. The element of desiring to monopolize all of the results and to enjoy some exclusive advantage over participants because they are business competitors would have to be entirely eliminated and managers would be obliged to take a broader and more comprehensive view of their problem and its purpose than at present. We have discussed the feasibility of this plan with competing interests in a number of cases and have frequently had the proposition pied by the insistence upon the part of some managers that his company would not be interested in a development that it could not monopolize. Coöperation on the part of several and a monopoly of the results by one is an insoluble problem from the standpoint here proposed.

It is not necessary or even desirable that the results of coöperative research be thrown open to public use. Such results should be and remain the exclusive property, for a limited period at least, by patent or otherwise, of those who contribute to the development. There is already, especially in this country, too little regard and protection for the rights of pioneers who have spent their money and taken their chances in order to further industrial development. Any scheme which would open greater opportunities to industrial piracy would be disastrous to development, and successful coöperation on specific research problems of common interest would have to carry with it a plan for the protection of the rights of the developers. The right to coöperate in the researches should not be denied to any one to whom the results would be of value, but the opportunity for pirating the results without proper compensation should be denied.

The Sherman law has been cited as a legal obstacle to the development of coöperative research. This law was enacted for the prevention of monopoly in restraint of trade. The prevention of industrial development was certainly not contemplated, and it is doubtful if such a construction could ever be put upon its provision. Well intended laws are sometimes diverted to strange uses and already we are confronted with the distortion of this law in ways calculated to produce political effect. The sundry civil bill passed by the last congress provided $300,000 for prosecuting combinations under the Sherman law but carried an additional provision, the motive for which can not be misunderstood, that none of the money was to be used in prosecuting combinations of labor or combinations of farmers.

If by any conceivable interpretation or motive the Sherman law should be construed as preventing the coöperation of industrial institutions in the study of scientific and engineering problems of mutual interest, it is our duty to show the malinterpretation of the law and indicate proper amendment. If chemistry is to be regarded as an important profession its organizations must consider affairs affecting its interest and the interests of its industrial constituents. Chemists and engineers have stood until recently, without protest, ridiculous abuses in our patent laws and practices. As soon as they concentrated their efforts on needed reforms the Supreme Court recognized the justice of their protests, recast the rules of practice, and now we are looking forward to a revision of the patent laws which will better protect the interests of the professions concerned.

It has been said that the most important step in invention is to realize a need. If the chemical profession will realize the need of more scientific study of industrial problems and the great possibilities of coöperation in the study of specific problems by interested industrial groups it is our duty to discover the way for the accomplishment of this need.

THE CONTROL OF PUBLIC UTILITIES

Up to the beginning of the legislative sessions of 1913, fourteen states—Wisconsin, New York, Maryland, New Jersey, Vermont, Ohio, Washington, California, Nevada, Oregon, Kansas, New Hampshire, Connecticut, and Rhode Island—had established commissions for the control of public utilities. Massachusetts divided many of the same powers among three commissions, and several states gave a part of the same powers to other commissions, such as, for example in Oklahoma, to the corporation commissions.

Following considerable agitation, eight states—Indiana, Illinois, Colorado, Missouri, Montana, Idaho, Pennsylvania, and West Virginia—created public utilities commissions during the legislative sessions of 1913. Massachusetts conferred the duties of the highway commission relating to telegraphs and telephones and the duties of the railroad commission upon a new public service commission; Ohio redrafted the public utility commission law, giving additional powers especially relating to valuation and to stock and bond issues; and New Hampshire amended her law by giving the commission power over accounting, including depreciation. In each case the commission is made appointive by the governor.

These laws uniformly require that public utilities shall give just and reasonable service at a just and reasonable rate, and in most states the commissions are given ample power for investigation and enforcement. The municipal utilities placed under control in the different states are mainly heat, light, water and power companies, street railways, and telephone and telegraph companies. In most of the states, railroads, other common carriers and similar services are also controlled.

Discrimination is prohibited in service and rates; free service to any but certain excepted classes is prohibited, and, in all but West Virginia, issues of stocks and bonds are placed under the regulation of the commission; uniform accounts are provided for, either in a mandatory or optional way, and valuation of the property used and useful for the convenience of the public is authorized in nearly all of the states. In Indiana and Ohio such valuation is required. In almost every state municipally owned utilities are subject to the same regulations as others. The laws make no exceptions for home rule. A strong effort was made in Illinois to except Chicago from the law, but it failed. It may be said in general that the state commission is supreme in most matters over the municipalities, although much power is left to the latter to regulate and control. The cities grant franchises and regulate by contract or otherwise the service and condition of occupying of the streets. In Indiana the indeterminate permit is provided for after the manner of the Wisconsin law.

A consideration of the new public utilities acts shows that there is a tendency to give real powers to the commissions. With the exception of the laws passed in Massachusetts and West Virginia, the acts of the year represent nearly all of the best which have been demonstrated to be empirically good in other states.

W. A. Hamor

ORIGINAL PAPERS

THE PROTECTION OF IRON AND STEEL BY PAINT FILMS

By Norman A. Dubois

Received October 4, 1913

The theories of corrosion of iron and steel which have received consideration and which still seem to have their defenders and opposers are interesting to note. The carbonic acid theory in brief requires the presence of carbonic acid to start corrosion. The peroxide theory supposes that hydrogen peroxide is formed in the presence of moisture and oxygen, and that this hydrogen peroxide causes corrosion. The electrolytic theory assumes that iron passes into solution in water in the form of a ferrous ion before it can oxidize. A more or less complete discussion of these theories may be found in the various journals and other publications. It is not the purpose of this paper to discuss them.

From the standpoint of the paint technologist the problem is that of finding the paint film which will enable him to protect the exposed surface of iron and steel from the various rusting influences for the longest possible time. The theories of corrosion and numerous discussions of them have been of inestimable value, and the proper interpretation of them has enabled the paint technologist to improve his paint film. Let us briefly consider these theories from the standpoint in question.

The carbonic acid theory requires the presence of carbonic acid that corrosion may proceed. In other words, considering a paint film properly applied over the surface of iron and steel it requires that carbon dioxide shall pass through this film, and also that water, either as such or in the form of aqueous vapor, shall pass through the film, and there in conjunction with the carbon dioxide react as carbonic acid. The imperviousness of the paint film to carbon dioxide gas and to aqueous vapor, then, is the vital quality from the standpoint of this theory. The more impervious the paint film to the gases carbon dioxide and aqueous vapor, the longer it will protect the iron or steel from corrosion.

The peroxide theory requires the formation of hydrogen peroxide on the surface of the iron or steel. Considering a paint film properly applied over the surface of iron or steel, therefore, this means that the less pervious the paint film is to the gases oxygen and aqueous vapor, the smaller will be the quantity of hydrogen peroxide formed on the surface of the iron or steel, and the longer it will protect the iron or steel from corrosion.

The electrolytic theory requires that iron first pass into solution in water as ferrous ion, and that it is then acted upon by oxygen dissolved in the water or by carbon dioxide and water to form rust. Again considering a paint film properly applied over iron or steel this theory requires the presence of water in which the iron may dissolve to form ferrous ions. Obviously, the only way the water can get to the iron or steel is to pass through the paint film, as such, or in the form of aqueous vapor. If we suppose the ferrous ions have been formed, the action can go no further in the absence of an oxidizing agent, presumably oxygen, which in turn must get through the paint film. The reasoning for the presence of other gases is similar. We find, therefore, that for corrosion to proceed according to the electrolytic theory the gases, aqueous vapor, oxygen, or others must pass through the paint film, and as in the other cases, the more impervious the paint film to gases and moisture, the longer it will protect the surface of the iron or steel from corrosion.

This is but to conclude that the paint film which will serve for the longest time as a protection to iron or steel against corrosion is the one which is the least pervious to aqueous vapor, the gases oxygen and carbon dioxide, or in fact any gas in the surrounding atmosphere which may in any way cause or accelerate corrosion.

If we assume the corrosion to be entirely due to the deterioration of the paint film rather than to its permeability to aqueous vapor and other gases, the same conclusion holds, as the rate of deterioration will be proportional to the permeability of the film to the deteriorating elements.

The electrolytic theory of corrosion has given rise to a division of pigments into three classes: corrosion accelerators, corrosion inhibitors, and inerts. While these pigments seem to give results as predicted by this theory in the presence of abundance of water or when the iron or steel is actually immersed in water, it does not necessarily follow that they will do so, to a like extent at least, when incorporated in a paint film where conditions are much different.

Assume, for instance, that our paint film is somewhat pervious to aqueous vapor and other gases. It follows that just as moisture may enter to the iron or steel surface and perhaps give conditions under which the electrolytic theory may apply when outside conditions are damp, this moisture may also pass from the steel surface outward when outside conditions are dry, and thus leave the steel surface dry in which case the electrolytic theory cannot possibly apply. As a matter of fact, the actual conditions existing on the surface beneath the paint film, in most instances, are very probably between the two extremes of somewhat damp and nearly dry, and this is far from being covered with an abundance of water at all times, the conditions under which the electrolytic theory seems to work out well. This reasoning is borne out by the fact that a piece of bright steel immersed in water containing a little zinc chromate in suspension will remain bright perhaps indefinitely, while the same pigment in a paint film under ordinary conditions will not protect the steel in a like manner.

Again, two paints composed of the same vehicle, but the first containing a so-called corrosion accelerator only, painted on a steel surface in a locality of ordinary dryness will outlast to a great extent the second containing a rust inhibitive pigment painted on a steel surface in a locality habitually very damp.

This reasoning seems to indicate and the evidence seems to bear out the conclusion that the problem of iron and steel preservation is rather to be solved by making our paint film as nearly impervious to gases as possible, than by trying to prevent corrosion by the addition of the so-called inhibitive pigments.

The problem is a physical one rather than a chemical one, and a comparison of paint films as to their relative obstruction to the diffusion of gases will tell more regarding their value as protection against corrosion than a study of the inhibitive action of their pigments. This is not to say that the inhibitive property of certain pigments is not worth consideration, but the imperviousness of the films is of far greater importance.

The work to be described here was carried out for the purpose of determining whether a special formula paint made according to the foregoing principles, embodying diffusion retarders, would not outlast in protecting qualities those made according to the formulas accepted as first quality paints for their respective purposes.

Our prime object is to make the film as impervious to gases as possible. This may be accomplished to a certain extent by special treatment of the vehicle and by incorporating special pigments and pigment combinations. It is well known that a film from the oxidation of pure linseed oil, *i. e.*, a film of linoxin, is more or less permeable to moisture and gases. It is more or less porous. If other oils or gums, or similar materials, can be incorporated with the linseed oil to form a homogeneous mass which as a whole acts as a perfect vehicle as regards compatibility of properties, it is readily understandable that such treatment may, to an extent, fill the intermolecular spaces between the linseed oil molecules, just as in other cases of solution, alloy, or mixture; and this compound vehicle will be more dense, will leave a film which offers more resistance to the diffusion of gases, and will, therefore, protect the iron and steel for a longer time (assuming other things equal) than a film which has not been treated in this way.

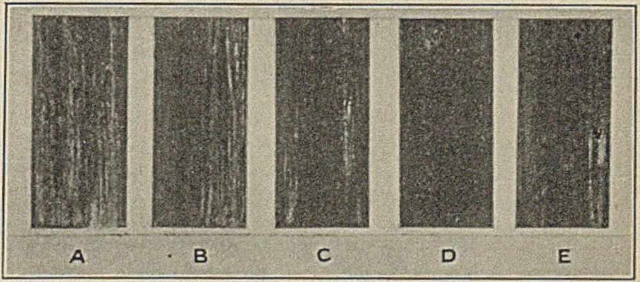

Plate I—Steel Panels Painted with Paints of Same Formula Except One Constituent of the Vehicle

Plate I shows five steel panels which, after thorough cleaning with hot 10 per cent solution of sulfuric acid for twenty minutes, washing by immersion in dilute caustic solution, thoroughly washing with water, and quickly drying, were painted as follows. All paints were of the same formula, with the exception of one constituent in the vehicle.

Panel A is a pure linseed oil vehicle.

Panel B contains 5 per cent of Kauri mixing varnish in the vehicle.

Panel C contains 10 per cent of Kauri mixing varnish in the vehicle.

Panel D contains 20 per cent of Kauri mixing varnish in the vehicle.

Panel E contains 30 per cent of Kauri mixing varnish in the vehicle.

These were exposed in a closed box with a glass front, in order that the conditions could be carefully watched. Oxygen and the corrosion accelerating gases in the atmosphere were passed into the box through wash bottles, to insure a slow but steady current, and a small quantity of steam was admitted to keep the atmosphere within the box always very moist, but not sufficient to raise the temperature materially. The panels were examined from day to day, and removed when it was judged that further exposure might obliterate the truths for which we were seeking.

It is very evident that the panels at both ends have failed before those between. A relation may also be seen between the duration of protection and the quantity of Kauri mixing varnish in the vehicle. The protecting qualities increase with the per cent of Kauri mixing varnish to a certain point, and then fall off again as the percentage of Kauri mixing varnish is increased beyond this point. This seems to indicate a definite point of maximum sealing effect for this particular material.

Another illustration of making a paint less pervious and therefore a better protection against corrosion, is the proper choice of pigments. Red lead and linseed oil have been long looked upon as the best primer for iron and steel. This may be true, but is it not possible to improve this red lead and linseed oil without seriously changing its nature and obtain a film which is less pervious to gases and moisture and thereby protect the iron and steel even more effectively than will the red lead and linseed oil? If we shake off some of the traditional bonds and apply the teachings of more recent scientific investigation we find it possible by using the foregoing principles and the proper choice of particle sizes, making use of the law of minimum voids, to produce a red lead primer, which has all the advantages of the traditional red lead and linseed oil, and is at the same time less pervious, and therefore a better protection against corrosion.

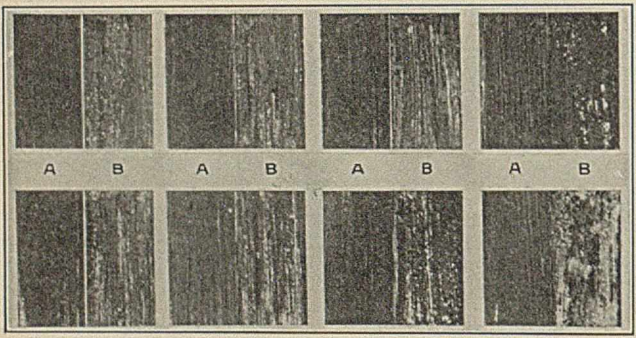

Plate II—Pairs of Steel Panels
A's primed with special red lead paint
B's primed with usual red lead paint
All painted with same second coat paint.

Plate II shows a series of pairs of steel panels, which have been cleaned in the usual manner with acid, etc. Both A and B of each pair were painted with the same second coat paint, and each pair with a different second coat paint, while A of each pair was primed with a special red lead paint, formulated according to the principles just mentioned, and B of each pair was primed with red lead and linseed oil mixed according to a formula considered to give the best results obtainable after many years of practical painting under more or less adverse conditions of moisture and corrosion accelerating gases. All the panels were painted in exactly the same manner on the same day, allowed the same time to dry between coats and also after the second coat, and exposed as previously described at the same time and for the same length of time. Since the second coat on A and B is the same in each instance its effect has nothing whatever to do with the comparison, this being dependent entirely on the difference in the red lead priming paints on A and B. It can be seen at a glance that the special red lead paint on A has given a much more efficient protection than that mixed according to the prevailing custom on B. One hundred and twenty comparison panels were exposed in this test and in every instance panel A showed a better film than did panel B.

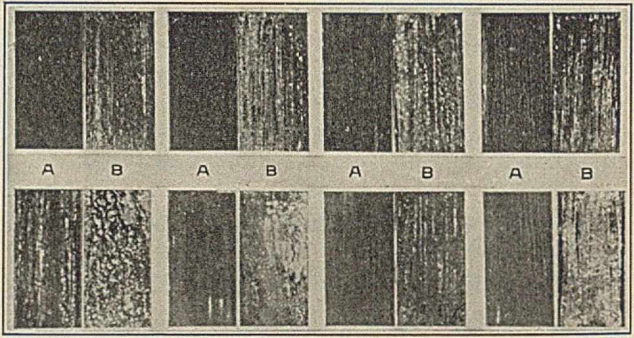

Plate III—Pairs of Steel Panels Painted with So-called Rust Proof Paints
A's primed with special red lead paint
B's primed with rust proof paint
All second coats of rust proof paint

Lastly, let us take up for a brief space the incoming of the throng of fantastically named "paints" which have been put on the market with claims equally as fantastic. Many of these have been claimed to protect the iron and steel as a primer and as a second coat better than anything on the market. It is only necessary to refer to Plate III, which is a photograph of some pairs of steel panels prepared as before mentioned and painted with a number of so-called rust inhibitive or rust proof paints. On panels marked B was painted two coats of a paint, and on panels marked A one coat of the same paint over a priming coat of the special red lead paint formerly mentioned. As a different paint is on each pair there are as many different paints as there are pairs of panels.

It is readily seen that the two coats of any of these paints, B, do not protect as well as where it is applied over the special red lead primer, A.

Blue lead seems to have certain properties very similar to red lead when used in a paint for the priming of iron or steel, and in fact it is very possible that it may be fully as good for this purpose as red lead, when properly used, if not better. Experiments are now being conducted by the writer to determine these relations.

Recently the idea has been set forth that certain pigments are rust inhibitive by virtue of their alkaline qualities. Further investigation seems necessary to determine whether it is simply the alkaline properties of these pigments considered as a rust inhibitive only which endows the paint film with superior protecting qualities.

The suggestion may not be out of place that the basic properties of certain pigments enable them to attack the vehicle to a sufficient extent to form a small quantity of metallic soap which acts as a binding material between the pigment particle and the linoxin, thus offering a greater obstruction to the passage of disintegrating elements between pigment particle and vehicle; or perhaps acting as a diffusion retarder in the linoxin.

It is not the intention of the writer to point out the shortcomings of any particular brand of paint or theory, but simply to give results of experiment and interpretation of the same with a view to bettering the paint conditions for all concerned.

In conclusion then, it would seem that whatever the correct theory of corrosion may be, it is of first importance to the paint technologist to construct his film in such a manner as to exclude gases and moisture to the greatest possible extent, as without these no corrosion can possibly take place.

LABORATORIES OF THE GORDON-HITTL CO.
BOSTON

THE OLEORESINS OF JEFFREY AND SINGLELEAF PINES

By A. W. SCHORGER

Received September 25, 1913

The Forest Service for a number of years has been investigating the possibilities of utilizing various species of conifers for the production of naval stores. The following work on Jeffrey and singleleaf pines is a continuation of the examination of the oleoresins obtained during the tapping experiments. The methods of analysis employed and the results obtained in the examination of other species will be found in another publication.[1]

The oleoresins of the pinon pine[1] (*Pinus edulis*, Engelm) and singleleaf pine (*Pinus monophylla*, Torr, and Frem.) are similar in composition, appearance, and odor. Both oleoresins contain large resin acid crystals and have a pungent characteristic odor. The volatile oils of the two species consist mainly of α-pinene and the sesquiterpene cadinene is found in the higher boiling portions. In addition, β-pinene and probably limonene[1] occur in the oil from *Pinus edulis* while limonene occurs in the oil of *Pinus monophylla*.

Attention has been previously[2] called to the confusion caused by lack of an exact knowledge of the species yielding heptane. The source of this substance has been variously ascribed to one or more of the following species: Western yellow pine (*P. ponderosa*, Laws); digger pine (*P. sabiniana*, Dougl.); and Jeffrey pine (*P. jeffreyi*). It has been previously[2] shown that the oil from *Pinus ponderosa* does not contain heptane and that the oil of *Pinus sabiniana* consists of nearly pure heptane. It is now possible to confirm the work of Blasdale[3] and Wenzell[4] since examination of authentic samples of the oleoresin of *Pinus jeffreyi* has shown that the oil consists largely of normal heptane.

The lack of uniform data in the literature regarding the resin acids is much to be regretted. The melting point of abietic acid from colophony varies from 135°[5] to 165°.[6] Tschirch[7] states that American colophony contains α-, β-, and γ-abietic acids melting at 155°, 158°, and 153–154°, respectively, and then obtains abietic acid, melting point 166–167°, from rosin oil.[8]

Leuchtenberger,[9] working under Tschirch, examined the colophony of *Pinus jeffreyi*. Extraction of an ether solution of the colophony with one per cent $(NH_4)_2CO_3$ gave four per cent of α-Jeffropinic acid, $C_{10}H_{14}O_2$, m. p. 160–161°; nine per cent β-Jeffropinic acid, $C_{12}H_{18}O_2$, m. p. 81–82°. Extraction with one per cent Na_2CO_3 solution gave 35 per cent α-Jeffropinolic acid, $C_{14}H_{20}O_2$, or $C_{14}H_{22}O_2$, m. p. 117–118°; 38.2 per cent β-Jeffropinolic acid, $C_{14}H_{20}O_2$, or $C_{14}H_{22}O_2$, m. p. 77–78°. The acid isolated by the author from the oleoresin of *P. jeffreyi* melted at 170–171°. The silver salt contained 26.16 per cent of Ag, agreeing with the formula $C_{20}H_{30}O_2$. The acid from the colophony melted at 137–8° crystallized from acetone and 145–6° crystallized from acetone and hydrochloric acid. α-Jeffropinic acid requires 39.51 per cent Ag and α-Jeffropinolic acid, $C_{14}H_{20}O_2$, requires 32.98 per cent Ag. To obtain acids of this formula it would be necessary for the resin crystals existing in the oleoresin to undergo profound alteration in heating to 145° C. which is not borne out by experience. The action of acids and alkalies has a material effect on the melting point of the resin acid. Valente[10] obtained an acid from French colophony melting in the crude state at about 160°. When purified by solution in dilute sodium carbonate and precipitation with dilute sulfuric acid, the resin acid melted at only 146–148°.

EXPERIMENTAL

Oleoresin of Pinus monophylla

Oleoresin.—Analysis of the crude oleoresin gave

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[1] "An Examination of the Oleoresins of Some Western Pines," by A. W. Schorger, Forest Service, *Bull.* **119**.

[1] *Loc. cit.*, 29.

[2] "An Examination of the Oleoresins of Some Western Pines," by A. W. Schorger, Forest Service, *Bull.* **119**.

[3] Blasdale, *J. Am. Chem. Soc.*, **23**, 162–4 (1901).

[4] Wenzell, *Pharm. Rev.*, **22**, 408–14 (1904).

[5] Flückiger, *J. prakt. Chem.*, **101**, 235 (1867).

[6] Maly, *Sitzungsber. d. k. Akad. d. Wis. zu Wien*, **44**, 121 (1861).

[7] "Die Harze und die Harzebehalter," 2nd ed., 1906, p. 660.

[8] *Arch. Pharm.*, **245**, 1 (1907).

[9] *Ibid.*, **245**, 701–7 (1907).

[10] *Atti della R. Accad. dei Lincei*, **1**, [4] 13 (1884).

the following percentages: Volatile oil 19.00 per cent; colophony (grade N) 79.63 per cent; trash, needles, bark, etc., 0.11 per cent; water 1.26 per cent.

Volatile oil.—The properties of the oil were as follows: $d_{15°}$ 0.8721–0.8733; $n_D^{15°}$ 1.4732–1.4733; $\alpha_D^{25°}$ +14.41° to +17.26°. Five hundred grams of the oil gave the following results on fractionation:

Temp. (corr.) ° C.	Distillate observed Per cent	Distillate cumulative Per cent	$d_{15°}$	$n_D^{15°}$
155.9–156.9	4.75	4.75	0.8602	1.4674
157.0	10.25	15.00	0.8603	1.4676
157.1	10.25	25.25	0.8602	1.4677
157.2	10.20	35.45	0.8599	1.4678
157.4	10.33	45.78	0.8598	1.4679
157.8	9.94	55.72	0.8594	1.4680
158.2	9.80	65.52	0.8588	1.4680
160.0	10.52	76.04	0.8576	1.4685
171.8	10.07	86.11	0.8536	1.4705
190.0	3.99	90.10	0.8511	1.4818
...	9.80	99.90	....	....

α-Pinene.—After repeated fractionation 398.5 grams of oil were obtained boiling below 160°. Ten grams of a fraction, b. p. 155.5–157°, $d_{15°}$ 0.8612, $\alpha_D^{26°}$ +35.36°, gave only 0.78 gram (7.8 per cent) of pinene nitrosochloride, m. p. 99°; nitrolpiperidine, m. p. 118°. The low yield of nitrosochloride is doubtless due to the high optical rotation of the pinene fraction. The fraction, b. p. 160–170°, weighing 21.5 grams was examined for β-pinene with negative results.

Limonene.—The limonene fraction weighing 17.5 grams had the following properties: b. p. 170–180°; $\alpha_D^{18°}$ —1.18°. A crystalline tetrabromide was not obtained but a dihydrochloride, m. p. 49°, was easily secured.

Cadinene.—The residue remaining from the original fractionation was distilled from a Ladenburg flask and two fractions collected: (1) b. p. 200–250°, 18.5 grams; (2) b. p. 250–280°, 20.2 grams; $\alpha_D^{25°}$ + 10.58°. Fraction (2) was found to contain cadinene as shown by a dihydrochloride, m. p. 117–118°. A 6.14 per cent ethereal solution gave $\alpha_D^{35°}$ —2.02°. In the examination of *d*- and *l*-cadinene from various oils the rotation of the cadinene dihydrochloride has always been found to be negative.

Colophony.—The colophony had the following constants: Acid no. 155.9 by direct titration; sap. no. 163.3. When the colophony was treated with an excess of *N*/2 alcoholic potash it yielded 7.22 per cent of resene soluble in petroleum ether. The colophony on being dissolved in acetone and allowed to stand in an ice box for a month deposited a mass of resin crystals. These crystals were mechanically freed from oily impurities so far as possible, rapidly stirred in cold acetone and the solvent decanted. After four crystallizations from the same solvent, the crystals obtained melted at 119–120°, and were completely liquid at 129°. The resin crystals contained in the original oleoresin were freed from the greater portion of the adherent oil by suction. The resulting white, waxy cake was recrystallized six times from acetone. The crystals obtained melted at 129–130° and were completely liquid at 135°. Analysis of the silver salt of the acid follows:

0.2214 gram of silver salt gave 0.0590 gram Ag = 26.65 per cent.

Silver abietate, $Ag(C_{20}H_{29}O_2)$, requires 26.37 per cent Ag.

Oleoresin of Pinus Jeffreyi

Oleoresin.—The analyses contained in the following table are of interest in that they represent samples from individual trees.

No.	Volatile oil Per cent	Water Per cent	Trash Per cent	Colophony Per cent	Volatile oil	
					$d_{15°}$	$n_D^{15°}$
1	11.25	1.23	0.46	87.06	0.7013	1.3963
2	8.81	1.50	0.44	89.25	0.7018	1.3958
3	9.73	2.29	0.23	87.75	0.6951	1.3927
4	10.96	1.42	0.80	86.82	0.7110	1.4002
5	9.05	2.00	0.40	88.55	0.7008	1.4060
Mean	9.96	1.69	0.47	87.88		

Volatile Oil.—The properties of the volatile oils are given in the preceding table. The oils from the five samples were mixed and 175 grams distilled from a Ladenburg flask with the following results:

Temp. (corr.) ° C.	Distillate observed Per cent	Distillate cumulative Per cent	$d_{15°}$	$n_D^{15°}$
98.2– 98.8	16.74	16.74	0.6880	1.3902
100.0	40.47	57.21	0.6889	1.3903
102.0	22.92	80.13	0.6897	1.3905
105.0	8.17	88.40	0.6906	1.3915
113.0	4.05	92.45	0.6965	1.3937
...	7.37	99.82	....	....

Heptane.—The first four fractions amounting to 150 grams were redistilled, using a 12-inch Hempel column with the following results:

No.	Temp. (corr.). ° C.	Distillate observed Per cent.	Distillate cumulative Per cent	$d_{15°}$
1	98.1–98.3	19.20	19.20	0.6878
2	98.4	40.95	60.15	0.6881
3	98.5	30.07	90.22	0.6881

The boiling points and specific gravities of the fractions are practically identical with the constants of pure *n*-heptane.

Citronellal.—The residue boiling above 113° distilled mainly between 200–215° C. The fraction with the latter boiling point weighed 6 grams (3.4 per cent) and had: $d_{15°}$ 0.8578; $n_D^{20°}$ 1.4570; $\alpha_D^{20°}$ —2.50°. The oil had a lemon odor and showed the following properties of an aldehyde: Combined with $NaHSO_3$ forming a flocculent precipitate, reduced an ammoniacal silver solution, and produced a rose-red coloration with a fuchsin solution decolorized with SO_2. The semicarbazone obtained separated as oil that crystallized after standing in the cold for several days. The semicarbazone was twice recrystallized from alcohol, finally from a mixture of chloroform and petroleum ether. The crystalline powder obtained melted at 91–92°. Lack of material prevented the satisfactory formation of other derivatives. Comparison with the properties of citronellal from Java lemon oil[1] follows:

Source	B. p.	$d_{15°}$	$n_D^{20°}$	Optical rotation
Java lemon oil	205–208°	0.8567	1.44791	α_D —3°
Pinus jeffreyi	200–215°	0.8578	1.4570	$\alpha_D^{20°}$ —2.50°

[1] Schimmel and Company, *Berichte*, April, 1903, p. 21

Active citronellal semicarbazone, $C_{10}H_{18} : NNHCONH_2$, melts at 82.5°, the racemic form at 96°. From the optical rotation of the aldehyde fraction of *Pinus jeffreyi* it is possible that the semicarbazone contained a small amount of the active form resulting in the low melting point obtained.

Colophony.—A sample of "ww" colophony had the following properties: Acid no. 147.6; sapon. no. 178.1. The rosin contained 12.5 per cent of resene obtained in the form of a yellow, very sticky, viscous syrup. The colophony crystallized from acetone after standing in the cold for several weeks, differing in this respect from the colophony of *Pinus sabiniana*. The crystals obtained after five recrystallizations from acetone softened at 130° and melted at 137–8°. When followed by a crystallization from a mixture of acetone and hydrochloric acid they softened at 136° and melted at 145–6°, becoming completely liquid at 151°.

The resin crystals obtained from the crude oleoresin melted at 170–171°. The silver salt of the acid was prepared and analyzed as follows:

0.3926 gram of silver salt gave 0.1027 gram Ag = 26.16 per cent Ag.

Silver abietate, $Ag(C_{20}H_{29}O_2)$, requires 26.37 per cent Ag.

SUMMARY

The volatile oil of *Pinus monophylla* contains 80–85 per cent *d*-α-pinene; 4–5 per cent *l*- or *i*-limonene; 4–6 per cent *d*-cadinene; losses by polymerization, etc., 4.5 per cent. The colophony contains 7.22 per cent resene and resin acids isomeric with abietic acid.

The volatile oil of *Pinus jeffreyi* contains about 95 per cent *n*-heptane and 5 per cent of an aldehyde, apparently citronellal. The colophony contains 12.5 per cent resene and resin acids isomeric with abietic acid.

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THE HYDROCARBONS OF UTAH[1]

By Carlos Bardwell, B. Arthur Berryman, Thomas B. Brighton and Kenneth D. Kuhre

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About fifteen kinds of hydrocarbons occur in Utah; the five of these occurring most abundantly—gilsonite, tabbyite, wurtzilite, ozocerite and rock asphalt—are the ones selected for this investigation.

Gilsonite[2] (uintaite) was first described by Blake in 1885. He gave it the name uintaite because of its occurrence in the Uinta Mountains. Later the name gilsonite was adopted because S. H. Gilson, a prospector, brought it into prominence as an article of commerce. The deposits of gilsonite are limited to the Uncompahgre Indian Reservation in Uinta County, being found in an area extending along the 40th parallel for about 60 miles.

Tabbyite receives its name from an Indian chieftain, Tabby. The deposits are in Tabby Canyon, a branch of the Duchesne, about 8 to 9 miles south and west of Theodore, Uinta County.

Wurtzilite[1] (elaterite or mineral rubber) from Utah was first described by Wurtz, who showed that it is a distinct mineral. The name elaterite had been used previously by Dana and other mineralogists to describe three different minerals of specific gravities ranging from 0.905 to 1.223. The region in which wurtzilite is found covers an area of about 100 square miles between Indian Canyon and Sam's Canyon, branches of Strawberry Creek, about 30 miles due north of Price, Utah.

Ozocerite (mineral wax) has been known for many years on account of the economic value of the large deposits in Galicia, Austria. The only other deposit known to be of commercial value is that in Utah. This deposit begins about two miles west of Colton, Utah County, and extends to about four miles west of Soldier Summit, a distance of 12 miles. The belt is 2 miles wide. This area may be divided into three parts:[2] (1) near Colton, on the north side of the Price River valley; (2) to the east of Soldier Summit where the railroad crosses the crest of the plateau; and (3) near Midway Station, on the north side of the canyon, near the source of Soldier's Creek.

Heretofore rock asphalt has usually been called bituminous sandstone, but the former name is growing in popularity, especially in Utah. The largest deposit in the state lies south and east of Vernal, north of the White River and between Ashley and Uinta valleys.[3] This deposit attains a thickness (in places) of twenty feet, but at present it is too far from a railroad for successful commercial exploitation. Another deposit occurs in Spanish Fork Canyon, southeast of Thistle, and still other immense deposits are found (1) in the tributaries of Whitmore Canyon, near Sunnyside, (2) at the head of Willow Creek, a tributary of the Green River, in the Book Cliff Mountains, and (3) in the Laramie sandstones near Jensen, on the Green River. A deposit of bituminous *limestone* occurs at the head of the right-hand branch of Tie Fork, a canyon entering Spanish Fork Canyon, 2 miles west of Clear Creek Station. An area underlaid by bituminous limestone, about 50 miles long east and west by 10 miles wide north and south, lies just north of Colton and south of Strawberry Creek, extending from Antelope Creek on the east to Thistle on the west.[4]

HISTORICAL

In reviewing the literature of these substances one finds that a great deal has been published concerning gilsonite and ozocerite, but not much about wurtzilite, tabbyite and rock asphalt. Day,[5] working with gilsonite, attempted to isolate "such single hydrocarbons or their derivatives as would give some information as to the real nature of the mineral itself." He gives an outline of the physical characteristics, solubilities, etc., of gilsonite, and describes the character of the residue from each solvent as well as the nature of the dissolved portion. Proximate and ultimate analyses

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[1] This work was done at the suggestion and under the direction of Dr. W. C. Ebaugh, to whom the authors' thanks are due.

[2] Blake, *Eng. Min. J.*, **40**, 431 (1885).

[1] Wurtz, *Ibid.*, **49**, 59 (1890).

[2] Taff and Smith, U. S. Geol. Survey, *Bull.* **285**, 369 (1905).

[3] Wigglesworth, *Trans. Am. Inst. Min. Eng.*, **17**, 115 (1888).

[4] Eldridge, U. S. Geol. Survey, *17th Ann. Rept.*, **1896**, 915, *et seq.*; *22nd Ann. Rept.*, **1900-01**, 332.

[5] Day, *J. Frank. Inst.*, Sept., **1895**, 221, *et seq.*

are given. From a study of the distillation products of gilsonite he concludes that the oil obtained belongs to the paraffin series of hydrocarbons, and is made up of a number of distinct substances, just as is petroleum. He obtained from the distillate volatile with steam, oils which seem to correspond to those described by Peckham[1] as obtained from California bitumens. These had an odor similar to quinoline, and to him this was an evidence of the relationship of California bitumen and of gilsonite and of their animal origin. Day gives also the results of treatment with nitric acid and descriptions of the products and their properties, concluding that some members of the naphthalene series are present.

Eldridge[2] described the location of the hydrocarbon deposits and the geology of the district. He states that the cracks in which gilsonite is found were formed by the gentle folding that produced the Uinta Valley syncline. He describes the properties of the gilsonite coming from near the surface where, through atmospheric agencies, it has lost its luster and become pencillated in structure. From a study of conditions he concludes that the gilsonite found its way into the fissures as a plastic mass, coming from below under pressure, and though of high viscosity, sufficiently fluid to be pressed between the grains constituting the wall rocks. He frankly confesses his lack of ability to suggest the condition under which the gilsonite existed prior to its flow into the cracks. An analysis of gilsonite by Day is quoted as follows:

	Percentages
Volatile matter	56.46
Fixed carbon	43.43
Ash	0.10
or	
Carbon	88.30
Hydrogen	9.96
Sulfur	1.32
Ash	0.10
Oxygen and nitrogen (undetermined)	0.32

Locke,[3] Blake,[4] Raymond,[5] and Wurtz[6] describe the uses of gilsonite, its solubilities, methods for "fluxing" it, etc. The earlier analyses of asphalts gave rather large percentages of oxygen, but this was probably because the presence of sulfur had not been recognized and the oxygen was supposed, with the carbon and the hydrogen, to make up the ash-free bitumen. Nevertheless some analyses which report sulfur and nitrogen also report small amounts of oxygen.[7] By some authorities, as Richardson and Peckham, oxygen is considered as foreign to natural asphalts.

In the first reference to wurtzilite, Blake[8] describes it from a physical standpoint, noting its occurrence, hardness, color, specific gravity, fusibility, electrical properties, etc. He explains the difference between wurtzilite and gilsonite,[9] and shows that the Utah wurtzilite is an entirely distinct mineral from the elaterite of Dana and other mineralogists. Wurtz[1] confirms the conclusions of Blake.

Utah ozocerite is very similar in properties to that from Galicia, but as it contains less oily material and is firmer, it is more valuable. Many popular accounts[2] of its mode of preparation, uses, etc., are to be found, but nothing concerning its chemical composition, distillation products, etc.

With the exception of occasional references to the location of bituminous sandstones in Utah, nothing could be found about rock asphalt.

USES OF UTAH HYDROCARBONS

An investigation of the uses of Utah hydrocarbons shows them to be surprisingly numerous and varied. Many of our commonest articles are made from these substances. Before the discovery of gilsonite in Utah, European and Asiatic asphalts were shipped into the United States; now, because of its abundance and purity large quantities of Utah asphalt are shipped to foreign countries. The production of gilsonite during the last two years has increased rapidly, due to the greater number of articles made from it. In 1910[3] the production was 30,000 tons; in 1912, over 50,000 tons. It is worth about $20.00 a ton, f. o. b. Utah.

Wurtzilite is little used because of its insolubility. About 1,000 tons are produced annually.

Ozocerite is of greater value than gilsonite, the price in New York being 15 to 28 cents per pound.[4] No data could be found as to the production of ozocerite, but at present the demand far exceeds the supply.

Perhaps the most extended use that has been made of Utah asphalts is in the paving industry. Gilsonite has been used in paving the streets of many important cities,[3] *e. g.*, Michigan Avenue, Chicago, where it is said to be giving satisfaction under the most exacting requirements. Rock asphalt was used[3] in paving Second South Street between West Temple and First West Streets, Salt Lake City, and the surface is now in fair condition, although it has had practically no repairs during its 16 years of service.

Another important use for Utah hydrocarbons is in the manufacture of varnishes and paints.[3] Only the purest and best materials are used for these purposes, the refined hydrocarbons being dissolved in turpentine and linseed oils. Wurtzilite has been used in the manufacture of a varnish in which the particles are simply held in suspension, but do not enter into solution.

Some of the uses of the individual Utah hydrocarbons are as follows:

Gilsonite.[5]—Paving industry, electrical insulators, roofing papers and compounds, water-proofing wooden and steel pipes and masonry aqueducts, preventing electrolytic action on iron plates of ship bottoms,

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[1] Peckham, *Am. J. Sci.*, **48**, III, 250.

[2] Eldridge, U. S. Geol. Survey, *22nd Ann. Rept.*, **1900-01**, 330.

[3] Locke, *Trans. Am. Inst. Min. Eng.*, **16**, 162 (1887).

[4] Blake, *Eng. Min. J.*, **40**, 431 (1885).

[5] Raymond, *Trans. Am. Inst. Min. Eng.*, **17**, 113 (1888).

[6] Wurtz, *Eng. Min. J.*, **48**, 114 (1889).

[7] Sadtler, THIS JOURNAL, **5**, 393 (1913).

[8] Blake, *Eng. Min. J.*, **48**, 542 (1889).

[9] Blake, *Trans. Am. Inst. Min. Eng.*, **18**, 497 (1889).

[1] Wurtz, *Eng. Min. J.*, **49**, 106 (1890).

[2] Higgins, *Salt Lake Mining Review*, **14**, 11–5 (Oct., 1912). Culmer, *Salt Lake Tribune* (Dec. 29, 1912); Taff and Smith, U. S. Geol. Survey, *Bull.* **285**, 369 (1905).

[3] Culmer, Address, Univ. of Utah, Nov. 15, 1912.

[4] Higgins, *Salt Lake Min. Rev.*, **14**, 11–5 (Oct. 15, 1912).

[5] Locke, *Trans. Am. Inst. Min. Eng.*, **16**, 162 (1887); New Internatl. Encyc. Article on "Asphalt;" Culmer. *loc. cit.*; Richardson and Parker, U. S. Geol. Survey, *Min. Resources of U. S.*, **1893**, 627–69; Taff and Smith, U. S. Geol. Survey, *Bull.* **285**, 369 (1905).

coating barb wire fencing, coating sea walls of brick or masonry, lining tanks for chemicals, coating poles, posts and ties, toredo-proof pile coating, smokestack paint, lubricant for heavy machinery, substitute for rubber, as binder pitch for culm in making briquettes and egette coal.

Tabbyite.—Compounds with Para rubber to manufacture floor mats, rubber paints and roofings; as a filler for rubber in automobile tires, etc.

Wurtzilite.—Varnishes, roofing compound, etc.

Ozocerite.[1]—Electrical insulator (said to have about four times the specific resistance of paraffin), altar candles, substitute for beeswax, ointments, pomades, salves, water-proofing, waxed paper, wax dolls and figures, telephone receivers, phonograph records, electroplating, water-proof crayons, shoe polish, buttons, ceresine, floor polishes and waxes, water-proofing cartridges, sealing wax, etc.

Rock Asphalt.—Paving industry.

EXPERIMENTAL RESULTS

The results of the first tests made upon eight samples of hydrocarbons are given in Table I.[2] They are the standard tests recommended by Richardson[3] and are meant primarily to determine the fitness of the materials for asphalt paving. No one of the materials as it occurs in nature comes up to the standards completely, but in the cases of Trinidad, Bermudez, rock asphalt and gilsonite the bitumen could be mixed with heavy petroleum oils and given the required penetration and other physical properties. As our work is concerned with the properties of the materials as they occur in nature no compounding was done. For the use of a standard machine for making the penetration tests we are indebted to the office of the City Engineer, Salt Lake City.

TABLE I

Original substance	Trin.	Ber.	Gils.	Tab.	Wur. 1	Wur. 2	Ozok.	R. A.
Loss 212° F., 1 hr., per cent	0.073	0.1765	0.353	0.91	0.53	0.21	0	0.14
Loss 325° F., 7 hrs., per cent	1.717	6.63	0.217	2.78	2.76	1.66	45.41	1.43
Penetration residue	0	30	0	0	0	0	15	0
New sample loss 400°, 7 hrs.	5.25	9.71	0.85	6.40	3.88	1.88	65.20	1.79
Penetration residue	0	0	0	0	0	0	0	0
Bitumen sol. in CS_2	60.36	90.93	99.64	94.63	10.83	8.10	99.46	11.34
Org. matter insol. in CS_2	3.94	3.74	0	0.72	87.68	88.54	0.50	0
Inorg. or mineral matter	35.70	5.32	0.36	4.65	1.50	3.36	0.046	88.66
					wt. increased			
Bit. sol. in 62° naphtha	41.00	34.40	61.70	58.50	2.76?	2.74?	81.71	9.25
This is per cent of total bit.	68.00	38.85	61.85	61.85	39.10	33.85	82.20	81.50
Carbenes: bit. insol. in CCl_4	could not filter	0	0.18	1.75	1.57	1.65	2.51	1.59
Bit. more sol. in CCl_4	....	1.37	0	0	0	0	0	0
Original loss on ignition	64.30	94.68	99.64	95.35	98.50	96.64	99.96	11.34
Fixed carbon	36.69	39.60	43.13	37.45	35.60	....	10.03	6.85
Sulfur on original	4.22	4.70	0.52	1.24	4.00	4.34	0.29	0.78
Specific gravity 78° F.	1.372	1.05	1.018	1.006	1.032	1.004	0.891	2.097
Streak	dark brown	nearly black	brown	brown	brown	brown	brown	brown
Luster	dull	glossy	glossy	slightly glossy	glossy	glossy	dull	dull
Fracture	conchoidal	conch.	conch.	conch.	conch.	conch.	conch.	....
Hardness	1	<1	2	<1	1	1	<1	....
Odor	tarry	tarry	slightly tarry	petroleum	tarry	tarry	petroleum	slightly oily
Softens ° F.	203	132	320	264	above b. p. mercury		134	....
Flows ° F.	266	181	377	275			140	....
Penetration at 78° F.	0	30	0	0	0	0	30	0

The bitumens in asphalts are divided into two general classes,[1] *viz.*, those soluble in 62° naphtha (malthenes) and those insoluble in carbon tetrachloride but soluble in carbon disulfide (carbenes). Our solubility tests were made by allowing one-gram samples, finely ground, to be in contact with excessive amounts of the solvents for 12 to 18 hours, filtering upon ignited asbestos in a Gooch crucible, washing with the pure solvent, drying at 100° C. and reweighing. Great difficulty was found in filtering some of the samples, especially the Trinidad asphalt.

Table II gives the ultimate composition of the samples as determined by the ordinary combustion method, with lead chromate and copper oxide in the combustion tube. Great care must be taken in starting a combustion to prevent the too rapid distillation of the volatile components present in the samples. Nitrogen was determined by a modified Kjeldahl method, with subsequent distillation into an excess of standard sulfuric acid. Sulfur was determined by a modification of the Eschka method,[2] *i. e.*, roasting a weighed sample of material with zinc oxide and sodium carbonate, leaching with water, filtering, acidulating with hydrochloric acid, and precipitating and weighing barium sulfate as usual. Ash was determined by (1) reweighing the boat after a combustion, or (2) by burning a one-gram sample in a platinum dish. In two cases the ash was analyzed. The results are given in Table II*a*.

TABLE II

Substance	Trin.	Ber.	Gils.	Tab.	Wur. 1	Wur. 2	Ozok.	R. A.
Carbon	51.06	77.52	85.25	81.32	76.90	79.40	85.35	9.55
Hydrogen	5.84	8.90	10.55	10.40	11.20	10.55	13.86	1.10
Sulfur	4.22	4.70	0.52	1.24	4.00	4.34	0.29	0.78
Nitrogen	0.66	0.89	2.21	2.10	2.18	2.10	0.36	0.31
Ash	35.70	5.32	0.89	4.65	1.50	3.36	0.04	88.05

TABLE II*a*

Ash analysis	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
Rock asphalt	78.20	2.20	9.00	5.60	2.10
Tabbyite	35.35	2.50	9.80	29.50	9.45

Table III records the results of a series of solubility

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[1] New Internatl. Encyc., Article on "Asphalt;" Higgins, *Salt Lake Min. Rev.*, **14**, 11–5 (Oct. 15, 1912).

[2] For purposes of comparison determinations were carried out also upon samples of refined Trinidad and Bermudez asphalt kindly supplied by the New York Testing Laboratory.

[3] Richardson, *The Modern Asphalt Pavement*, **1905**, 168.

[1] Richardson, *loc. cit.*

[2] Ebaugh and Sprague, *Jour. Am. Chem. Soc.*, **29**, 1475 (1907).

tests. The treatment with solvent lasted for 18 hours, and a motor-driven shaking device produced thorough mixture of sample and solvent. The hot extractions were made with boiling solvent in a flask fitted with a reflux condenser.

TABLE III

Solvent	Trin.	Ber.	Gils.	Tab.	Wur. 1	Ozok.	R. A.
Amyl alcohol	Insol.	Insol.	Inl.	4	Insol.	Insol.	Insol.
Ethyl ether	109	145	∞	46	Insol.	13	14
Ethyl acetate	30	24	*5 3	*7 3	Insol.	1	*7 4
Amyl nitrate	84	39	51	Insol.	*5 Insol.	7	16
Amyl acetate	132	37	86	Insol.	Insol.	1	Insol.
Benzol	48	36	71	35	Insol.	18	12
Toluol	39	33	72	57	0.09	Very sol.	14
Turpentine	115	116	60	65	45	Very sol.	29
Nitrobenzene	39	24	9	14	*12 Insol.	Insol.	3
Aniline	3	Insol.	*33 Insol.	Insol.	*2 Insol.	Insol.	Insol.
Chloroform	10	23	54	33	*1.5 0.96	∞	83
Carbon disulfide	∞	∞	∞	55	13.45	∞	Very sol.
Carbon tetrachloride	∞	∞	44.30	36.00	1.8	∞	12
62° Naphtha	Very sol.	63	5	6.80	2.8	7	18
Ethyl alcohol	Insol.	Insol.	Insol.	*1 Insol.	Insol.	Insol.	Insol.
Propyl alcohol	Insol.	Insol.	*1 Insol.	*11 Insol.	Insol.	Insol.	Insol.

Numbers refer to grams soluble in 100 grams cold solvent.

* Grams soluble in 100 grams boiling solvent.

Table IV gives the results of the fractional distillations of the hydrocarbons. A number of distillations at reduced pressure were tried, but the results were not satisfactory, and work along this line was discontinued for lack of time. It was noticed, however, that (1) gilsonite is soluble in its own distillate and in those from wurtzilite and tabbyite, (2) tabbyite is soluble in the distillates from gilsonite and wurtzilite, but (3) wurtzilite is insoluble in its own distillate and in the distillates from gilsonite and tabbyite. Gilsonite is soluble in stearin and hot paraffin, but wurtzilite is insoluble in both of these materials.

TABLE IV

Substance	Trin.	Ber.	Gils.	Tab.	Wur. 1	Ozok.	R. A.
0–150° C.	14.93	9.89	9.34	3.12	16.15	0.21	0.91
150–200° C.	10.42	7.99	5.34	11.93	21.70	8.91	3.22
200–250° C.	2.26	16.08	12.84	24.87	22.82	8.38	0.29
250–300° C.	....	21.12	28.99	13.21	0.91	17.69	....
300–350° C.	....	....	....	4.77	....	25.89	....
350–400° C.	....	....	....	....	....	26.85	....
Total volatile	27.61	55.08	56.51	57.90	61.58	87.93	4.42
Fixed carbon	36.69	39.60	43.13	37.45	36.92	10.03	7.53
Ash	35.70	5.32	0.36	4.65	1.50	0.04	88.05
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

CONCLUSIONS

The marked differences in the physical and chemical properties and in the compositions of the five hydrocarbons are established. Tabbyite is shown to be a distinct substance. The reported insolubility of wurtzilite is amply confirmed.

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WINKLER'S METHOD FOR THE DETERMINATION OF OXYGEN IN WATER; THE EFFECT OF NITRITE AND ITS PREVENTION[1]

By FRANK E. HALE AND THOMAS W. MELIA

The accuracy of Winkler's method[2] for the determination of dissolved oxygen in water under usual conditions has been shown by many investigators. Comparison with Bunsen's direct estimation of the oxygen by boiling off the gas and determining the amount by gasometric analysis was carefully made by Winkler, himself, and later by Chlopin,[3] by Gill,[4] and by Birge and Juday.[5]

EFFECT OF NITRITE AND ITS CORRECTION

Considerable criticism has arisen of late regarding the Winkler method because of the effect of nitrites upon the results. If the effect were quantitative, a correction could be applied according to the following formula:

$$\mathrm{H{-}O{-}N{=}O + H{-}I = H{-}O{-}H + N{=}O + I}$$

in which N is equivalent to I and to $^1/_2$ O, and each part per million of nitrogen as nitrite would increase the apparent oxygen content by $8/14 \times 1$ or 0.57 p. p. m.

But the reaction is catalytic, the N=O taking up oxygen from the air to again form nitrous acid so that the effect under certain conditions may be considerable.

The present experiments were undertaken to ascertain the extent of the error with varying amounts of nitrite and if possible to find a simple method of prevention.

It is hardly necessary to describe the Winkler method as the details are in many text-books. The water to be examined, in our work, was poured through a funnel, keeping the funnel full, to the bottom of 300 cc. bottles, having tight fitting, well ground glass stoppers, and overrun until all water in contact with air in the bottle was removed. Then 1 cc. of a nitrite solution was introduced by a pipette at the bottom, the stopper inserted so as to exclude any air bubbles and the oxygen determined. In order to keep conditions alike a solution of nitrite was made of such strength that it contained 500 p. p. m. of nitrite, expressed as nitrogen. Varying quantities of this solution were then made up to 10 cc. and 100 cc. volumes from which 1 cc. was introduced into the bottles according to the amount of nitrite desired. Table I shows the amounts needed.

The results were tested by the usual colorimetric method of Griess and found to be correct.

In the determination of the oxygen the manganous sulfate and the potassium hydroxide-potassium iodide solutions were carefully measured, 2 cc. of each being introduced at the bottom of the bottle so as to displace an equal amount of the water tested. The bottle was well shaken and the precipitate allowed to

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[1] Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8–14, 1913

[2] L. W. Winkler, *Ber. d. chem. Ges.*, **21**, 2843 (1888); **22**, 1764 (1889).

[3] Chlopin, *Archives f. Hygiene*, **27**, 18 (1896).

[4] Report of Metropolitan Sewerage Commission, N. Y., 401 (1910).

[5] Birge and Juday, *Wisconsin Survey Bulletin*, **22**, 11, 12 (1911).

TABLE I—NITRITE SOLUTIONS

Amount of original sol.			Nitrite p. p. m.
0.6 cc.	diluted to 100 cc.	then 1 cc. added to 300 cc. equal	0.010
1.2 cc.			0.020
1.8 cc.			0.030
2.4 cc.			0.040
3.0 cc.			0.050
0.6 cc.	diluted to 10 cc.		0.100
1.2 cc.			0.200
1.8 cc.			0.300
2.4 cc.			0.400
3.0 cc.			0.500
6.0 cc.			1.000
1.2 cc.	added to 300 cc.		2.000
1.8 cc.			3.000
2.4 cc.			4.000
3.0 cc.			5.000

settle well before adding the acid. Hydrochloric acid, concentrated, reacts most quickly. About 2 cc. are needed. This is also better introduced at the bottom because the catalytic nitrite action can take place only in acid solution and in the presence of air. Correction for displacement is required only for the first two solutions. The titrations were made upon 100 cc. using *N*/100 thiosulfate.

The following table shows the effect of varying quantities of nitrite upon the oxygen determination:

TABLE II—SHOWING EFFECT OF NITRITE

Nitrite p. p. m.	Water used	Cc. *N*/100 thiosulfate per 100 cc.	Oxygen p. p. m.	Differences p. p. m.
0.003	Brooklyn tap	12.70	10.31	..
0.010	Brooklyn tap	12.60	10.23	−0.08
0.020	Brooklyn tap	12.70	10.31	±0.00
0.030	Brooklyn tap	12.60	10.23	—0.08
0.040	Brooklyn tap	12.60	10.23	—0.08
0.050	Brooklyn tap	12.55	10.19	—0.12
...	distilled	13.10	10.64	......
0.100	distilled	13.15	10.68	+0.04
0.100	distilled	13.20	10.72	+0.08
0.200	distilled	13.30	10.80	+0.16
0.200	distilled	13.50	10.96	+0.32
0.300	distilled	13.00	10.56	−0.08
0.300	distilled	13.60	11.04	+0.40
0.400	distilled	13.60	11.04	+0.40
0.500	distilled	13.70	11.12	+0.48
1.000	distilled	15.50	12.58	+1.94

It will be seen from these results that the effect of nitrite is inappreciable with amounts below 0.200 p. p. m. and the ordinary run of waters rarely contain sufficient nitrite to affect the accuracy of the results. Winkler himself placed the danger point at 0.100 p. p. m. nitrite.

As the nitrite is increased the end reaction is not permanent and the starch blue color comes back so quickly that considerable error is caused. That the action is catalytic and accumulative is shown by the following facts:

A sample with 0.500 p. p. m. nitrite kept three days tightly stoppered after the reagents had been added ready to titrate gave the same result as above, the error, 0.48 p. p. m., occurring during titration. The same sample kept three days exposed to air required 21.3 cc. *N*/100 thiosulfate, equivalent to 17.30 p. p. m. oxygen, an error of 6.66 p. p. m. A sample with 1.000 p. p. m. nitrite kept three days in acid condition in contact with air required 23.85 cc. thiosulfate, equivalent to 19.37 p. p. m. oxygen, an error of 8.73 p. p. m.

Winkler,[1] and also Max Müller,[2] tried to correct the error by adding acid and iodide and making a separate titration and correction, but this could not accomplish the result since the reaction is catalytic and varies with the time of exposure to the air. Rideal and Stewart[3] in 1901 recommended preliminary treatment with permanganate in acid condition and neutralization of excess permanganate by oxalate to eliminate the nitrite error. Rideal and Burgess[4] advised a colorimetric method in 1909 in the bottle, correcting for nitrite.

As nitrite may be oxidized and quantitatively determined by permanganate by the method of Kinnicutt and Nef[5] it was hoped that by allowing for a certain length of time contact in alkaline condition before acidifying, the manganese oxyhydrate could be made to destroy the nitrite and introduce thereby a known error. The following table gives the results of our experiments, using distilled water:

TABLE III—SHOWING RESULTS AFTER STANDING IN ALKALINE CONDITION

Nitrite p. p. m.	Time in alkaline condition	Cc. *N*/100 thiosulfate per 100 cc.	Oxygen p. p. m.	Difference p. p. m.
..	3 hours	11.40	9.26	..
...	3 hours	11.40	9.26	..
...	18 hours	11.38	9.24	—0.02
...	18 hours	11.42	9.27	+0.01
1.000	0 hour	14.50	11.77	+2.51
1.000	$^1/_4$ hour	14.20	11.53	+2.27
1.000	$^1/_2$ hour	16.00	12.99	+3.73
1.000	1 hour	14.70	11.94	+2.68
1.000	1.5 hours	14.90	12.10	+2.84
1.000	2 hours	14.80	12.02	+2.76
1.000	18 hours	15.20	12.34	+3.08

This procedure failed completely as the errors remained high and irregular.

The next attempt was to try a weaker acid, acetic, instead of hydrochloric. This gave unsatisfactory results since the precipitate would not readily entirely dissolve even though a large excess of acid was added to the portion titrated. But as the results were not high the procedure was modified by adding hydrochloric acid to dissolve the precipitate, being careful to exclude all air, then crystals of sodium acetate were introduced quickly to neutralize the hydrochloric acid and render the solution acid with acetic acid. After the solution contains only free acetic acid it may be exposed to the air without any danger of nitrite interference. The color never comes back. The end reaction is slightly slower in titration but not so as to appreciably lengthen the operation, simply requiring a little care not to overrun the end point. It was found that 2 cc. of hydrochloric acid, introduced at the bottom of the bottle to prevent the acidified solution coming in contact with air, was sufficient to dissolve all of the precipitate, and 4 grams of sodium acetate crystals would neutralize the excess of hydrochloric acid added and produce sufficient free acetic acid to bring about a proper reaction. As the crystals entrained air, it was feared that a slight error might be introduced in that way, but such did not

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[1] L. W. Winkler, *Ber. d. chem. Ges.*, **21**, 2843 (1888); **22**, 1764 (1889).

[2] Max Müller, *J. Soc. Chem. Ind.*, **8**, 923 (1889).

[3] S. Rideal and C. G. Stewart, *Analyst*, **26**, 141 (1901).

[4] Rideal and Burgess, *Ibid.*, **34**, 193 (1909).

[5] Sutton, "Volumetric Analysis," 10th Edition, p. 288.

seem to be the case as the solution contained free acetic acid before the air affected the nitrite. Pellets were compressed containing 4 grams of sodium acetate and tried also, but while the results were as accurate the pellets dissolved very slowly and introduced just as much air. The crystals were tried with the idea of displacing as little liquid as possible, but both crystals and pellets displace three cc. of solution for which correction must be made as it contains iodine previously set free by the hydrochloric acid. The following table gives the results of these experiments:

Table IV—Showing Results with Sodium Acetate Crystals

Nitrite p. p. m.	Acid used	Sodium acetate 4 grams	End reaction	Cc. N/100 thiosulfate per 100 cc.	Oxygen p. p. m.	Difference	Remarks
...	4 cc. HCl conc.(a)	....	......	11.15	9.05	..	Blank
1.0	Acetic conc.(a)	...	uncertain	11.00	8.93	—0.12	Failure
1.0	4 cc. HCl conc.(a)	crystals	returned	14.00	11.48	+2.43	Excess HCl
1.0	4 cc. HCl 1 : 1(a)	crystals	sharp	11.30	9.26	+0.21	
1.0	2 cc. HCl conc.(b)	crystals	sharp	11.00	9.02	—0.03	.....
...	4 cc. HCl 1 : 1(a)	....	....	10.90	8.85	—0.05	Blank
...	4 cc. HCl 1 : 1(a)	....	....	11.02	8.95	+0.05	Blank
...	4 cc. HCl 1 : 1(a)	crystals	sharp	10.85	8.90	..	Blank
1.0	4 cc. HCl 1 : 1(a)	crystals	sharp	11.24	9.22	+0.32	
0.5	4 cc. HCl 1 : 1(a)	pellet	sharp	11.00	9.02	+0.12	
1.0	4 cc. HCl 1 : 1(a)	pellet	sharp	11.22	9.20	+0.30	.....
2.0	4 cc. HCl 1 : 1(a)	pellet	sharp	11.15	9.14	+0.24	
5.0	4 cc. HCl 1 : 1(a)	pellet	sharp	11.03	9.05	+0.15	
...	2 cc. HCl conc.(b)	....	....	11.00	8.93	—0.09	Blank
...	2 cc. HCl conc.(b)	crystals	sharp	11.00	9.02	..	Blank
1.0	2 cc. HCl conc.(b)	crystals	sharp	10.65	8.74	—0.28	.....
1.0	2 cc. HCl conc.(b)	crystals	sharp	11.20	9.18	+0.16	Excess starch
1.0	2 cc. HCl conc.(b)	crystals	sharp	10.90	8.94	—0.08	Little starch
1.0	2 cc. HCl conc.(b)	crystals	sharp	11.05	9.06	+0.04	Careful end-point

(a) Acid added at top of bottle.
(b) Acid added at bottom of bottle.

It will be noticed that when the acid was added at the top of the bottle there was a slight tendency for a positive error. This was counteracted by adding the acid at the bottom of the bottle, as shown in last results.

Some of the above solutions were allowed to stand over night in contact with air and were then again titrated. All gave considerably lower results, not varying with the amount of nitrite, 1–5 p. p. m., but constant, showing a complete prevention of the nitrite reaction, and also showing that solutions acidified ready for titration should not stand in contact with air for several hours before titrating.

In order to further simplify the procedure a strong solution of potassium acetate (which is much more soluble than the sodium salt) was made by dissolving 100 grams of the crystals in 25 cc. of hot water and filtering. The crystals increased the volume to about 80 cc. At first this syrup was used. Later the syrup was diluted to 100 cc. This makes a stable solution, 1 cc. of which contains 1 gram of potassium acetate.

The following table shows the excellent results obtained in the presence of 1 p. p. m. nitrite with the use of this potassium acetate solution.

Table V—Showing Results with Potassium Acetate Solution

Nitrite p. p. m.	Acid used(b)	Potassium acetate solution	End reaction	Cc. N/100 thiosulfate per 100 cc.	Oxygen p. p. m.	Difference
	2 cc. HCl conc.	......	sharp	9.5	7.70	—0.03
	2 cc. HCl conc.	1 cc. = $1^1/_4$ grams	sharp	9.5	7.73	..
1	2 cc. HCl conc.	1 cc. = $1^1/_4$ grams	returned	9.5	7.73	±0.00
1	2 cc. HCl conc.	1 cc. = $1^1/_4$ grams	returned	9.7	7.90	+0.17
1	2 cc. HCl conc.	2 cc. = $2^1/_2$ grams	sharp	9.5	7.77	+0.04
1	2 cc. HCl conc.	2 cc. = $2^1/_2$ grams	sharp	9.3	7.61	—0.12
1	2 cc. HCl conc.	2 cc. = 2 grams	sharp	9.6	7.85	+0.12

(b) Acid added at bottom of bottle.

Note.—Since this paper was written the method has been used by the Sewer Bureaus of N. Y. City in a study of N. Y. harbor. Several hundred determinations have been made with nitrite sometimes as high as 2 p. p. m., with entire satisfaction.

EFFECT OF ORGANIC MATTER

It is also claimed that the Winkler method cannot give accurate results in the presence of organic matter. Hefelmann and Barth[1] make this criticism of Müller's method which appears to be identical with Winkler's. The same criticism has been made as to sewage.

The writers have found no appreciable difference in results to be caused by heavy microscopic growths in water, and the following experiments were undertaken to ascertain to what extent the results might be lowered by either oxidation or direct combination of iodine with the organic matter present in sewage. The sewage employed contained total solids 950 p. p. m., loss on ignition 340 p. p. m., fixed solids 610 p. p. m., chlorine 185 p. p. m., free ammonia 13.6 p. p. m., albuminoid ammonia 8.0 p. p. m., and was taken from a Brooklyn sewer at Atlantic Ave. and Clinton St.

In a preliminary experiment 0.1 cc. of N/100 iodine when added to 25 cc. of sewage containing 1 cc. each of manganous sulfate solution and concentrated hydrochloric acid gave a deep blue with starch solution which did not fade out in thirty minutes.

Bottles of 300 cc. capacity were then filled as for oxygen determination with the sewage, 2 cc. of manganous sulfate solution added, 2 cc. of concentrated hydrochloric acid, and then N/100 iodine added. After standing stoppered five and also thirty minutes, 100 cc. portions were titrated with N/100 thiosulfate. The loss of iodine, expressed as parts per million of equivalent oxygen, was inappreciable, at least not over 0.2 p. p. m. Upon standing in presence of air over night, even, no more iodine was used up apparently since an increased amount of iodine was present, due to the effect of the nitrite in the sewage.

The experiment was then tried in a different manner. The oxygen was determined in distilled water, the sewage, and mixtures of the two containing 10%, 25%, and 50% of sewage. These mixtures were obtained by filling the bottle with distilled water through a funnel, as previously described, and then adding by pipette at the bottom the required amount of sewage, forcing out distilled water at the top.

The results were within experimental error. The starch blue color returned after titration showing the presence of some nitrite but there was not sufficient to affect the accuracy of the results.

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[1] R. Hefelmann and K. Barth, *Chem. Ztg.*, **13**, 1337 (1889).

The experiment was repeated on 10% sewage mixtures containing an addition of 1 p. p. m. nitrite with and without the use of potassium acetate solution. As was to be expected, the results were high without the acetate and within experimental error with the acetate.

The following table gives the results of these experiments:

TABLE VI—SHOWING LACK OF EFFECT OF ORGANIC MATTER

Liquid	Cc. HCl conc.	Cc. K acetate, 1 cc. = 1 gram	Cc. mn. sulfate	Nitrite p. p. m.	Cc. *N*/100 iodine per 100 cc.	Time min.	Cc. *N*/100 thiosulfate per 100 cc.	Oxygen p. p. m.	Oxygen theory p. p. m.	Difference as oxygen	End reaction
Sewage........	2	..	2	..	2.3	5	2.00	..	..	—0.24	ret.
Sewage........	2	..	2	..	2.3	30	2.05	..	..	—0.20	ret.
Sewage........	2	..	2	..	4.6	5	4.75	..	..	+0.12	ret.
Dist. water....	2	..	2	..	..	..	9.60	7.80	7.80	..	sharp
Sewage 10%...	2	..	2	..	..	..	8.80	7.15	7.22	—0.07	ret.
Sewage 25%...	2	..	2	..	..	..	7.55	6.13	6.36	—0.23	ret.
Sewage 50%...	2	..	2	..	..	..	6.00	4.87	4.91	—0.04	ret.
Sewage 100%..	2	..	2	..	..	..	2.50	2.03	2.03	..	ret.
Sewage 10%...	2	..	2	1	..	..	9.85	8.00	7.22	+0.78	ret.
Sewage 10%...	2	1	2	1	..	..	9.15	7.45	7.22	+0.23	ret.
Sewage 10%...	2	2	2	1	..	..	8.45	6.91	7.22	—0.31	sharp

PRESERVATION OF SAMPLES

Some experiments were also carried out to determine the possibility of preserving samples of water for oxygen determination unchanged so that they may be transported to a laboratory for analysis. Birge and Juday[1] give some results on samples which stood up to six hours. They also quote Spitta,[2] Gill,[3] Seyler[4] and Dost,[5] that the oxygen does not change greatly in 24 hours, even with a 10° rise in temperature, with exposure to the air, and though the water become supersaturated.

TABLE VII—SHOWING RESULTS WITH USE OF BULB PIPETTE AND STORAGE

Source of sample	Time of standing	Temperature	Cc. *N*/100 thiosulfate per 100 cc.	Oxygen p. p. m.	Remarks
Mt. Prospect Res. 12 foot depth..............	......	15.5° C.	15.10	12.26	Supersaturated
Mt. Prospect Res. 12 foot depth..............	$1^1/_2$ hours	25° C.	14.40	11.73	Supersaturated
Mt. Prospect Res. 12 foot depth..............	18 hours	25° C.	13.00	10.56	Supersaturated
					8.35 saturation
Mt. Prospect Res. 12 foot depth..............	....	15.5° C.	15.95	12.95	10.04 saturation
Mt. Prospect Res. 12 foot depth..............	$1^3/_4$ hours	13° C. (icebox)	16.05	13.03	
Mt. Prospect Res. 12 foot depth..............	20 hours	13° C. (icebox)	15.55	12.63	
Gowanus canal..............................	2 hours	room	0.00	0.00	

From our experience it seems preferable to make determinations on the field, but satisfactory results may be obtained by using the device that D. D. Jackson[6] recommends for putrescibility bottles, that is, a medicine pipette passing through a rubber stopper. If the samples are below saturation with oxygen, the bulb may be collapsed and the sample transported without ice, but if the samples are saturated or supersaturated with oxygen the bulbs should be left filled with the water and the samples iced. The bulbs take care of the change in volume and thus prevent loosening of the stopper and consequent leakage of air. The icing holds the excess oxygen of supersaturated samples in solution. Samples of sewage should preferably be iced to prevent loss of oxygen by combination with the organic matter present, and also preserved by 1 cc. of 40% formaldehyde as recommended by A. Lederer.[1] The samples should be collected in the usual way by passing the water to be examined through the bottle until all water in contact with air is removed. The bulb should be filled with some of the same water from a dish and all air carefully forced out of the bulb with the pipette pointed upward. It is then quickly inserted in the filled bottle, which has been protected by a glass stopper until now, and either left full or collapsed according as the samples are iced or not, respectively. The effect of exposure to air of the water which fills the bulb is inappreciable, but the presence of any air bubbles would be serious.

Table VII gives some results with water so collected and stored.

The first three supersaturated samples lost oxygen upon storing at room temperature exposed to diffused daylight, although the sample kept 18 hours still contained more than 2 p. p. m. oxygen over saturation at room temperature. Bubbles of gas could be seen collected under the stopper.

The ice-box samples kept very well even though containing about three parts of oxygen over saturation. The three samples were of course taken separately at as near the same depth and spot as possible.

Samples low in oxygen keep perfectly without ice.

SUMMARY

I. Winkler's method for dissolved oxygen in water is very easy, rapid and accurate. Duplicate samples in routine work ordinarily check within 0.1 p. p. m. oxygen.

II. Nitrite as present in the usual run of waters has no appreciable effect upon the accuracy of the results.

III. Nitrite in quantities upward of 0.2 p. p. m. increases the results by a catalytic reaction, increasing with increasing amounts of nitrite.

IV. The effect of high nitrite present in any amount ever occurring in water may be counteracted by the use of potassium acetate solution (or sodium acetate crystals) to neutralize the hydrochloric acid before exposure to the air.

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[1] Birge and Juday, *Wisconsin Survey Bulletin*, **22**, 17, 18 (1911).

[2] Spitta, *Archives f. Hygiene*, **38**, 215 (1900).

[3] Gill, *Tech. Quart.*, **5**, 250 (1892).

[4] Seyler, *Chem. News*, **67**, 87 (1893).

[5] Dost, *Chem. Centralbl.*, **77**, 1457.

[6] D. D. Jackson and W. A. Horton, THIS JOURNAL, **1**, 328 (1909).

[1] Lederer, "The Influence of Storage and Various Preservatives upon the Dissolved Oxygen in Waters," Sewage Disposal Investigations, the Sanitary District of Chicago, 1910.

The procedure then is to add at the bottom of the bottle 2 cc. of manganous sulfate solution (480 grams per liter) followed by 2 cc. of potassium hydroxide-iodide solution (360 grams hydroxide and 100 grams iodide per liter). Shake and settle. Add at the bottom 2 cc. concentrated hydrochloric acid and shake until the precipitate is entirely dissolved. Then add 2 cc. potassium acetate solution (1000 grams per liter) at the bottom and mix. Withdraw by pipette 100 cc. into an Erlenmeyer flask and titrate with $N/100$ thiosulfate, adding a little starch solution at the end. Correction must be made for 6 cc. of water displaced by the first two solutions and by the acetate solution. The acid needs no correction, since it displaces only water from which oxygen has been removed.

Precautions must be taken to exclude contact with air as much as possible until the solution is ready to titrate by replacing the stopper as quickly as possible after each reagent is introduced; to get complete solution of the precipitate by the hydrochloric acid; to give the thiosulfate a little more time to react at the end point in the acetic acid condition; to use small amounts of starch solution. For introducing the solutions it is advisable to use pipettes with two marks, measuring 2 cc., well up on the pipette so as to give head and not contaminate the upper liquid in the bottle more than necessary while actually displacing liquid from the bottle in proportion to the amount introduced.

V. Samples for oxygen may be taken and transported elsewhere for titration in ground glass stoppered bottles with part of the chemicals added, either in alkaline or acid condition, if kept out of contact with air. The alkaline condition is preferable, since changes in temperature cannot change results, all the oxygen being in the precipitate. In either condition if air leaks in it may increase results, in alkaline condition by direct absorption, in hydrochloric acid condition by catalytic action of nitrite. It is not advisable to add the acetate until ready for titration.

Samples for oxygen may best be transported elsewhere for determination by using medicine pipettes. If samples are not saturated with oxygen, the bulbs should be collapsed and samples transported without ice; if supersaturated the bulbs should be full of the water and samples iced.

Acknowledgment is due Mr. W. A. Horton for assistance in many of the determinations.

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SULFUR DIOXIDE IN GELATINE[1]

By Paul Poetschke

Edible gelatin, according to the tentative standard prepared by the Committee on Food Standards of the Association of Official Agricultural Chemists, is the purified, dried, inodorous product of the hydrolysis, by treatment with boiling water, of certain tissues, as skin, ligaments, and bones, from sound animals, and contains not more than two (2%) per cent of ash and not less than fifteen (15%) per cent of nitrogen. It is used extensively in the preparation of various articles of food, such as jellies, jams, candy and ice cream, and it is, therefore, of importance to eliminate, as far as possible, all contaminating chemical substances.

Sulfur dioxide was formerly employed as a bleaching agent and also in the treatment of the raw materials used in the manufacture of gelatin, with the result that the finished product contains considerable quantities of this substance. It was not until the Food and Drugs Act of June 30, 1906 went into effect, that the attention of food chemists was seriously directed to the determination of this substance, not only in gelatin but also in other food materials such as wine, dried fruits and sugar products. The products in which sulfur dioxide was used were readily distinguishable on account of the considerable amounts present, but as the use of this substance was discontinued in all stages of manufacture, the problem became more difficult, since sulfur dioxide was still found in gelatin prepared without the use of this substance. The origin of the sulfur dioxide found by analysis, then became a recurring question and the opinion of many manufacturers and chemists was that the existing methods of analysis gave inconsistent and fallacious results. The main object of the present investigation was to determine the sources of error involved in the determination of sulfur dioxide and to develop a uniform and satisfactory method of analysis. Incidentally, the origin of the relatively small quantities of sulfur dioxide found in gelatin prepared without the addition of this substance was taken up.

EXPERIMENTAL PART—ANALYTICAL

Owing to the wide discrepancies which were observed in the determination of SO_2 in gelatin, when the same sample was analyzed by different chemists, an investigation of the cause of these discrepancies was undertaken. Much experimental work was required and, therefore, the various sources of error are taken up in detail.

In the distillation method, a known weight of the sample is dissolved in water and distilled, after the addition of phosphoric acid, in an atmosphere of CO_2. The distillate is collected in an excess of iodine and the iodine used up in oxidizing the SO_2 determined volumetrically or the resulting H_2SO_4 determined gravimetrically as $BaSO_4$. Bromine water is also used as an oxidizing agent, but in this case the gravimetric method is employed.

I—ADVANTAGES OF GRAVIMETRIC OVER VOLUMETRIC METHOD

The gravimetric method of estimation of the sulfuric acid formed is the best method, since the volumetric method, in which the excess iodine is titrated with a solution of sodium thiosulfate, is subject to considerable error owing to the possible presence of reducing substances other than SO_2, which may come over with the distillate. A comparison of the gravimetric and the official volumetric method[1] on a sample of gelatin gave the following result:

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[1] Presented at the 48th meeting of the A. C. S., Rochester, September 8–12, 1913.

[1] U. S. Dept. of Agric., Bur. of Chemistry, *Bull.* **107**.

	Gravimetric Per cent	Volumetric Per cent
Sulfur dioxide	0.0085	0.0102

Owing to the fact that the sample contained a small quantity of SO_2, a $N/50$, instead of a $N/10$, iodine solution was used. This sample was selected for this purpose since the influence of reducing substances is rendered more apparent when the SO_2 is low. The result on this sample demonstrates that reducing substances are evolved and that these are a source of error to be avoided. It has been repeatedly observed that the iodine containing distillates becomes turbid, in some cases the cloudiness is very marked, and this in itself is evidence of the fact that the error introduced will depend entirely upon the nature of the sample under examination.

II—HYDROCHLORIC ACID USED FOR GENERATING CARBON DIOXIDE

Commercial HCl is frequently used for generating CO_2 from marble. It is absolutely necessary to use chemically pure acid for this purpose since the commercial acid contains free chlorine. In a number of experiments it was found that free chlorine could be detected in the distilling flask by means of starch iodide when commercial HCl was used, even though the CO_2 was washed by bubbling through a wash bottle containing dilute copper sulfate solution. The free chlorine would naturally oxidize an equivalent amount of SO_2 in accordance with the following equation:

$$SO_2 + 2H_2O + 2Cl = H_2SO_4 + 2HCl.$$

III—ADVANTAGES OF IODINE OVER BROMINE

In the gravimetric determination of SO_2, iodine is preferable to bromine since it does not oxidize H_2S to H_2SO_4. Horne[1] separated the H_2S by passing the distillate through a 2 per cent neutral solution of cadmium chloride and states that the SO_2 is not precipitated but passes on to the iodine, where it is oxidized to H_2SO_4, to be afterwards precipitated as $BaSO_4$. The fact is that when the gravimetric method is employed using iodine as the oxidizing agent, it is not necessary to remove H_2S. This is, however, a necessary precaution when the volumetric method is used. When H_2S is passed into an iodine solution the following reaction takes place:

$$H_2S + 2I = 2HI + S.$$

Two experiments were conducted in order to verify this reaction, especially as to the possibility of oxidizing some of the H_2S to H_2SO_4.

1. 50 cc. of $N/20$ iodine solution were diluted to 200 cc. with distilled water and a current of H_2S passed into the solution until it was decolorized; 5 cc. of concentrated HCl were then added, the solution concentrated to about 75 cc. by boiling, filtered and precipitated with $BaCl_2$. $BaSO_4$ obtained = 0.0023 gram.

2. This experiment was conducted in the same manner except that the HCl was added before passing in H_2S. $BaSO_4$ obtained = 0.0020 gram.

A blank determination conducted by diluting 50 cc. of iodine solution to 200 cc. with water and boiling down to 75 cc., filtering and precipitating with $BaCl_2$, gave 0.0008 gram of $BaSO_4$.

Taking the average $BaSO_4$ obtained in Experiments 1 and 2 and deducting the blank, we have 0.0014 gram of $BaSO_4$, equivalent to 0.0004 gram of SO_2. Considering the quantity of H_2S passed through the iodine and also the fact that no attempt was made to purify the gas, it is evident that the amount of $BaSO_4$ is negligible and that these facts show that none of the H_2S is oxidized to H_2SO_4.

When H_2S is passed into a solution of bromine, sulfur is first precipitated but further oxidation to H_2SO_4 takes place. This was verified by diluting 50 cc. of saturated bromine water to 200 cc. with water and passing in H_2S until the solution was decolorized. The liquid was then acidified with 5 cc. of HCl, concentrated to 75 cc. by boiling, filtered and precipitated with $BaCl_2$. A heavy precipitate of $BaSO_4$ was obtained, indicating that bromine water oxidizes H_2S to H_2SO_4.

That bromine oxidizes H_2S and other volatile sulfur compounds, thus yielding high results for SO_2, is evident from the following experiment: A pound of fresh round steak was freed from fat and passed through a meat chopper. A determination of SO_2 on the same day by the gravimetric-iodine method gave two (2) parts of SO_2 per million. The meat was allowed to decay and on the fourth day another determination by the same method gave six (6) parts per million. On the ninth day the meat had a strongly ammoniacal odor. Two determinations were made, one by the gravimetric iodine method and the other by substituting saturated bromine water for the iodine solution. Blank determinations were made in both cases. The following results were obtained:

	Sulfur dioxide in parts per million
With iodine	11
With bromine	37

Winton and Bailey[1] obtained similar results by distillation of beef which was allowed to decompose. They collected the distillate in bromine after first passing through a dilute solution of copper sulfate in order to remove sulfides and mercaptans, the resulting copper sulfide being weighed and reported as H_2S. In two separate series of experiments on beef which was allowed to decompose for nine days (calculating their H_2S figures to SO_2) they obtained as follows:

	Sulfur dioxide in parts per million	
	1	2
Obtained by copper sulfate	38	8
Obtained by bromine	12	10
Total,	50	18

The authors found that the amount of sulfur as H_2S was larger than the amount of sulfur as SO_2, especially in the case of veal.

It is, therefore, obvious that iodine is preferable to bromine since it is not necessary to pass the distillate through a solution of a metallic salt, such as copper sulfate or cadmium chloride, in order to remove sulfides when iodine is used.

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[1] "The Chemical Determination of Sulfites in Sugar Products," U. S. Dept. Agr., Bur. of Chemistry, *Bull.* **105**.

[1] *J. Am. Chem. Soc.*, **29**, 1499 (1907).

IV—DISSOLVING THE GELATIN

The fact that gelatin is insoluble in cold water, but swells up in it, and is readily soluble in hot water, naturally leads some analysts to use hot water in order to facilitate solution and to prevent the flask containing the mixture of gelatin and water from breaking, which frequently results if the flask is heated directly over a small flame before the gelatin is completely dissolved. The addition of hot water, although the flask is quickly stoppered, causes a loss of SO_2. The results of three determinations on a sample of gelatin which was finely ground and well mixed, gave the following:

Per cent sulfurous acid	*a.* 0.0350
	b. 0.0350
	c. 0.0355

The same sample of gelatin was treated in exactly the same way, except that instead of adding cold, recently boiled distilled water, hot water was used, the flask connected to the apparatus and the usual distillation carried out. It usually required from five to ten minutes to dissolve the gelatin and during this time the flask was stoppered. The loss of SO_2 incurred by this treatment is apparent from the following three determinations:

Per cent sulfurous acid	*a.* 0.0247
	b. 0.0265
	c. 0.0212

The above results show that a loss of from 25 to 40 per cent of the total sulfurous acid occurs when hot water is used to dissolve the gelatin. The same sample of gelatin was sent to a large commercial laboratory and the following result was reported:

Per cent sulfurous acid = 0.0173.

It appears highly probable that hot water was used in this case to dissolve the gelatin, since the determination shows a loss of about 50 per cent of the total sulfurous acid.

V—CONCENTRATION OF THE DISTILLATE

Zerban and Naquin,[1] in their work on sulfurous acid in molasses, call attention to the fact that if it is necessary to concentrate the distillate, this should be done in flasks with narrow openings when gas is used as a source of heat for concentrating the distillate.

Kühn and Rühle[2] have conducted a series of experiments in which it was shown that when a solution of iodine is boiled over a gas burner in a beaker, contamination from the products of combustion of the illuminating gas takes place and this gives rise to serious errors. The conclusion is drawn that the SO_2 obtained in the distillation of meat is not due to its formation from sulfur compounds but to contamination from the surrounding atmosphere.

Repeated blank determinations, run on successive days, demonstrated that a variable contamination with sulfur took place, since careful tests of the reagents used failed to account for the $BaSO_4$ obtained in the blanks. The following experiments were conducted in order to trace this source of error:

Several blank determinations were made by placing 300 cc. of recently boiled and cooled distilled water in the distilling flask (Fig. 1), phosphoric acid added and distilled in a current of CO_2, collecting 200 cc. of distillate in a beaker containing 25 cc. of $N/10$ iodine solution. The beaker was kept closely covered with a clock glass provided with a hole in the center so as to fit over the exit tube of the condenser. The contents of the beaker were then acidified with 5 cc. of concentrated HCl, the solution boiled to expel the iodine and precipitated with 10 cc. of $BaCl_2$ solution. After standing over night the precipitate was filtered off and weighed as $BaSO_4$.

Number	Date of experiment	Gram of barium sulfate obtained
1	Nov. 14, 1910	0.0045
2	Nov. 30, 1910	0.0054
3	Nov. 30, 1910	0.0067
4	Oct. 15, 1910	0.0016
5	Oct. 15, 1910	0.0016

Experiments 2 and 3 were run side by side, and including 1, on the same iodine solution. Experiments 4 and 5 were run on a new iodine solution.

The following experiments were conducted by direct precipitation, that is, 25 cc. of iodine solution, used in 4 and 5, were diluted to 100 cc., 5 cc. of concentrated HCl added, boiled to expel the iodine, and precipitated with $BaCl_2$. Experiments 6 and 7 were run simultaneously, and 8 on the following day.

Number	Date of experiment	Gram of barium sulfate obtained
6	Oct. 15, 1910	0.0055
7	Oct. 15, 1910	0.0057
8	Oct. 16, 1910	0.0039

Two blank determinations were made using in one case a closely covered beaker as a receiver and in the second, the special "beaker-flask" shown in Fig. 1. The results were as follows:

Receiver	Gram barium sulfate obtained
Beaker........................	0.0017
	0.0052
"Beaker-flask".................	0.0004
	0.0004
	0.0005

Table I gives a series of results, obtained by both methods, on samples of gelatin.

TABLE I

Sample No.	Barium sulfate Total		Barium sulfate Blank		Per cent sulfur dioxide in sample	
	Flask	Beaker	Flask	Beaker	Flask	Beaker
59344	0.0040	0.0117	0.0004	0.0052	0.0036	0.0065
59406	0.0041	0.0085	0.0004	0.0031	0.0037	0.0054
59551	0.0011	0.0043	0.0005	0.0037	0.0006	0.0006
59622	0.0014	0.0137	0.0004	0.0128	0.0010	0.0009
59647	0.0026	0.0103	0.0004	0.0049	0.0022	0.0054
59648	0.0015	0.0043	0.0005	0.0025	0.0010	0.0018
59800	0.0036	0.0164	0.0004	0.0078	0.0032	0.0086
59846	0.0045	0.0147	0.0009 ?	0.0135	0.0036 ?	0.0012
60008	0.0066	0.0127	0.0004	0.0057	0.0062	0.0070
60009	0.0049	0.0056	0.0004	0.0033	0.0045	0.0023

It is evident that the blank determinations made by collecting the distillate in beakers show very divergent results, whereas those collected in the "beaker-flasks" show excellent agreement, with the exception of the result on Sample 59846, in which case the blank is evidently too high, no doubt owing to accidental error since all of the determinations were conducted on the same iodine solution. While good agreement was obtained in several instances for percentage of SO_2 in the gelatin by both flask and "beaker-flask" when the corresponding blanks were deducted from the total $BaSO_4$, it is impossible, even under these condi-

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[1] F. Zerban and W. Naquin, U. S. Dept. of Agriculture, Bureau of Chemistry, *Bull.* **116**.

[2] *Z. Nahr. Genussm.*, **20**, 10–9.

tions, when running blanks side by side, to obtain uniformly satisfactory results. It is, therefore, evident that the somewhat prevalent custom of running a blank once a day, or even that of running a blank with each determination, cannot be relied upon to give sufficiently accurate results when beakers are used to collect and concentrate the distillate. The uniformity of the blank results obtained with the "beaker flasks" demonstrates that contamination from the surrounding atmosphere is obviated in this case and it is, therefore, necessary to run a blank only with each change in the reagents.

The following duplicate determinations on two samples of gelatin show the uniformity of results obtained by providing against contamination from the surrounding atmosphere:

TABLE II

Sample number		Barium sulfate Total	Barium sulfate Blank	Per cent sulfur dioxide in sample
63181	*a*	0.0155	0.0004	0.0151
	b	0.0146	0.0004	0.0142
63182	*a*	0.0260	0.0004	0.0256
	b	0.0263	0.0004	0.0259

VI—COMPARISON OF STEAM DISTILLATION AND DIRECT DISTILLATION

Gudeman[1] recommends distillation with steam in order to eliminate errors arising from decomposition due to concentration of the mass during distillation, on the ground that many food products normally contain sulfur compounds which yield volatil sulfur compounds on distillation with acids and that these are increased with corresponding increase in acidity and concentration of the mass.

A number of analyses were made in order to determine whether it is necessary to observe this precaution in the case of gelatin. In all cases the distillation was conducted in a current of carbon dioxide, using steam in one case and heating directly with a Bunsen burner, as in the usual method, in the analyses made for comparison. The same volume of distillate was collected in both methods. Table III gives the results of these determinations.

TABLE III

Sample number	Percentage sulfur dioxide by distillation				Variation from steam distillation
	With steam		Without steam		
26226	*a*	0.1661	*a*	0.1723	+0.0034
	b	0.1678	*b*	0.1570	
			c	0.1707	
	Average =	0.1669	Average =	0.1703	
26227	*a*	0.0885	*a*	0.0886	+0.0017
	b	0.0862	*b*	0.0894	
	Average =	0.0873	Average =	0.0890	
26229		0.0277		0.0252	—0.0025
25915		0.0375		0.0374	—0.0001
26795		0.0618		0.0637	+0.0019
26796		0.0247		0.0257	+0.0010
26797		0.0130		0.0121	—0.0009
26798		0.0504		0.0516	+0.0012
26890		0.2732		0.2749	+0.0017
26885		0.0812		0.0828	+0.0017
26884		0.1084		0.1098	+0.0014
60232		0.0009		0.0000	—0.0009
60233		0.0000		0.0002	+0.0002
60234		0.0000		0.0010	+0.0010
60471		0.0027		0.0014	—0.0013
60419		0.0057		0.0072	+0.0015
61420		0.0026		0.0024	—0.0002
62123		0.0032		0.0042	+0.0010
62124		0.0048		0.0052	+0.0004

The above analyses were conducted on routine samples of gelatin and it is very likely that the variations in the two methods are due to lack of uniformity in the samples. The variations occur in both directions and are not of sufficient magnitude to indicate that distillation with steam is necessary in the case of gelatin.

VII—RECOVERY OF KNOWN AMOUNTS OF SULFUR DIOXIDE

A number of experiments were made by distilling known amounts of sodium sulfite solution under the conditions observed in the regular method. It was necessary to prepare a solution of sodium sulfite and to measure aliquot portions, for standardization and distillation, at the same time so as to avoid oxidation. The standardization of the sulfite solution was carried out by titration in an atmosphere of CO_2, adding the sulfite solution to an excess of iodine and titrating the excess of iodine with sodium thiosulfite. The following results were obtained:

Sulfur dioxide by titration Gram	Sulfur dioxide by gravimetric determination after distillation Gram
0.0145	0.0145
0.0183	0.0170
0.0218	0.0207
0.0218	0.0206
0.0487	0.0482
0.0487	0.0477

VIII—METHOD OF CARRYING OUT THE DETERMINATION OF SULFUR DIOXIDE IN GELATIN

Apparatus Required.—Fig. 1 shows the apparatus and its arrangement in detail. Two units are represented, providing for two determinations which can be conducted at the same time. A Woulff bottle having two necks and an outlet at the bottom, fitted with a cylindrical open top, glass stoppered, long stem funnel, is used for generating the CO_2. The outlet tube at the bottom of the Woulff bottles is connected to a long tube leading to a reservoir for receiving the spent acid which is drawn off by opening the pinchcocks as required. The aforementioned

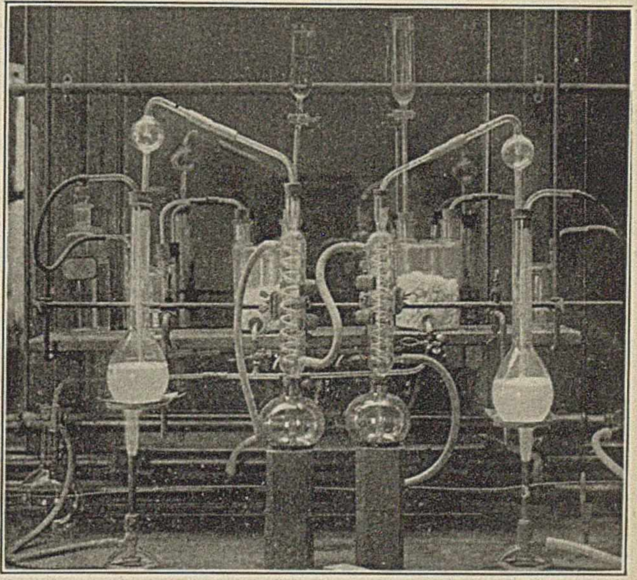

FIG. 1

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[1] THIS JOURNAL, 1, 81.

Woulff bottle is connected to a smaller one provided with two necks, this bottle serving to wash the CO_2. The wash bottle is connected to the distilling flask, consisting of a long neck Kjeldahl flask of 500 cc. capacity, by means of a glass tube reaching to within $^1/_2$ inch of the bottom of the flask. The distilling flask is connected to the condenser through a Hopkins bulb. The glass tubes at the rubber connection are brought closely together and the tube leading into the condenser is extended so as to lead directly into the worm of the condenser. A special condenser was designed for this purpose, consisting of an eight-inch worm condenser provided with an exit tube 4 inches in length and $^3/_8$ inch internal diameter, so as to give a sufficient length of tube without requiring additional connections. The inlet tube of the condenser is $2^1/_2$ inches in length and $^3/_4$ inch internal diameter, and permits of convenient connection with the distilling bulb by means of a rubber stopper. A special receiving flask was designed, to serve also as a flask for concentrating the distillate and for precipitation of the H_2SO_4. The main advantages of this "beaker-flask" have been discussed under V, but it is also efficient in avoiding contamination with sulfurous gases while the distillate is being collected and does not require transferring of the distillate to another receptacle for concentration. The flask is connected to the condenser by means of a paraffined flat cork having a small angular slit in the side to allow for the escape of the carbon dioxide. The "beaker-flask" has a capacity of 400 cc. and is 4 inches high. It is provided with a lipped neck $^3/_4$ inch high and $^3/_4$ inch in diameter.

Reagents Required.—1. Ordinary white marble broken into pieces small enough to pass through the neck of the Woulff bottle.

2. HCl for generating the CO_2. Chemically pure concentrated HCl is diluted with an equal volume of water. Commercial HCl must not be used, owing to the presence of excessive amounts of free chlorine.

3. Phosphoric acid. Glacial phosphoric acid in sticks is broken into pieces weighing approximately 5 grams each.

4. Iodine solution. A $N/20$ solution.

5. HCl for acidifying the distillate. Chemically pure concentrated HCl.

6. $BaCl_2$. An approximately $N/5$ solution, which should be perfectly clear and free from sediment.

7. Recently boiled and cooled distilled water.

NOTE.—Duplicate blank determinations are conducted on the reagents using the same amounts as in an actual analysis of gelatin. A label bearing the result of this standardization is placed on the iodine bottle and a corresponding correction is made in every determination. Two liters of iodine solution and a corresponding amount of the other reagents, except the distilled water, are set aside at one time for a series of analyses.

Determination.—Twenty-five cubic centimeters of iodine solution are measured into the receiving flask and the flask is connected to the condenser so that the end of the condenser reaches below the surface of the solution.

Twenty-seven and one-half grams of gelatin are weighed into the distilling flask and 300 cc. of distilled water added, together with a piece of phosphoric acid. The flask is then connected to the apparatus and the air is displaced by CO_2 generated by allowing the dilute HCl to fall upon the marble. The rate of flow of CO_2 is easily regulated by adjusting the flow of acid. When the air has been displaced, the gelatin is liquefied by immersing the flask in boiling water contained in a sauce pan, and the water is kept boiling until the gelatin is completely dissolved. Solution of the gelatin is facilitated by frequently agitating the flask by means of a rotary motion. When the gelatin is completely dissolved, the boiling water bath is removed, the flask dried and heat applied directly with a Bunsen burner.

A current of CO_2 is allowed to flow through the apparatus until the distillation is completed. When 200 cc. of distillate have been collected, the apparatus is disconnected, the receiver lowered and the condenser rinsed with a little hot distilled water.

After adding 5 cc. of concentrated HCl to the distillate, it is concentrated by boiling to approximately 75 cc., using a Bunsen burner. The solution is then filtered into a clean "beaker-flask," the filter and receiver being thoroughly washed with hot distilled water. The filtered solution is then heated to boiling and 10 cc. of $BaCl_2$ solution slowly added, stirring continuously. The flask is lightly stoppered with a clean cork and allowed to stand over night on a steam bath.

On the following morning the solution is decanted through a 9 cm. blue ribbon ashless filter paper, the precipitate then washed onto the filter and completely removed from the flask with the aid of a rubber tipped rod bent in an angle so as to reach the sides of the flask. The filter is then washed with hot distilled water until the washings are free from chlorides. The filtrate should be perfectly clear and it is advisable to allow the solution to stand on a steam bath for about one hour, when by giving the solution a rotary motion, even traces of precipitate will collect in the center of the flask. If no precipitate appears, the $BaSO_4$ obtained in the first filtration is ready for ignition; otherwise the solution must be refiltered.

The filter paper, containing the $BaSO_4$, is removed from the funnel, at the same time wiping off any trace of precipitate which may have crept over the paper, and it is then placed in a weighed platinum crucible. The paper is ashed, the crucible allowed to cool and the precipitate treated with a drop of pure concentrated H_2SO_4 in order to convert any barium sulfide, which may have been formed by reduction, to $BaSO_4$. After expelling the excess of H_2SO_4, the crucible is heated to a bright red for five minutes, cooled in a desiccator and weighed. The treatment with H_2SO_4 is repeated until a constant weight is obtained. The blank obtained on the reagents is deducted from this weight and the difference gives the percentage of SO_2 in the sample.

NOTE.—27.5 grams of the sample are used, since the weight of $BaSO_4$ obtained directly gives the percentage of SO_2 without further calculation. It is not necessary to weigh this sample closer than to 0.1 gram.

ORIGIN OF SULFUR DIOXIDE IN GELATIN

I—EFFECT OF DISTILLATION OR POSSIBLE LIBERATION OF VOLATIL SULFUR COMPOUNDS

Alexander,[1] in a paper on the determination of sulfur dioxide in gelatin, considered it likely that some of the organic sulfur in the gelatin is carried over, in the form of volatil sulfur compounds, when distilled with phosphoric acid in a current of CO_2. He also considered it probable that the time and intensity of heating and the concentration of the solution influenced the quantity which appeared in the distillate. This subject has already been discussed in part in connection with steam distillation and direct distillation, but the following experiments have a more direct bearing on the effect of time and intensity of heating:

1. 27.5 grams of gelatin were dissolved in 300 cc. of water and heated in an autoclave at 20 lbs. pressure for 30 minutes. After the addition of phosphoric acid the flask was connected to the distillation apparatus and the amount of SO_2 determined in the usual manner. The result of this determination, expressed in per cent by weight of the original gelatin, was 0.0007 against 0.0013 in the original sample, thus showing a loss of SO_2.

2. Same as Experiment 1, except that the solution was heated for one hour in the autoclave at 20 lbs. pressure. The amount of SO_2 found was 0.0002 per cent, showing a still greater loss of SO_2.

3. Same as Experiment 1, except that the solution was heated for two hours in the autoclave at 20 lbs. pressure. In this experiment 0.0003 per cent of SO_2 was obtained, practically the same amount as found in Experiment 2.

It is evident from these experiments that the heating of the gelatin solution in an unstoppered flask in the autoclave resulted in a loss of SO_2. As the time of heating was increased, the gelatin lost considerably in gelatinizing power and deposited a grayish coagulum. The sample of gelatin selected for this experiment contained an exceptionally small amount of SO_2, the object being to determine whether the heating, in the absence of phosphoric acid, caused a cleavage of the gelatin which would render it more susceptible to attack and possible liberation of volatil sulfur compounds on distillation with phosphoric acid.

4. A fourth experiment was conducted in which 27.5 grams of the same gelatin used in the previous experiments was placed in the distilling flask of the apparatus (Fig. 1), 300 cc. of water added, acidified with phosphoric acid and distilled in the usual manner, collecting 200 cc. of distillate in iodine. By means of a separatory funnel, attached to the distilling flask, 200 cc. of water were added to the residue in the distilling flask, thus replacing the volume of water collected in the distillate: 200 cc. of distillate were again collected in a receiver containing a fresh supply of iodine. This operation was repeated once more, three successive distillates being collected. The amount of SO_2 found in each distillate, expressed in per cent by weight of the original gelatin, was as follows:

Distillate I = 0.0014%
Distillate II = 0.0001%
Distillate III = 0.0000%

This experiment shows that prolonged heating in the presence of phosphoric acid, with the resultant increase in concentration and acidity, does not cause a dissociation of the organic sulfur of the gelatin with liberation of volatil sulfur compounds which are oxidized to H_2SO_4 by iodine.

The fact that 16 samples, out of over 1000 samples, were found to contain absolutely no SO_2 is convincing evidence that dissociation of the natural sulfur in gelatin, with liberation of volatil sulfur compounds oxidizable to H_2SO_4 by iodine, does not occur under the conditions observed in the determination of SO_2.

It is interesting to note that the only sulfur-containing dissociation-product obtained so far from gelatin[1] by Harbaczewski,[1] is H_2S. Even if this were liberated under the analytical conditions, it would not be oxidized to H_2SO_4 by the iodine solution.

II—SIGNIFICANCE OF SULFUR DIOXIDE IN GELATIN FOR BACTERIOLOGICAL PURPOSES

The fact that the heating of a solution of gelatin under pressure results in a loss of SO_2 is of interest in connection with the preparation of nutrient media for bacteriological work. A sample of sheet gelatin which contained 0.1108 per cent of SO_2 was used to prepare a quantity of nutrient media. Twenty tubes of the preparation, containing in all 26.04 grams of the original gelatin, were analyzed for SO_2 with the following result:

	Found Per cent	Calculated from original SO_2 content of gelatine Per cent
SO_2 in nutrient media.............	0.0009	0.0133

The loss in SO_2 which resulted in the process of preparation was, therefore, 93 per cent of the original content of SO_2. Another preparation from the same gelatin contained 0.0006 per cent of SO_2 which corresponds to a loss of 95 per cent. Leffmann and LaWall[2] have reported the SO_2 content of two samples of imported gelatin, used largely for bacteriological work, as 265 and 835 parts per million and believe that such gelatin is unsuitable for culture medium. They suggest that bacteriologists establish a strict standard for gelatin. The above results on a culture medium prepared from a gelatin containing 1108 parts of SO_2 per million, indicate that this precaution is unnecessary and also account for the fact that bacteriologists have not experienced difficulty when employing media prepared with such gelatin.

III—OCCURRENCE OF SULFUR DIOXIDE IN GELATIN PREPARED FROM RAW MATERIALS FREE FROM SULFUR DIOXIDE

A number of experiments were conducted in which two samples of gelatin were prepared in the laboratory. The bones used for this work were obtained from a calf which was killed in the laboratory in connection with another investigation, so that there was no question as to the origin of the raw material. The bones were carefully freed from adhering meat, chopped into small pieces, thoroughly washed, and 3133 grams were then digested for three days with four times their weight of HCl (sp. gr. 1.15). The material was then washed free from acid, covered with a saturated solution of calcium hydrate and allowed to stand for three

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[1] *J. Am. Chem. Soc.*, **29**, 783.

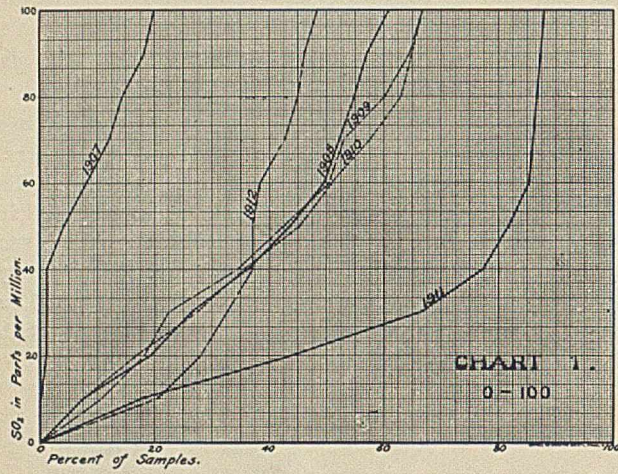
[1] Gustav-Mann, "Chemistry of the Proteids," **1906**, p. 562.

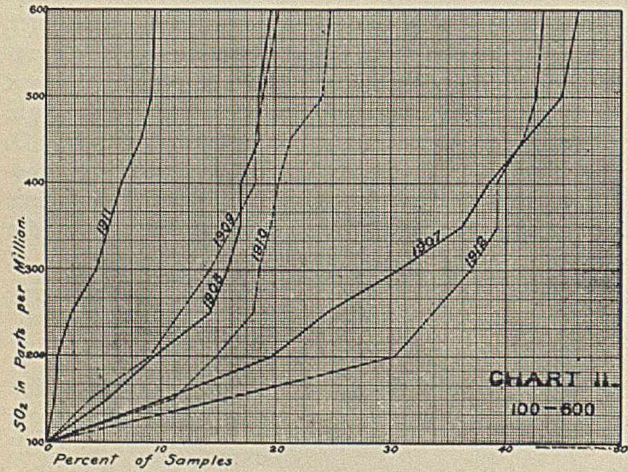
[2] *Analyst*, **36**, 271.

days. The material was then thoroughly washed and pressed to remove as much water as possible. The resulting wet "stock" weighed 1589 grams and this was divided in three portions for the following experiments:

1. The wet "stock" was dried in a current of air and when air-dry it weighed 228 grams, thus showing 57 per cent of water lost from the original to the air-dry condition. A determination of SO_2 on this air-dry material gave 0.0006 per cent.

2. The wet "stock" was digested with three times its weight of water for 30 minutes in an autoclave at 22 lbs. pressure, which gave a transparent solution. This was poured into a glass tray in which it gelatinized on cooling. This jelly was superficially dried in a current of air from an electric fan and then removed to a wire netting to complete the drying. The entire drying was conducted in a room separated from the main laboratory so as to avoid unusual contamination with sulfurous gases. An analysis of the air-dried product gave 0.0189 per cent of SO_2.



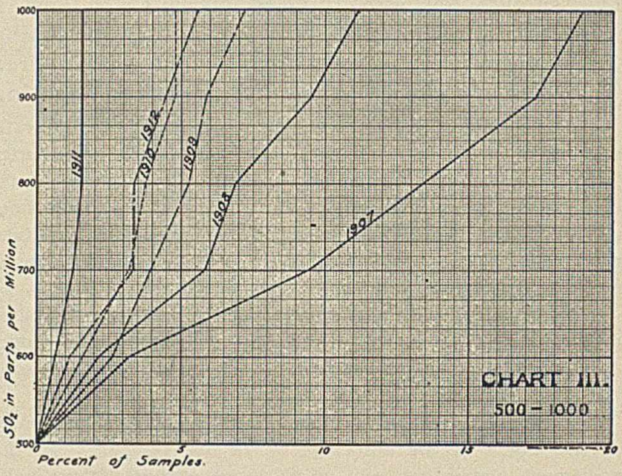


3. This portion was digested with the same amount of water, as in the case of Experiment 2, for 5 hours under reduced pressure, but solution took place so slowly that it was necessary to place the mixture in an autoclave. After 50 minutes' heating at 19 to 22 lbs. pressure, the solution was poured into a tray and then dried as in the case of Experiment 2. An analysis of this product gave 0.0199 per cent of SO_2.

These experiments show that the SO_2 could only have been absorbed from the air passed over the jelly during the drying. The dry "stock" contained but traces of SO_2 which in all probability was also absorbed in the drying. Gas burners were used occasionally in the room where the drying process was carried out and this undoubtedly augmented the SO_2 content. Both products were free from odors of decomposition, so that bacterial influences were not responsible for the rather high SO_2 content.

SULFUR DIOXIDE CONTENT OF COMMERCIAL GELATIN

A large number of samples of commercial gelatin obtained from various sources have been examined in this laboratory. These products include domestic and foreign gelatins and represent the materials produced by more than twenty different manufacturers. From 1907 to 1912 inclusive, 1060 samples were examined. A tabulation of the individual analyses would be unnecessarily burdensome and, therefore, the results have been arranged in groups, expressing the SO_2 content in parts per million and giving the percentage of samples found within various limits during the years 1907 to 1912 inclusive. Table IV gives the percentage of samples within these limits and Table V gives the same results tabulated in four groups so as to show the total percentage of samples occurring within the limits given for the different groups. In Charts I to IV the data contained in Table V are represented graphically.



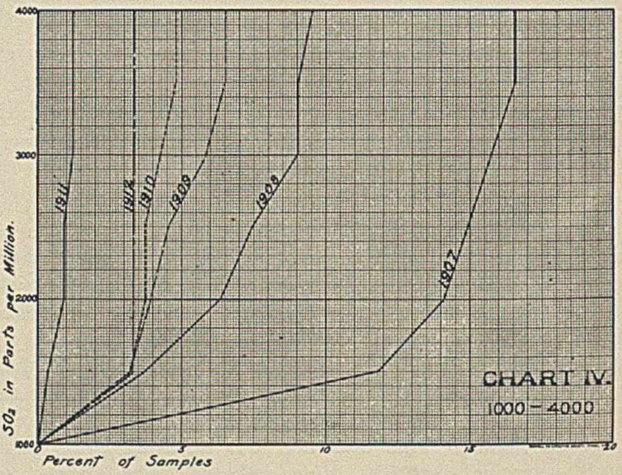


TABLE IV

SO_2 Parts per million	Percentage of samples					
	1907	1908	1909	1910	1911	1912
0– 10	0.00	7.45	10.45	7.45	17.46	20.22
10– 20	0.78	11.70	7.84	9.09	26.35	7.86
20– 30	0.00	7.45	5.23	10.64	22.85	4.49
30– 40	0.00	9.56	11.11	9.50	10.47	4.49
40– 50	3.15	7.45	7.84	9.56	4.76	0.00
50– 60	3.93	5.85	7.84	5.32	3.17	1.12
60– 70	3.93	2.66	2.62	6.92	0.95	4.49
70– 80	2.36	2.66	7.19	5.32	0.63	2.24
80– 90	3.93	2.12	4.57	2.12	0.63	1.12
90– 100	1.57	3.72	1.95	1.60	0.63	2.24
100– 150	10.23	5.32	3.90	11.17	0.63	15.73
150– 200	9.45	4.25	5.23	3.72	0.31	14.60
200– 250	4.72	4.78	2.62	3.20	1.26	3.36
250– 300	6.30	1.60	2.62	0.53	2.22	3.36
300– 350	5.51	1.06	1.95	1.06	0.95	2.24
350– 400	2.36	0.00	1.95	0.53	1.26	0.00
400– 450	3.15	1.60	0.00	1.06	1.58	2.24
450– 500	3.15	0.00	0.65	2.66	0.95	1.12
500– 600	3.15	2.12	2.62	1.60	0.63	1.12
600– 700	6.30	3.72	1.31	1.60	0.63	2.24
700– 800	3.93	1.06	1.31	0.53	0.31	0.00
800– 900	3.93	2.66	0.65	1.06	0.00	1.12
900–1000	1.57	1.60	1.31	0.00	0.00	1.12
1000–1500	11.81	3.72	3.26	3.20	0.31	3.36
1500–2000	2.36	2.66	0.65	0.53	0.63	0.00
2000–2500	0.78	1.06	0.65	0.00	0.00	0.00
2500–3000	0.78	1.60	1.31	0.53	0.31	0.00
3000–3500	0.78	0.00	0.65	0.53	0.00	0.00
3500–4000	0.00	0.52	0.00	0.00	0.00	0.00
Above 4000	0.00	0.00	0.65(*a*)	0.00	0.00	0.00

(*a*) Contained 0.7410 per cent, or 7410 parts per million.

TABLE V

SO_2 Parts per million	Percentage of samples					
	1907	1908	1909	1910	1911	1912
0– 10	0.00	7.45	10.45	7.45	17.46	20.22
0– 20	0.78	19.15	18.29	16.54	43.81	28.08
0– 30	0.78	26.60	23.52	27.18	66.66	32.57
0– 40	0.78	36.16	34.63	35.62	77.13	37.06
0– 50	3.93	43.61	42.47	45.19	81.89	37.06
0– 60	7.86	49.46	50.31	50.51	85.06	38.18
0– 70	11.79	52.12	52.93	57.43	86.01	42.67
0– 80	14.15	54.78	60.12	62.75	86.64	44.91
0– 90	18.08	56.90	64.69	64.87	87.24	46.03
0– 100	19.65	60.62	66.64	66.47	87.90	48.27
100– 150	10.23	5.32	3.90	11.17	0.63	15.73
100– 200	19.68	9.57	9.13	14.89	0.94	30.33
100– 250	24.40	14.35	11.75	18.09	2.20	33.69
100– 300	30.70	15.95	14.37	18.62	4.42	37.05
100– 350	36.21	17.01	16.32	19.68	5.37	39.29
100– 400	38.57	17.01	18.27	20.21	6.63	39.29
100– 450	41.72	18.61	18.27	21.27	8.21	41.53
100– 500	44.87	18.61	18.92	23.93	9.16	42.65
500– 600	3.15	2.12	2.62	1.60	0.63	1.12
500– 700	9.45	5.84	3.93	3.20	1.26	3.36
500– 800	13.38	6.90	5.24	3.73	1.57	3.36
500– 900	17.31	9.56	5.89	4.79	1.57	4.48
500–1000	18.88	11.16	7.20	4.79	1.57	5.60
1000–1500	11.81	3.72	3.26	3.20	0.31	3.36
1000–2000	14.17	6.38	3.91	3.73	0.94	3.36
1000–2500	14.95	7.44	4.56	3.73	0.94	3.36
1000–3000	15.73	9.04	5.87	4.26	1.25	3.36
1000–3500	16.51	9.04	6.52	4.79	1.25	3.36
1000–4000	16.51	9.57	6.52	4.79	1.25	3.36
1000–4000+	16.51	9.57	7.17	4.79	1.25	3.36

The results show that the 1907 samples contained the largest amount of SO_2, only 19.65 per cent of the samples containing less than 100 parts per million and 35.39 per cent above 500 parts per million. The 1908 samples show 60.62 per cent of the samples below 100 parts per million and 20.73 per cent above 500 parts per million. The 1909 and 1910 samples are quite similar throughout. In 1911 the analyses show 87.90 per cent of the samples with less than 100 parts per million and only 2.77 per cent above 500 parts per million. The 1912 samples contained more SO_2 than the 1911 samples, this being due to the fact that a large number of the 1912 samples, 42.65 per cent, contained from 100 to 500 parts per million.

Comparatively few samples contained less than 10 parts per million. A number of the samples containing less than 10 parts per million were found to contain hydrogen peroxide evidently added to destroy SO_2.

In this connection, the results obtained on the two samples of gelatin prepared in the laboratory are significant. These samples contained 189 and 199 parts per milion of SO_2, respectively, whereas the air-dried "stock" from which they were prepared contained only 6 parts per million. Two more samples of gelatin prepared in the laboratory from fresh calf bones, purchased in a butcher shop, contained 23 and 78 parts per million. In this case the jelly was also dried on glass plates in a current of air from an electric fan. It is, therefore, not surprising that even excessive amounts of SO_2 may be found in gelatin prepared from selected stock. In the manufacture of gelatin, the thin gelatin solutions are concentrated to the desired consistency so that gelatinization will take place on cooling. The jelly is then sliced and dried in a continuous current of air at 85 to 95° F. If the factory is situated in a manufacturing district, where much coal is burned, it is to be expected that the SO_2 absorbed by the gelatin would be greater than in the case of gelatin manufactured in outlying districts.

Naturally, the selection of the stock is also important, since it may contain considerable amounts of SO_2. Thirty-six samples of stock examined in 1908, 1909 and 1910 gave the following results:

	Sulfur dioxide Parts per million
Maximum	1695
Minimum	9
Average	407

In conclusion, I wish to acknowledge my indebtedness to my assistant, Mr. E. S. Liebscher, for his painstaking work in carrying out a considerable part of the analyses and experiments.

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EXPERIMENTAL DATA ON THE DETERMINATION OF SACCHARIN IN FOODS WITH A MODIFICATION OF SCHMIDT'S METHODS

By HALSEY DURAND

Received October 13, 1913

A recent ruling of the Board of Health of the Department of Health of New York City prohibited the use of saccharin in foods and drinks (see Section 68, Sanitary Code). The enforcement of this law required the examination of a large number of samples of various foodstuffs and soft drinks in which violations were expected.

A method for the detection of saccharin was sought which could be done positively and with as much speed as possible.

A review of the literature gave five methods, as follows:

I. Taste Test.—The aqueous solution of the sample is acidified and shaken out with ether. The ethereal layer separated and evaporated to dryness and a small portion of the residue applied to the tongue. An extremely sweet taste followed by a bitter taste indicates saccharin.

II. Bornstein's Test.—(*Z. anal. Chem.*, **27**, s. 165). Aqueous solution is shaken as above and the ether residue heated with resorcin and a few drops of concentrated sulfuric acid, till the mass begins to swell. Cool. Repeat heating and cooling several times. Cool, dilute with water and neutralize with sodium hydrate. Red-green fluorescence indicates presence of saccharin.

III. Kastle's Test.—(*Bull.* **26**, Hyg. Lab., U. S. Pub. Health & Mar. Hosp. Serv.) The ether residue is treated with a few drops of a mixture of 5 cc. of phenol and 3 cc. of pure concentrated sulfuric acid. It is then heated for 5 minutes to 160–170° C. and the mass dissolved in water and made alkaline with sodium hydrate. A dark purplish red or pink indicates the presence of saccharin.

IV. Schmidt's Test.—(*Rep. Anal. Chem.*, **30**.) Residue from ether extraction is heated in a porcelain dish with about 1 gram sodium hydrate for one-half hour at 250° C. in air oven or linseed oil bath. This converts saccharin to sodium salicylate. The melt is dissolved in water, acidified with hydrochloric acid and shaken with ether. Evaporate ether, take up residue with water and add dilute ferric chloride solution. A violet color indicates the presence of saccharin. The absence of salicylic acid must first be ascertained before applying this method. If salicylic acid is present the ether residue is treated with dilute hydrochloric acid and bromine water added in excess. The liquid is well shaken and filtered. The salicylic acid is completely removed as a bromine derivative. The filtrate is made strongly alkaline and evaporated and heated as above. By this means the false saccharin frequently found in wines and giving faint reactions for saccharin is also eliminated.

V. Allen's Test.—(*Allen's Com. Organ. Anal.*, **2**, Pt. 3, p. 38.) The ether residue is rendered alkaline with sodium hydrate and ashed. The ash is taken up with water made acid with hydrochloric acid and tested with barium chloride or sulfur. The presence of sulfur indicates saccharin.

This test, a little potassium nitrate being added during ignition, is also used for the quantitative determination of saccharin, the barium sulfate being weighed and the weight x 0.783 = saccharin. This quantitative method was not tried as the presence of saccharin is sufficient ground for prosecution.

Test I.—The taste test was tried and found to be very satisfactory, the absence of the sweet taste being a good indication in most cases of the absence of saccharin. However, the possibility of other substances producing the sweet taste, and also of the sweet taste being masked by bitter substances in the residue, made it necessary to have some further test as confirmation.

Test II was tried and gave good reactions. It was found, however, that a large number of organic compounds give the same reaction as saccharin, so this method was discarded.

Test III was tried and excellent results were obtained when pure saccharin was used. When ether residues obtained from shaking out aqueous solutions of foods and drinks were treated with the phenol-sulfuric acid mixture and neutralized with sodium hydrate the characteristic color did not appear. The failure of this reaction is evidently due to the presence of small amounts of impurity in the residue. Efforts were made to obtain the pure phenol compound from the aqueous solution after treating the residue with phenol-sulfuric acid mixture, by shaking out with amyl alcohol and isobutyl alcohol and treating the separated alcohol solutions with sodium hydrate, without results.

Test IV (Schmidt's) was tried repeatedly by the laboratory force using the various modifications as suggested by different authorities. Invariably the ether residue, obtained by shaking out the acidified aqueous solution of the mass after heating, gave a benzoic acid reaction on addition of dilute ferric chloride solution. It was found also that the saccharin in the original ether residue was converted into benzoic acid when treated with saturated sodium hydrate solution and allowed to stand over night at room temperature. Excellent results were obtained in this way and this method was adopted by this laboratory as a confirmatory test to be used with the taste test. This method while giving good results required too long a time for its completion.

METHOD ADOPTED

The writer has recently succeeded in obtaining the salicylic acid by Schmidt's method (IV) both in pure saccharin and in ether residues containing saccharin, by proceeding as follows:

One hundred cc. of an aqueous solution of the sample to be examined for saccharin are acidified with phosphoric acid and shaken out with ether in the usual manner. The separated ether is filtered through double folded filter papers, to remove moisture, into a nickel dish of convenient size and evaporated to dryness. After ascertaining the absence of salicylic, (see description of Schmidt's method), the residue is treated with about 1 cc. of saturated sodium hydrate solution, allowing the alkali to come in contact with the entire residue. Place the dish on a piece of asbestos board about 3 mm. in thickness, heat for 8–10 minutes over a Bunsen flame, cool, take up with water, acidify with hydrochloric acid, and shake out with ether. Evaporate ether, to which a small amount of ammonium hydrate has been added, in a glass dish on water bath, take up residue with a little water and test with dilute ferric chloride for salicylic acid. This method gave very satisfactory results requiring about three-quarters of an hour.

The writer has further simplified and shortened the time required for the method and also eliminated the possibility of the sublimation of the salicylic acid on the water bath by omitting the treatment of the final ether residue with ammonium hydrate and its evaporation to dryness. The ether residue, after separation, is poured into a test tube and about 5 cm. of water containing a small amount of ferric chloride are added. The test tube is then shaken vigorously and the ether and water layers allowed to separate. The presence of salicylic acid is indicated by a violet coloration of the water layer.

CHEMICAL LABORATORY, DEPARTMENT OF HEALTH
NEW YORK CITY

BOUILLON CUBES

By F. C. Cook[1]

Received September 13, 1913

INTRODUCTION

Bouillon cubes consist of a large amount of common salt mixed with varying amounts of meat and plant extract, a small per cent of fat, and a little condiment. Some of the products sold under the name "bouillon cubes" contain but a small per cent of meat stock or extractives, and are not entitled to the term "bouillon" unless it is modified. They are extensively advertised as capable of making a stimulating and appetizing hot drink simply by being dissolved in hot water. They have, therefore, a legitimate place among our dietary accessories.

Several brands of these cubes have appeared on the American market in the past five years, most of them manufactured in this country, and some imported from Germany. Many are wrapped in tin foil, while others are wrapped in paraffin paper, and occasionally a brand of cubes is found in both foil and paper. As the moisture content is low and a large amount of salt is present, they will keep indefinitely, although certain makes tend to lose their form during warm weather.

TABLE I—ANALYSIS OF BOUILLON CUBES—ORIGINAL BASIS

Sample No.	Brand	Solids Per cent	Organic material Per cent	Ether extract Per cent	Ash Per cent	Total chlorine as sodium chloride Per cent	Total phosphoric acid (P_2O_5) Per cent	Acidity (cc. twentieth-normal sodium hydroxid per 1 gram)	Total nitrogen Per cent	Nitrogen precipitated by absolute alcohol in hydrochloric acid Per cent	Total creatinin Per cent
1977	Behrend	96.60	22.86	1.93	73.74	72.13	1.02	6.20	2.19	0.13	0.84
1978	Oxo	95.06	25.31	3.10	69.75	65.00	1.51	6.50	2.97	0.86	1.07
1979	Steero	96.05	28.41	1.20	67.64	62.15	1.83	9.15	3.62	0.76	1.67
1980	Burnham	96.87	41.94	1.00	54.93	52.90	0.58	6.10	2.11	0.05	0.88
1981	Sunbeam	95.73	45.23	1.44	50.50	49.26	0.54	7.30	2.36	0.02	0.92
1982	Armour	96.05	26.48	0.96	69.57	67.44	0.62	6.00	2.79	0.17	1.07
1983	Morris	96.77	33.00	3.79	63.77	59.17	1.69	9.68	3.67	0.56	1.07
1984	Standard	95.81	21.76	4.19	74.05	72.22	0.48	5.01	2.09	0.07	0.50
1985	Liggitt	96.00	21.91	4.58	74.09	71.98	0.41	4.75	2.11	0.05	0.49
1986	Knorr	95.44	26.24	4.57	69.20	65.00	1.55	7.40	3.20	0.91	1.38

The bouillon cubes which are reported in this paper were collected on the New York market in 1912.

METHODS OF ANALYSIS

The samples were prepared for analysis by grinding fifteen to twenty cubes in a mortar as thoroughly as possible and placing the composite paste in small screw-cap jars. The solids were obtained by drying to constant weight *in vacuo* at 65° C. The ash, sodium chloride, phosphoric acid (P_2O_5), nitrogen, and ether extract were determined by the methods of the Association of Official Agricultural Chemists,[1] total creatinin by the Benedict-Myers[2] autoclave method, and precipitation with alcohol in hydrochloric acid solution was carried out according to Rippetoe's method,[3] which is as follows:

Rippetoe's Method.—Transfer 10 cc. of an aqueous solution containing 2 grams of the sample to a 200 cc. glass-stoppered measuring cylinder, add 1.2 cc. of 12 per cent hydrochloric acid, mix and add absolute alcohol to the 200 cc. mark, shake and let stand several hours at 20 to 25° C. If necessary make to mark, filter, and determine total nitrogen in 100 cc. of filtrate.

The acidity figures were obtained by titrating one gram of the sample dissolved in 100 cc. of water with twentieth-normal sodium hydroxide, using phenolphthalein as indicator. The results obtained on the ten samples of cubes analyzed are given in Tables I and II.

The water content of the cubes examined was under 5 per cent and the ether extract figures varied from 1 to 4.58 per cent. These last figures represent the amount of fat added to these cubes during the process of manufacture. The ash, which is largely sodium chloride, varied from 50 to 74 per cent. A large amount of sodium chloride is necessary to give a salty taste to the cup of water in which the cube is dissolved, and to furnish body to the cube. Sudendorf[4] analyzed 18 samples of cubes bought on the market at Hamburg, Germany, and two samples prepared in his laboratory. The latter contained sufficient salt to give a satisfactory taste to the cup of bouillon. The

TABLE II—ANALYSIS OF BOUILLON CUBES—WATER, FAT, AND ASH-FREE BASIS

Sample No.	Brand	Phosphoric acid (P_2O_5) Per cent	Total nitrogen Per cent	Total creatinin Per cent	Ratio of creatinin to total nitrogen
1977	Behrend	4.86	10.50	4.01	1 : 2.6
1978	Oxo	6.80	13.37	4.82	1 : 2.8
1979	Steero	6.73	13.30	6.14	1 : 2.2
1980	Burnham	1.41	5.03	2.10	1 : 2.4
1981	Sunbeam	1.23	5.39	2.10	1 : 2.6
1982	Armour	2.43	10.94	4.19	1 : 2.6
1983	Morris	5.78	12.57	5.82	1 : 2.2
1984	Standard	2.73	11.88	2.84	1 : 4.2
1985	Liggitt	2.37	12.18	2.83	1 : 4.3
1986	Knorr	7.14	14.75	6.36	1 : 2.3

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[1] Physiological Chemist, Animal Physiological Chemistry Laboratory, Bureau of Chemistry.

[1] *Bull.* **107**, Rev., Bureau of Chemistry, U. S. Dept. Agr.

[2] *Am. J. Phys.*, **18**, 397 (1907).

[3] Private communication.

[4] *Z. Nahr. Genussm.*, **23**, 577 (1912).

results showed that 65 per cent of sodium chloride is sufficient to be added to a cube.

The figures for total creatinin vary according to the amount and kind of the meat extract present. The total creatinin includes the original creatinin of the cube and the creatin which has been changed to creatinin in the autoclave. As both substances are structurally closely related, and have a common origin in the creatin of the muscle, only the figure for total creatinin is given in this table. The determination of creatinin is very important in this work as it is of value in showing how much meat extract was used in preparing the cube. According to Seiger,[1] if we place the creatinin content of meat extract at 6 per cent, then bouillon cubes should contain the following amounts of creatinin:

Meat extract used Per cent	Creatinin contained Per cent
25	1.5
20	1.2
15	0.9
10	0.6

The creatinin determination is applied to the water solution of the cube or meat extract. As noted[2] by the writer before, there is not sufficient protein present in ordinary meat extract to interfere with the creatinin test. Geret[3] has recently stated that the meat extract content of different cubes, based on the analyses of Liebig's meat extract, varies from 20 to 25 per cent for the superior cubes while the inferior cubes contain no creatinin. He also stated that gelatin increases the creatinin results. In a previous publication the writer stated that egg albumen and Witte's peptone, when added to solutions containing creatinin, decreased the creatinin result. The figures on which these statements are based were obtained by the Benedict-Myers method. It is likely that solutions of creatin containing gelatin or egg albumen, when evaporated to dryness or otherwise treated, would give high creatinin figures due to caramel or other colored products formed during the process, which might account for the high figures obtained by Geret.

Meat extract contains a higher per cent of total nitrogen than plant extract; therefore, a cube prepared largely from meat extract has a higher total nitrogen content than one prepared largely from plant extract. A good cube is indicated by high creatinin and high nitrogen figures. The results obtained by precipitation with absolute alcohol in hydrochloric acid solution, as outlined above, show that a larger per cent of nitrogen is precipitated in a high-grade than in a low-grade cube, and the figures are of some value in determining how much meat extract has been used in the preparation of the cube. The nitrogen precipitated by absolute alcohol in hydrochloric acid is not appreciably affected by the sodium chloride present. The acidity figures are of little value in determining the nature of the constituents present in a bouillon cube.

The phosphoric acid (P_2O_5) results, especially when calculated to a water, fat, and ash-free basis, show higher figures for the superior cubes than for the inferior ones. The value of the phosphoric acid (P_2O_5), total nitrogen and total creatinin results are more apparent on the water, fat, and ash-free basis than on the original basis. The creatinin-total nitrogen ratios show little in regard to the composition of the cubes, as a low creatinin figure due to the use of a small amount of meat extract, and a low total nitrogen figure due to the use of a large amount of plant extract would be found in the same product. From a survey of Sudendorf's analyses of cubes collected on the German market it is apparent that the cubes sold on the market in this country are very similar in composition to those on the German market, that is, both consist of a large amount of salt, together with smaller amounts of meat and plant extracts.

SUMMARY

Bouillon cubes on the market at present consist of about 5 per cent of water, 1 to 4.5 per cent of ether extract (fat), and 50 to 74 per cent of ash which is practically all sodium chloride. The nitrogen bodies and undetermined organic material amount to 20 to 40 per cent. The phosphoric acid (P_2O_5) varies from 0.4 to 1.8 per cent, the total nitrogen from 2.1 to 3.6 per cent, and the total creatinin from 0.49 to 1.67 per cent.

A cube prepared largely from meat extract gives high total phosphoric acid (P_2O_5), total nitrogen, and total creatinin figures. The amount of nitrogen precipitated by absolute alcohol and hydrochloric acid is also markedly higher than in a cube containing much plant and little meat extract.

Bouillon cubes are extensively advertised and are sold on account of their flavoring and stimulating properties, rather than for any slight food value they may possess. The large per cent of sodium chloride, which need not exceed 65 per cent, is used to furnish body to the cube and to give a salty taste to the cup of water in which the cube is dissolved.

Bouillon is a clear broth, the basis of which is meat; consequently a true bouillon cube should show high creatinin and high total nitrogen figures, and should be prepared entirely, or largely from meat stock or meat extract in addition to the salt and fat present. Several of the cubes on the market contain much more plant than meat extract and are not entitled to the name "bouillon" unless modified.

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THE INFLUENCE OF BRAN-EXTRACTS ON THE BAKING QUALITIES OF FLOUR

By H. L. White

Received September 6, 1913

It is generally recognized that bran and shorts contain valuable food constituents such as fat, carbohydrates other than cellulose, mineral matter and some nitrogenous material. Attempts have been made to improve the bread-making qualities of a flour, by in-

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[1] *Konserven Ztg.*, **48**, 378 (1912).

[2] *J. Am. Chem. Soc.*, **31**, 673 (1909).

[3] *Z. Nahr. Genussm.*, **24**, 570 (1912).

troducing into the flour extracts of bran made with various solvents. Thus cold water extracts and hot water extracts[1] have been mixed with flour in varying proportions with beneficial results. A process has been patented[2] for treating bran in order to recover the mineral constituents for admixture with flour. The bran is treated with water to extract soluble salts and the residue treated with an acid solvent and water and subsequently with an alkaline solution. The acid and alkali solutions are neutralized, and the whole of the extracts are evaporated to dryness, and the residue is reduced to a powder.

In connection with some experimental work on the mineral content of flour, it was found advisable to determine the effect of a dilute hydrochloric acid-extract of bran on the baking qualities of flour made from several varieties of wheat. It has been claimed[3] that a 0.2 per cent HCl extract of bran contains phytin from which an acid identical with Posternak's[4] anhydro-oxymethylen diphosphoric acid is obtained. That phytin is obtained in this manner is denied by Anderson[5] who claims that the extract thus obtained does not correspond in composition with salts of the true phytic acid. Without entering into the discussion of this point, the fact remains that the dilute acid extract contains, in addition to other constituents, both organic and inorganic phosphorous compounds.

EXPERIMENTAL

The acid-extract used in these experiments was prepared by soaking bran in 0.2 per cent HCl for sixteen hours. The proportions used were, bran 300 grams, acid 1800 cc. The liquid was first filtered through cheese-cloth and then through paper, a clear liquid of a brown color being thus obtained. Analysis of this clear liquid gave the following results:

TABLE I—COMPOSITION OF ACID-EXTRACT OF BRAN

Total Solids Grams per 100 cc.	Ash Grams per 100 cc.	Total P_2O_5 Grams per 100 cc.	Inorganic P_2O_5 Grams per 100 cc.	Organic P_2O_5 (by diff.) Grams per 100 cc.	Acidity cc. N/20 NaOH per 10 cc. ext.
3.584	0.917	0.464	0.200	0.264	13.6

In one series of baking tests the acid-extract was neutralized with 0.1 *N* NaOH, using phenolphthalein as an indicator. In another series a water-extract (bran 300 grams, water 1800 cc.) was used, and in still another, 0.2 per cent HCl was used in place of a bran extract. A comparison of these various extracts is afforded in the following table:

TABLE II—COMPOSITION OF VARIOUS EXTRACTS USED IN BAKING TESTS

	Total solids Grams per 100 cc.	Ash Grams per 100 cc.	Total P_2O_5 Grams per 100 cc.	Inorganic P_2O_5 Grams per 100 cc.	Organic P_2O_5 (by diff.) Grams per 100 cc.	Acidity cc. N/20 NaOH for 10 cc. ext.
Acid-extract	3.584	0.917	0.464	0.200	0.264	13.6
Water-extract	2.776	0.444	0.163	0.110	0.053	3.0
Acid-extract, neutralized	3.785	1.145	...	...	...	...
0.2% HCl	...	...	...	...	...	10.65

BAKING TESTS

Several series of baking tests were made, some months apart, using flour made from the same samples of wheat but freshly ground for each series of tests. In Series I (spring of 1912) varying amounts of extract were used, while in Series II (fall of 1912) the same amount (150 cc.) was used in every case. The bread was made in the usual way, the extracts being used instead of water to make the dough. Straight flours from each of three varieties of wheat were used in these experiments: Bluestem (Lab. No. 568), Durum (Lab. No. 481), and Velvet Chaff (Lab. No. 993).

TABLE III—RESULTS OF BAKING TESTS—SERIES I—BLUESTEM WHEAT

1st Baking	Extract Cc.	Water Cc.	Volume loaf Cc.	Color	Texture
	Acid-Extract				
568A (check)	...	201	2460	95	96
568B	80	123	2760	97	98
568C	150	52	2820	100	100
568D	150	50	3020	100	100
2nd Baking	Acid-Extract				
568A (check)	...	200	2460	95	96
568E	80	120	2850	97	98
568F	170	30	2920	98	100
3rd Baking	Acid-Extract Neutralized ("Soapy")				
568A (check)	...	196	2640	...	...
568G	80	122	2590	...	...
568H	170	36	2280	...	...
4th Baking	Dilute Hydrochloric Acid (0.2%)				
568A (check)	...	205	2690	99	98
568I	80	121	2680	101	98
568J	140	65	2700	99	97

In both the first and second bakings using acid-extract there was an increase in volume, amounting to 18 per cent, and an improvement in both color and texture. With the neutralized acid-extract there was a decrease in loaf volume amounting to 13 per cent.

In order to determine if the use of acid-extract resulted in an increase of acid-reacting material in the bread, the soft portions of loaves, Nos. 568A (check) and 568D (150 cc. extract) were extracted with water and the filtered solution titrated with 0.05 normal NaOH, with the following results:

TABLE IV—ACIDITY OF INNER PORTIONS OF LOAVES OF BREAD

Lab. No.	N/20 NaOH Cc.	Calculated as lactic acid Per cent	Calculated as HCl Per cent
568A (check)	4.3	0.193	0.078
568D (extract)	8.35	0.373	0.152

The average acidity of the inner portion of twenty-one samples of fresh bread was found[1] to be equivalent on a dry basis to 0.289 per cent lactic acid or 0.215 per cent hydrochloric acid. Therefore, the acidity of the water-soluble portions of 568A and 568D is about the same as the average of home-made bread and of bakers' bread.

TABLE V—SERIES I—DURUM WHEAT

1st Baking	Extract Cc.	Water Cc.	Volume loaf Cc.	Color	Texture
	Acid-Extract				
481A (check)	..	190	2040	97	94
481B	80	107	2090	97	95
481C	140	51	2170	97	96

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[1] Willard and Swanson, *Chem. News*, **105**, 97–9.

[2] U. S. Patent, No. 1,018,441.

[3] Patten and Hart, New York Exp. Sta., *Bull.* **250**.

[4] Posternak, *Compt. rend.*, **137**, 439.

[5] Anderson, New York Agric. Exp. Sta., *Technical Bull.* **22** (1912).

[1] Congdon, Twenty-second Annual Report, North Dakota Agricultural Experiment Station, **1911**, Part II.

This flour did not respond to treatment with acid-extract as the gain in loaf volume was only 5 per cent, color and texture remaining about the same in each loaf.

Table VI—Series I—Velvet Chaff Wheat

1st Baking	Extract Cc.	Water Cc.	Volume loaf Cc.	Color	Texture
		Acid-Extract			
993A (check)....	...	190	1980	96	92
993B..........	80	110	2260	99	96
993C..........	160	30	2400	98	96
2nd Baking		Acid-Extract			
993A (check)....	...	187	2090	96	95
993D..........	80	108	2340	97	98
993E..........	150	38	2380	98	98
3rd Baking		Acid-Extract, Neutralized			
993A (check)....	...	190	2200	100	93
993F..........	80	113	2090	99	92
993G..........	140	55	1970	99	90
4th Baking		Dilute Hydrochloric Acid (0.2%)			
993A (check)....	. .	187	2090	96	95
993H..........	80	108	2230	97	95
993I..........	150	38	1910	94	85

As shown in the above table there was an increase in the loaf volume of from 13 per cent to 21 per cent when acid-extract was used, and both color and texture were improved. With neutralized extract there was a decrease in loaf volume. With dilute acid alone there was a decrease of 9 per cent in loaf volume, a slight change in color, and a poor texture.

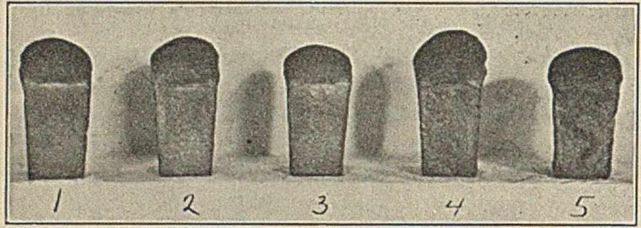

Plate I

1. Check loaf
2. Water-extract
3. Acid-extract, neutralized
4. Acid-extract
5. Acid alone

After a study of these results, it was decided to make a second series of baking tests, including in each baking all of the extracts which had been used in the several bakings of Series I and in addition a filtered cold-water-extract of bran.

Table VII—Series II—Bluestem Wheat—No. 568

Flour No. 568	Extract Cc.	Water Cc.	Volume loaf Cc.	Color	Texture
Check..........	. .	190	2490	94	97
Check..........	. .	189	2480	95	97
Acid-extract....	150	40	2600	96	98
Acid-extract.....	150	40	2690	96	98
Water-extract....	150	40	2600	92	98
Water-extract....	150	39	2515	93	97
Acid-ext., neutral	150	39	2240	94	92
Acid-ext., neutral	150	45	2360	92	92
Dilute acid......	150	39	2250	94	90
Dilute acid.... .	150	40	2200	94	90

A consideration of data submitted in Table VII shows that the acid-extract and water-extract gave somewhat larger loaves than the check, in the order named; and that with the acid-extract both color and texture were slightly improved. Plate I gives some idea of the external appearance of the loaves.

Table VIII—Series II—Durum Wheat

Flour No. 481	Extract Cc.	Water Cc.	Volume loaf Cc.	Color	Texture
Check..........	...	200	1920	96	95
Check..........	...	199	1870	96	95
Acid-extract.....	150	48	2030*	96	94
Acid-extract.....	150	51	1870*	96	98
Water-extract....	150	50	2010	95	96
Water-extract....	150	51	2030	95	96
Acid-ext., neutral	150	51	1910	97	96
Acid-ext., neutral	150	51	....	..	..
Dilute acid.....	150	50	1630	94	85
Dilute acid.... .	150	50	1650	94	85

* Baker's comment: "Dough broke slightly."

A consideration of the data submitted in Table VIII indicates but little improvement in loaf volume, color, or texture by the use of acid-extract. The water-extract gave better results than the acid-extract. The dilute acid decreases loaf volume and unfavorably modifies the texture.

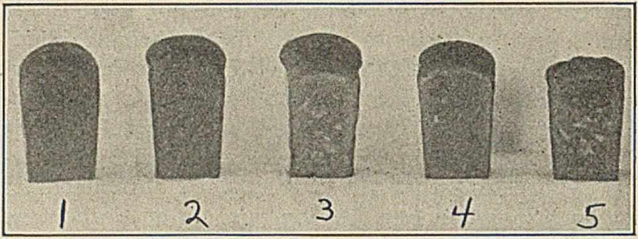

Plate II

1. Check loaf
2. Water-extract
3. Acid-extract
4. Acid-extract, neutralized
5. Acid alone

Table IX—Series II—Velvet Chaff Wheat

Flour No. 993	Extract Cc.	Water Cc.	Volume loaf Cc.	Color	Texture
Check..........	..	188	2030	95	95
Check..........	..	187	2060	95	95
Acid-extract.....	150	36	2480	98	97
Acid-extract....	150	36	2460	98	97
Water-extract....	150	36	2340	94	96
Water-extract....	150	34	2200	94	96
Acid-ext., neutral	150	35	2020	95	95
Acid-ext., neutral	150	36	2040	95	95
Dilute acid......	150	36	1870	92	80
Dilute acid......	150	36	1700	92	80

As will be noted in Table IX, the acid-extract exerted a favorable influence on the baking qualities of flour from velvet chaff wheat, increasing the loaf volume, and giving a better color and texture. The water-extract increased loaf volume, but had little influence on color and texture. The dilute acid on the other hand had a marked unfavorable influence on

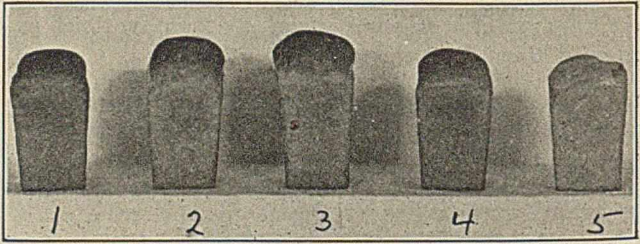

Plate III

1. Check loaf
2. Water-extract
3. Acid-extract
4. Acid-extract, neutralized
5. Acid alone

loaf volume and texture, and, to a lesser degree, the color.

In view of the fact that in the larger number of baking tests the acid-extract had a greater influence than the water-extract to increase loaf volume and to improve the color and texture, the question naturally arises as to whether the improvement is due to the stimulating effect of acid, or phosphate, or other constituent of the extract on the yeast; or to some other factor. Experiments undertaken to determine the stimulating effect of acid-extract on yeast were not convincing. A possible explanation is that the gluten may have become more coherent in the presence of acid and soluble salts (particularly phosphates) as is suggested by Wood.[1] At any rate, the baking tests show clearly that it is not acid alone, but acid plus extractive material that gives the best results.

SUMMARY AND CONCLUSIONS

In two series of baking tests of flour made from three varieties of wheat, acid-extract of bran, water-extract, acid-extract neutralized, and dilute acid, were used to replace a part of the water necessary to make the dough.

In general, the acid-extract produced larger loaves of bread (from 6 per cent to 20 per cent increase in volume) of a better color and texture than the check loaf, or those in which other extracts were used. The water-extract produced loaves somewhat larger than the check loaves. The dilute acid gave a loaf of decreased volume and very poor texture.

Analyses of acid- and water-extracts show the presence of 0.464 gram P_2O_5 and 0.163 gram P_2O_5, respectively, in 100 cc. extract.

Experiments made to show the stimulating effect of acid-extract on yeast were not convincing. It is thought the presence of both acid and soluble salts makes the gluten more coherent.

In general the better the flour, that is the stronger the gluten, the more marked is the improvement by use of acid-extract; but all samples of flour show greater or lesser improvement.

The inner portions of the loaves of bread made with acid-extract show no greater amount of water-soluble acid reacting material than the average of home-made, or bakers' bread.

In conclusion, the writer wishes to acknowledge his indebtedness to L. M. Thomas, of the Division of Grain Standardization, Bureau of Plant Industry, U. S. Dept. of Agriculture, for his cöoperation in making the baking tests, scoring the bread and for making the photographs that are used in this report.

North Dakota Agricultural College

THE ANALYSIS OF MAPLE PRODUCTS, II

A Comparative Study of the Delicacy of Methods[2]

By J. F. Snell and J. M. Scott

In studying the usefulness of the electrical conductivity test[3] for the detection of adulteration in maple syrup it appeared desirable to compare the delicacy of this test with that of other methods in vogue. For this purpose three syrups, A, B, and C, were chosen. A, a light-colored syrup of high quality, and B, a mixture of several pure maple syrups, were kindly donated by Mr. John H. Grimm, of Montreal, while C was a syrup made at Macdonald College in the season of 1913.

These were diluted with water and boiled to 219° F., after which their specific gravities at 60° F. were: A, 1.325; B, 1.320; C, 1.318. Cane-sugar syrups of the same specific gravities were prepared from granulated sugar and mixtures of the cane and maple syrups made up and analyzed.

The following determinations were made upon each of the mixtures:

(1) Total ash by ignition in an electric muffle at a low red heat (600–650° C.).

(2) Insoluble ash.[1]

(3) Soluble ash by difference.

(4) Alkalinity of insoluble ash.[1]

(5) Alkalinity of soluble ash.[1]

(6) Conductivity value, *i. e.*, 100,000 times the specific conductivity at 25° C. of a mixture of one volume syrup with two volumes of water.[2]

(7) Canadian lead number.[3]

(8) Winton lead number. In Syrups B and C this determination was made upon 25 grams of syrup as originally directed by Winton,[4] the blank being treated with acetic acid as directed by Bryan.[5]

In Syrup A, however, the determination was made upon the quantity of syrup (38.462 grams) containing 25 grams of dry matter, the procedure prescribed by the Canadian standard of purity for maple syrup.[6]

(9) Ross's modified Winton number.[7]

This determination also was made on 25 grams of syrup in Syrups B and C, but upon 38.462 grams in syrup A.

(10) Sy lead value.[8] Weight of lead precipitated from normal lead acetate by 100 cc. of syrup.

The results obtained are shown in Tables I, II, and III. In Tables IV, V, and VI the actual percentage of maple syrup in each mixture is compared with the "estimated percentages" derived from the ratios of the various values in the mixture to those in the pure syrup.

EFFECTS PRODUCED UPON THE VARIOUS DATA BY PROGRESSIVE DILUTION WITH SUCROSE SYRUP

It will be noted that the ratios of the weights and also those of the alkalinities of the soluble ash to the insoluble ash remain nearly constant down to the 50 per cent mixture. In mixtures containing less than 50 per cent. of maple syrup, these ratios fluctuate greatly. These fluctuations are doubtless due to the

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[1] T. B. Wood, *Jour. Agr. Sci.*, **2**, 267 (1907); Abstract in *J. Soc. Chem. Ind.*, **27**, 175 (1908).

[2] Paper presented at the 48th Meeting of the A. C. S., Rochester, September 8–12, 1913.

[3] Snell, This Journal, **5**, 740 (1913).

[1] Jones, Vermont Agr. Expt. Sta., *18th Ann. Rept.*, **1904-5**, 321; Bryan Bur. Chem., U. S. Dept. Agr., *Bull.* **134**, 17 (1910); McGill, Lab. Inland Revenue Dept., Ottawa, *Bull.* **228**, 5 (1911).

[2] Snell, *loc. cit.*

[3] McGill, *loc. cit.*

[4] Winton and Kreider, *J. Am. Chem. Soc.*, **28**, 1204 (1906).

[5] Bryan, *loc. cit.*

[6] Canadian Order-in-Council, G, 994, Nov. 8, 1911; McGill, Lab. Inland Rev. Dept., *Bull.* **228**, 5 (1911).

[7] Ross, Bur. Chem., U. S. Dept. Agr., *Circ.* **53**, 8 (1910).

[8] Sy, *J. Frank. Inst.*, Dec., 1908, page 68 of reprint.

TABLE I—MAPLE SYRUP A

Per cent maple syrup	Per cent total ash	Per cent insoluble ash	Per cent sol. ash	Sol. ash: Insol. ash	Alkalinity insol. ash	Alkalinity sol. ash	Alk. sol. ash: Alk. insol. ash	Conductivity value	Canadian lead number	Modified Winton* lead no.	Modified Ross* lead no.	Sy lead value
100	1.14	0.45	0.69	1.53	56	47	0.84	136	2.26	1.46	1.78	0.342
90	1.08	0.38	0.70	1.89	54	52	0.96	126	1.71	1.44	1.69	0.309
80	0.86	0.35	0.51	1.46	46	42	0.91	115	1.58	1.23	1.60	0.273
70	0.68	0.26	0.42	1.62	38	36	0.92	101	1.38	1.18	1.50	0.229
60	0.71	0.25	0.46	1.84	36	31	0.86	90	1.10	1.04	1.39	0.194
50	0.68	0.20	0.48	2.40	31	26	0.84	78	0.70	0.72	1.33	0.179
40	0.32	0.14	0.18	1.29	20	20	1.00	65	0.36	0.55	1.23	0.104
30	0.20	0.14	0.06	0.43	22	12	0.55	50	0.14	0.30	1.04	0.075
20	0.15	0.06	0.09	1.50	16	14	0.87	35	turbidity only	0.16	0.80	0.052
10	0.09	0.02	0.07	3.50	10	4	0.40	20	faint turbidity	0.00	0.44	0.020

* Winton and Ross methods on 25 grams dry sugar = 38.462 grams syrup.

TABLE II—MAPLE SYRUP B

Per cent maple syrup	Per cent total ash	Per cent insoluble ash	Per cent water-sol ash	Sol. ash: Insol. ash	Alkalinity insol. ash	Alkalinity sol. ash	Alk. sol. ash: Alk. insol. ash	Conductivity value	Canadian lead number	Winton* lead number	Ross* lead number	Sy lead value
100	0.92	0.40	0.52	1.30	65	52	0.80	170	3.18	1.46	1.72	0.460
90	0.80	0.37	0.43	1.16	62	48	0.77	147	2.67	1.34	1.64	0.378
80	0.71	0.25	0.46	1.84	57	41	0.72	144	2.12	1.19	1.48	0.296
70	0.62	0.26	0.36	1.38	52	38	0.73	126	1.81	1.03	1.34	0.259
60	0.55	0.22	0.33	1.50	46	31	0.67	109	1.60	0.89	1.16	0.239
50	0.49	0.20	0.29	1.45	38	28	0.74	95	1.06	0.73	1.08	0.177
40	0.38	0.12	0.26	2.17	26	26	1.00	77	0.74	0.54	0.82	0.128
30	0.32	0.09	0.23	2.56	19	23	1.21	58	0.31	0.38	0.66	0.074
20	0.22	0.06	0.16	2.67	12	14	1.17	47	turbidity only	0.23	0.37	0.050
10	0.08	0.02	0.06	3.00	10	9	0.90	24	no turbidity	0.11	0.10	0.022

* Winton and Ross methods on 25 grams syrup.

TABLE III—MAPLE SYRUP C

Per cent maple syrup	Per cent total ash	Per cent insol. ash	Per cent sol. ash	Sol. ash: Insol. ash	Alkalinity insol. ash	Alkalinity sol. ash	Alk. sol. ash: Alk. insol. ash	Conductivity value	Canadian lead number	Winton lead number	Ross lead number	Sy lead value
100	0.70	0.27	0.43	1.59	48	40	0.83	128	2.02	1.34	1.49	0.415
90	0.63	0.24	0.39	1.62	45	38	0.84	117	1.80	1.28	1.37	0.351
80	0.54	0.21	0.33	1.57	44	35	0.80	107	1.38	1.10	1.21	0.308
70	0.47	0.21	0.26	1.24	38	31	0.82	96	1.09	0.98	1.07	0.265
60	0.39	0.18	0.21	1.17	30	28	0.93	85	0.64	0.74	0.86	0.166
50	0.34	0.14	0.20	1.43	26	24	0.92	70	0.37	0.67	0.79	0.126
40	0.31	0.12	0.19	1.58	20	21	1.05	59	0.24	0.56	0.66	0.072
30	0.23	0.09	0.14	1.56	18	17	0.94	47	0.14	0.44	0.52	0.058
20	0.17	0.06	0.11	1.83	14	12	0.86	31	faint turbidity	0.38	0.31	0.032
10	0.06	0.02	0.04	2.00	6	6	1.00	18	no turbidity	0.18	0.23	faint turbidity

TABLE IV—MAPLE SYRUP A. ESTIMATED MAPLE SYRUP CONTENT CALCULATED FROM DETERMINATIONS GIVEN IN TABLE I

Actual per cent maple syrup	Estimated from total ash	Estimated from insol. ash	Estimated from sol. ash	Estimated from alk. insol. ash	Estimated from alk. sol. ash	Estimated from conductivity	Estimated from Canadian lead no.	Estimated from modified Winton lead no.	Estimated from modified Ross lead no.	Estimated from Sy lead value
90	94.7	84.4	101.4	96.4	110.6	92.6	75.7	98.6	94.9	90.3
80	75.4	77.8	73.9	82.1	89.4	84.6	69.9	84.2	89.9	79.8
70	59.6	57.8	60.9	67.9	76.6	74.3	61.1	80.8	84.3	67.0
60	62.3	55.5	66.6	64.3	66.0	66.2	48.7	71.2	78.1	56.7
50	59.6	44.4	69.6	55.4	55.3	57.4	31.0	49.3	74.8	52.3
40	28.1	31.1	26.1	35.7	42.6	47.8	15.9	37.7	69.7	30.4
30	17.5	31.1	8.7	39.3	25.5	36.8	6.2	20.5	58.4	22.0
20	13.2	13.3	13.0	28.6	29.8	25.7	....	11.0	44.9	15.2
10	7.9	4.4	10.1	17.9	8.5	14.7	....	0.0	24.7	5.8

TABLE V—MAPLE SYRUP B. ESTIMATED MAPLE SYRUP CONTENT CALCULATED FROM DETERMINATIONS GIVEN IN TABLE II

Actual per cent maple syrup	Estimated from total ash	Estimated from insol. ash	Estimated from sol. ash	Estimated from alk. insol. ash	Estimated from alk. sol. ash	Estimated from conductivity	Estimated from Canadian lead no.	Estimated from Winton lead no.	Estimated from Ross lead no.	Estimated from Sy lead value
90	87.6	92.5	82.7	95.4	92.3	86.5	83.9	91.8	95.3	82.2
80	77.2	62.5	88.5	87.7	78.8	84.7	66.7	81.5	86.0	64.3
70	67.4	65.0	69.2	80.0	73.1	74.1	56.9	70.5	77.9	56.3
60	59.8	55.0	63.5	70.8	59.6	64.1	50.3	61.0	67.4	52.0
50	53.3	50.0	55.8	58.5	53.9	55.9	33.3	50.0	62.8	38.5
40	41.3	30.0	50.0	40.0	50.0	45.3	23.3	37.0	47.7	27.8
30	34.8	22.5	44.2	29.2	44.2	34.1	9.7	26.0	38.4	16.1
20	23.9	15.0	30.8	18.5	26.9	27.6	....	15.8	21.5	10.9
10	8.7	5.0	11.5	15.4	17.3	14.1	....	7.5	5.8	4.8

Table VI—Maple Syrup C. Estimated Maple Syrup Content from Determinations Given in Table III

Actual per cent maple syrup	Estimated from total ash	Estimated from insol. ash	Estimated from sol. ash	Estimated from alk. insol. ash	Estimated from alk. sol. ash	Estimated from conductivity	Estimated from Canadian lead no.	Estimated from Winton lead no.	Estimated from Ross lead no.	Estimated from Sy lead value
90	90.0	88.9	90.7	93.7	95.0	91.4	89.1	95.5	91.9	84.6
80	77.1	77.8	76.7	91.7	87.5	83.6	68.3	82.1	81.2	74.2
70	67.1	77.8	60.5	79.2	77.5	75.0	54.0	73.1	71.8	63.9
60	55.7	66.7	48.8	62.5	70.0	66.4	31.7	55.2	57.7	40.0
50	48.6	51.9	46.5	54.2	60.0	54.7	18.3	50.0	53.0	30.4
40	44.3	44.4	44.2	41.7	52.5	46.1	11.9	41.8	44.3	17.3
30	32.9	33.3	32.6	37.5	42.5	36.7	6.9	32.8	34.9	14.0
20	24.3	22.2	25.6	29.2	30.0	24.2	....	28.4	20.8	7.7
10	8.6	7.4	9.3	12.5	15.0	14.1	....	13.4	15.4	....

greater influence of experimental errors in the ash determinations in mixtures of low, as compared with those of high, maple content. In the 10 per cent mixtures the actual quantity of insoluble ash weighed was in each instance one milligram, while the quantities of tenth normal acid used were 0.20, 0.45 and 0.30 cc., respectively, in the soluble ash of Syrups A, B, and C, and 0.50, 0.50 and 0.30 cc. in the insoluble ash. A similar variability is noticeable in most of the other values for the mixtures of low maple content.

The true Winton and Ross lead numbers (Syrups B and C) and the conductivity value come nearest to decreasing proportionally to the maple content. The conductivity value gives estimated results a little higher than the actual, with the single exception of the 90 per cent mixture in case of Syrup B. That this exception is not due to experimental error is evidenced not only by the fact that repetition of the measurement on this syrup confirmed the result at first obtained, but that in the case of four other syrups, 90 per cent mixtures gave estimated values of 86.6, 87.0, 87.2, and 87.3. In this respect, accordingly, Syrups A and C appear exceptional rather than Syrup B. Accordingly, small adulteration with cane sugar appears often to have somewhat more than its proportional effect on conductivity, while greater adulteration has always less than its proportional effect.

Table VIII—Comparison of Winton and Ross Lead Numbers on Syrups D and E

Actual per cent maple syrup	Syrup D Winton lead no.	Syrup D Maple content estimated from Winton lead no.	Syrup D Ross lead no.	Syrup D Maple content estimated from Ross lead no.	Syrup E Winton lead no.	Syrup E Maple content estimated from Winton lead no.	Syrup E Ross lead no.	Syrup E Maple content estimated from Ross lead no.
100	1.71	....	2.01	....	1.635	....	2.155	....
90	1.56	91.2	1.85	91.8	1.325	81.0	1.94	90.0
80	1.30	75.7	1.63	81.1	1.18	72.2	1.75	81.2
70	1.14	66.7	1.41	70.1	1.06	64.8	1.625	75.4
60	1.03	60.2	1.40	69.7	0.825	50.5	1.355	62.9
50	0.875	51.2	1.19	59.2	0.645	39.4	1.12	52.0
40	0.605	35.4	0.825	41.0	0.46	28.1	0.905	42.0
30	0.425	24.9	0.76	37.8	0.29	17.7	0.72	33.4
20	0.265	15.5	0.43	21.4	0.145	8.9	0.445	20.7
10	0.09	5.3	0.135	6.7	0.060	3.7	0.190	8.8

The Ross lead number when determined by the original method (Syrups B and C) does not decrease as rapidly as the actual maple syrup content. (In the case of Syrup A where the determinations are made on a quantity of syrup equivalent to 25 grams of dry sugar the results obtained are high throughout and further from the actual proportions of maple syrup than are those obtained without the use of potassium sulfate.) These results—particularly those on Syrup B (Tables II and V)—are not in agreement with Dr. Ross's experience, and in correspondence with us he suggested that our high results might be due to our neglect to observe his caution to use only freshly boiled distilled water in diluting the syrup. Unfortunately we were not able to test this point with Syrup B as our material was exhausted. We have, however, made a series of experiments on some of the mixtures of Syrup C, the results of which are given in Table VII. No difference of consequence was observed due to the boiling of the water. In order to make a further study of the Winton and Ross methods we prepared two composite samples (D and E) from 100 pure syrups made in the season of 1913. The syrups from which these composites were made were obtained directly from the sugar bushes of Quebec and Ontario by graduate representatives of the College, so that there can be no doubt as to their purity. Mixtures of these syrups with cane syrup were made up and the Ross and Winton lead determinations made upon each, freshly boiled water being used in the Ross method. As will be seen from the results which are tabulated in Table VIII, the Ross method gives estimated results much closer to the actual maple content than does the Winton method. Especially is this the case in regard to Syrup E. In most instances the estimated results with the Winton method are lower than the actual maple content, while on the other hand the Ross method gives results slightly higher than the actual.

Table VII—Comparison of Ross Lead Numbers on Mixtures of Syrup C, Using Freshly Boiled and Unboiled Water

Actual per cent maple syrup	Ross lead number with freshly boiled water	Calculated per cent maple syrup	Ross lead number with unboiled distilled water	Calculated per cent maple syrup
100	1.42	....	1.49	....
80	1.17	82.0	1.21	81.2
50	0.78	54.9	0.79	53.0
20	0.32	22.5	0.31	20.8

The Canadian lead number drops off much more rapidly than the actual maple syrup percentage and vanishes in the three series at a maple content of 20 per cent. This fact gives the Canadian method a distinct advantage as far as the detection of small adulteration is concerned, but renders it useless for distinguishing compound maple syrups containing a small proportion of maple from imitation syrups containing none. Moreover, the advantage of the Canadian method for the former purpose is somewhat offset by the great variability of the Canadian lead number in genuine maple syrups. In its investigation of some 450 Canadian syrups of the season of 1911, obtained directly from the makers accompanied by a declaration of genuineness,[1] the Laboratory of the Inland Revenue Department found twelve syrups with values below that adopted in the standard, *viz.*, 1.70. Six samples yielded lead values of over 4.50, and of these three were above 5.00. In an uncompleted investigation of 125 genuine Canadian syrups of the season of 1913 we have found even a greater variation in the Canadian lead number, 9 samples having values above 4.50, 8 of which are also above 5.00. As will be seen by referring to the Canadian lead numbers in Table II, a syrup of high lead value may be adulterated with a comparatively large proportion of cane sugar without falling below the Canadian standard. Syrups A and C, however, with original lead values of 2.26 and 2.02, respectively, have already reached the limit of the standard when the adulteration amounts to 10 per cent.

The Sy lead number, like the Canadian, drops off more rapidly than the maple content. But it does not show this propensity to the same degree as the Canadian value. We are unable to see any advantage in Sy's method over the other methods which would compensate for the extra time and labor involved in making the determination.

RANGE OF VARIATION IN GENUINE SYRUPS

The delicacy of any method of detecting adulteration of maple syrup with pure sucrose obviously depends upon: (1) The limits of natural variation of the value in question in genuine syrups. (2) The rate at which the value falls off as the proportion of genuine syrup is decreased. As we have seen, the Canadian lead value excels in the second point but not in the first. The range of variation of the different values may readily be seen from Table IX, which shows percentage variation of the different values in the natural product as found by Bryan, McGill, and ourselves. Bryan's figures were obtained from 481 samples of maple syrup representing all the maple-producing states of the Union and the Province of Quebec. McGill's figures on the Canadian lead number are based upon analyses of 456 samples of Canadian syrups; those on Winton lead number, total ash and malic acid upon a study of 47,115 and 452 of these samples, respectively. Our limits for the conductivity method are the result of measurements made upon over 200 syrups. It will be noticed that the range is somewhat wider than that reported in the first paper of this series, *viz.* 82%. This is due to the fact that since the publication of the paper on electrical conductivity we have found syrups which gave conductivity values above the maximum previously obtained (200) and which from our present information we must regard as genuine. We have, however, found none below the minimum reported (110). Our figures for the other values are based upon an uncompleted investigation of 125 samples of Canadian syrup of the season of 1913 and are to be regarded as merely tentative. When the investigation is completed the range of some of the values may prove to be narrower than here reported. From the figures given in Table IX it is evident that the conductivity value shows the narrowest limits of variation of any of the data.

TABLE IX—RANGE OF VARIOUS ANALYTICAL VALUES IN GENUINE MAPLE SYRUPS. EXPRESSED IN PERCENTAGE OF THE MINIMUM

Investigator	Total ash	Winton lead no.	Malic acid value	Canadian lead no.	Conductivity value
Bryan	147	151(*a*)	452	...	...
McGill	100	127(*b*)	287	380	. .
Snell and Scott	125	190	329	331	109

(*a*) Original Winton method. (*b*) Modified.

COMPARATIVE PRECISION OF LEAD METHODS

The Laboratory of the Canadian Inland Revenue, which originated the Canadian lead method, admits that the Winton method gives more precise results, *i. e.*, closer duplicates, than can be obtained with the Canadian method. Our own experience is to the same effect. It occurred to the authors that it might be possible to combine the advantages of these two methods by using the same proportion of lead subacetate solution as in the Canadian method, and determining the amount of residual lead in solution as in the Winton method. Some experiments have been carried on in this connection, the results of which will be published in a subsequent paper.

MODES OF WASHING PRECIPITATE IN CANADIAN LEAD METHOD

Experiments have also been made upon the effect of temperature and volume of wash-water upon the weight of the lead subacetate precipitate as obtained by the Canadian method. The results given in Table X clearly indicate that wash waters of 80° and 100° C.

TABLE X—EFFECT OF VARIATIONS OF TEMPERATURE AND VOLUME OF WASH WATER UPON THE CANADIAN LEAD NUMBER

Syrup I

	Total quantity of wash water(*a*)			
Temp. of wash water 80° C.	50 cc.	100 cc.	150 cc.	Average
1st time	4.56	4.29	4.20	
	4.52	4.32	4.62	
2nd time	4.68	4.63	4.12	
	4.80	4.60	4.21	
Average at 80°	4.64	4.46	4.29	4.46
100° C.				
1st time	4.77	4.37	4.70	
	4.66	....	4.50	
2nd time	4.84	4.26	4.36	
	....	4.35	4.42	
Average at 100°	4.76	4.33	4.50	4.53
Average	4.70	4.40	4.40	
Max. deviation	0.18	0.23	0.30	

(*a*) Applied in five equal portions in every instance.

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[1] Lab. of the Inland Revenue Dept., Ottawa, *Bull.* **228** (1911).

Syrup II

Temp. of wash water 80° C.	Total quantity of wash-water(a) 50 cc.	100 cc.	150 cc.	Average
1st time	2.83	2.40	2.58	
	2.92	2.54	2.69	
2nd time	2.95	2.74	2.75	
	2.98	2.75	2.79	
Average at 80°	2.92	2.61	2.70	2.74
100° C.				
1st time	2.93	2.72	2.51	
	2.82	2.70	2.65	
2nd time	2.82	2.81	2.43	
	2.98	2.76	2.54	
Average at 100°	2.89	2.75	2.53	2.72
Average	2.91	2.68	2.62	
Max. deviation	0.09	0.28	0.19	

(a) Applied in five equal portions in every instance.

give identical results. Higher results are obtained with 50 cc. of wash water (applied in five portions) than with 100 cc. or 150 cc. There is no material difference between the results obtained with 100 cc. and with 150 cc. of wash water.

MODES OF REDUCTION OF LEAD NUMBERS TO DRY MATTER BASIS

In the investigation made by the Laboratory of the Inland Revenue Department preliminary to the setting of standards, the Canadian and Winton lead determinations were made upon fixed quantities of syrup (5 grams and 25 grams, respectively) and the results calculated to a dry matter basis. The standards, however, prescribe the use of a quantity of syrup equivalent to the same fixed quantity of *dry matter*, *i. e.*, 5 grams and 25 grams of dry matter, respectively. We have made a comparison of results obtained directly by the methods of the Canadian standard with those obtained by calculation from the determinations on the wet basis. As will be seen from Table XI, with the Canadian method the results obtained by calculation to a dry basis are lower than those determined directly upon the dry basis, the average difference on the four syrups being 0.36. With the Winton method, on the other hand, the calculated results are uniformly higher than those directly determined, the average difference in this case being 0.18. All results given are the average of closely agreeing duplicates. It would appear, therefore, that material differences exist between the results obtained, on the one hand, by determination upon a fixed quantity of syrup and calculation to a dry basis and, on the other hand, by direct determination upon a definite quantity of dry matter.

TABLE XI—COMPARISON OF LEAD NUMBERS ON DRY BASIS, ACTUAL AND CALCULATED

	Canadian lead method			Winton lead method		
Syrup number	Actual lead no.	Calculated lead no.	Difference	Actual lead no.	Calculated lead no.	Difference
1	1.80	1.36	0.44	1.35	1.53	0.18
2	3.20	2.95	0.25	1.96	2.11	0.15
3	3.02	2.63	0.39	1.98	2.20	0.22
4	2.86	2.51	0.35	2.01	2.16	0.15
		Average,	0.36			0.18

THE BLANK IN THE WINTON METHOD

In making the determination of lead in the blank for the Winton method, Bryan recommends the addition of acetic acid to the lead subacetate solution to prevent formation of a precipitate upon the addition of water, "as pure sugar would do."[1] Upon making determinations in duplicate on two blanks, one treated with acetic acid, the other with 25 grams cane sugar syrup, we found that smaller amounts of lead were held in solution by the cane sugar than by the acetic acid. This was the case, whether the determinations were made immediately upon the unfiltered blank or upon the settled (3 hours) and filtered blank, as will be seen from the figures of Table XII. It would seem to be more rational to make the Winton blank in the presence of cane sugar syrup rather than with acetic acid, as in this way we should approximate more closely to the conditions obtaining in the determinations upon maple syrup.

TABLE XII—EXPERIMENT ON WINTON BLANK

	Weight of lead sulfate precipitate Immediately unfiltered	At end of 3 hours filtered
Acetic acid used as clarifier in blank	0.1593	0.1600
25 grams cane sugar syrup in blank	0.1571	0.1558

SUMMARY

1. The rates at which the conductivity value, ash data and various lead values fall off as maple syrup is diluted with cane sugar syrup are determined for three samples of maple syrup.

2. The range of variation of these data in genuine syrups is studied with reference to the work of Bryan and McGill, as well as to our own work.

3. The Canadian lead value shows the most rapid falling off.

4. The conductivity value shows the narrowest range.

5. The Winton lead method gives better agreement of duplicates than the Canadian method.

6. In the Canadian method no material difference is obtained by washing the precipitate with water at 80° and 100° C. Practically identical results are obtained with 100 cc. and 150 cc. wash water, but higher results with 50 cc.

7. Results obtained in the Canadian method, using the quantity of syrup containing 5 grams of dry matter, are higher than those obtained with use of 5 grams of syrup and calculated to the dry basis. On the other hand, in the modified Winton method, prescribed in the Canadian standards, lower results are obtained with the use of the quantity of syrup containing 25 grams dry matter than when 25 grams syrup are used and the results calculated to the dry basis.

8. The use of cane-sugar syrup instead of acetic acid in the Winton blank is suggested.

(The expenses of this investigation were defrayed out of the grant of the Dominion Government for the advancement of agriculture, 1912.)

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[1] Bryan, *loc. cit.*, p. 18.

ON THE PREPARATION OF NEUTRAL AMMONIUM CITRATE SOLUTION[1]

By Paul Rudnick and W. L. Latshaw

It has been the custom in this laboratory for several years past to determine the strength of neutral ammonium citrate solution by the analytical method recommended by the Committee on Ammonium Citrate Solution of this Division in 1909,[2] except that no attempt was made to determine the citric acid content by titrating back the residue after distillation of the ammonia. It was found simpler and easier to determine the strength in this way and to calculate from this strength the extent of dilution necessary to bring the solution to the strength recommended, *i. e.*, 43.7 grams of ammonia per liter, than to dilute to the required specific gravity by cut-and-try methods. A determination of the specific gravity of the solution thus prepared is always made as a final check and is always found to be 0.09 ± 0.001, substantially as required by the official method.[3]

The determination of the neutrality proper, however, has not been made by determining the citric acid as recommended by the committee, but is made by the indicator method recommended by Hand,[4] which has proven fairly satisfactory in our hands so far as ease of manipulation and simplicity were concerned.

The electrical conductivity methods proposed by Hall and Bell[5] and later by Patten and Robinson[6] as well as the extraction and temperature methods proposed by Bell and Cowell[7] do not seem applicable to the problem as presented in routine fertilizer work for various reasons, chiefly because of the difficulties of manipulation involved. A most practical method of attacking the problem was advised by Patten and Marti[8] and presented at the last meeting of this Division in Milwaukee. The great advantage of this method lies both in its simplicity and ease of accurate reproduction, as well as in the fact that it is based upon reliable and accurate physico-chemical measurements summarized in a definite strength of both ammonia and citric acid.

It became a matter of interest to compare this method with the method used in this laboratory heretofore as described above, and the following is an account of the preliminary work undertaken and of the results so obtained.

Two solutions of ammonium citrate were prepared as follows:

Solution I upon analysis by the Patten and Marti method showed a content of 158.1 grams of citric acid and 37.23 grams of ammonia per liter. From this the proper correction for both citric acid and ammonia were calculated and a re-analysis of the corrected solution showed a content of 168.6 grams of citric acid and 44.54 grams of ammonia per liter. The gravity of this solution was 1.09. This solution was assumed to be practically neutral and of the proper strength, although when tested by the indicator method of Hand it seemed to be very slightly acid. This was in accordance with the ratio of ammonia to citric acid, namely 1 : 3.786 instead of 1 : 3.765.

Solution II was made up of a higher concentration than that required by the official method and was then brought to neutrality as follows:

Instead of following strictly the method of Hand a series of tubes was prepared from Solution I as described by Hand, namely adding 5 cc. of the ammonium citrate solution to 45 cc. of neutral water containing the prescribed amount of azolitmin indicator. One of these tubes was left unchanged and to the remainder were made successive additions, differing by 0.5 cc. each, of *N*/10 ammonia and *N*/10 citric acid, respectively. From these tubes the one apparently nearest neutral was chosen and Solution II was then adjusted to this color by the method of Hand. Instead of comparing the tubes as described by him, however, we found it much easier to compare them in a Craven-Jennings colorimeter[1] in the same manner as in nesslerization of water.

Solution II was then analyzed by the Patten and Marti method and was found to contain 179.2 grams of citric acid and 47.80 grams of ammonia per liter, giving a ratio of 1 : 3.748 as against 1 : 3.765, the ratio given by Patten and Marti. Solution II was then brought to a gravity of 1.09.

We now had two solutions, one of which (Solution II) was obviously slightly alkaline, the other (Solution I) slightly acid. Comparative analyses of a sample of acid phosphate were made with these two solutions, giving the following results:

Percentages Insoluble P_2O_5 by	
Solution I	Solution II
1.10	1.11
1.11	1.10
Lost	1.12

These results would indicate that the variation of these solutions from the ratio given by Patten and Marti was not sufficient to affect the results obtained on the sample of acid phosphate in question. Further work on this subject is in progress.

Chemical Laboratory of Armour & Company
Union Stock Yards, Chicago

A STUDY OF THE PEMBERTON-KILGORE METHOD FOR DETERMINATION OF PHOSPHORIC ACID

By P. L. Hibbard

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After using the Pemberton-Kilgore volumetric method for phosphoric acid quite successfully for some time, sources of error in it became apparent. Endeavor to avoid these errors led to the making of this study, which is now published with the hope that others may be helped in the use of this very good method.

In the beginning it is well to understand that the method is not, nor can it be made scientifically exact. Good results obtained in the use of it must always be

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[1] Paper presented at the 48th meeting of the A. C. S., Rochester, September 8-12, 1913.

[2] W. D. Richardson, *et al.*, This Journal, **1**, 616 (1909).

[3] *Bur. Chem., Bull.* **107**, page 1.

[4] *Ibid.* **132**, page 11.

[5] *J. Am. Chem. Soc.*, **33**, 711 (1911).

[6] This Journal, **4**, 443 (1912).

[7] *J. Am. Chem. Soc.*, **35**, 49 (1913).

[8] This Journal, **5**, 567 (1913).

[1] Supplied by the Bausch & Lomb Optical Company.

due to a proper balancing of tendencies to error. Nevertheless, with proper handling, it is capable of giving results which for accuracy and reliability compare favorably with those obtained by most analytical methods in common use, and which are obtained with an ease and speed not equalled by any other method for determination of phosphoric acid known to the writer. Much similar work has been done by others. (See Bibliography.)

Publication of this study has been long delayed, with the hope of better clearing up several points. Pressure of other work now makes it likely that this is very remote. But for practical purposes the work is complete and is now given publicity with the hope that it may assist some to successfully use the Pemberton-Kilgore method, who would not otherwise overcome some of its difficulties.

This work includes a study of the influence of the chief factors likely to have any bearing on the successful use of the method, as apparent to the writer. The method is not well adapted for estimating very small amounts of phosphoric acid. Many of the results are given in tabular form for easy reference. This is followed by a summary and bibliography.

A. PRINCIPLES OF THE METHOD

The phosphate solution is mixed with an acid solution of molybdic acid, which causes precipitation of an acid double salt of phosphoric and molybdic acids of uniform and definite composition (E 26). This salt, here spoken of as yellow precipitate, is filtered out, washed free of other acid, and its acidity determined by titration with standard caustic alkali, which thus measures the amount of P_2O_5 in the solution analyzed. Apparently this should give scientifically exact results. In practice this is not true because of the influence of the numerous other substances usually present in the phosphate solution. Inexperienced operators will usually get as good results with this method as with most others. Experienced analysts will need considerable practice with it before then can safely rely on their results, though it is hoped that careful reading of this study will soon enable such persons to use it very successfully. In case but few determinations art to be made at one time, it is scarcely worth while to prepare the apparatus and solutions needed. The gravimetric method would be more convenient.

The method is suitable for determination of P_2O_5 in almost any substance, with great speed and adequate accuracy. After the solution of the phosphate is prepared the assay may be completed in 20 minutes or in much less time, at slight sacrifice of accuracy. In the analysis of fertilizers by this method, I have been able to complete 21 determinations, including weighing out to final result, in a little over six hours of actual working time, on various occasions. About one-third of those were determinations of citrate-insoluble P_2O_5 which require much more time to prepare the solutions. After the solutions were prepared I have been able to precipitate, wash and titrate to final result 22 samples in two and one-third hours.

B. THE FILTER AND PREPARATION OF ASBESTOS

Lack of a suitable filter is the probable cause of more failures in the use of this method than any other one thing. The usual paper filter, or the Gooch crucible, is not well suited to the work, and any one depending on them is likely soon to be discouraged. The filter tube described by Kilgore is very satisfactory (G 7). Commonly known as a carbon tube or sugar filter, this is a glass tube about $1^1/_4$ inches wide, $2^1/_2$ inches long, open at one end and narrowed at the other end to a stem $^1/_4$ inch diameter and 2 inches long. A perforated porcelain disk $1^1/_8$ inches diameter has a stiff piece of platinum or copper wire 5 inches long fastened in its center. By extending into the narrow stem this wire holds the disk level in the bottom of the filter tube. The disk supports a layer of prepared asbestos about $^1/_8$ inch thick which forms the filter. The stem of the filter tube is pushed through one hole of a two-hole rubber stopper which is placed in the mouth of an ordinary 12-ounce wide mouth bottle. A bent glass tube in the other hole of the stopper is connected with the vacuum pipe. Suction equal to 10 inches of mercury is sufficient. In forming the filter, suction should not be applied until most of the water has run out of the asbestos pulp after it is poured into the filter tube.

A suitable quality of asbestos is very important for rapid and clear filtering. In order to prepare the asbestos, shred it to small pieces, pack into a wide mouthed flask, cover with dilute HCl (1 to 3). Place the flask in a water bath and heat to boiling several (five) hours. (Cannot well be heated over flame.) Filter on a Buchner filter, wash free of acid, return to the flask and cover with 5 per cent caustic soda, heat again in a water bath three hours, filter, wash free of alkali, then with dilute acid, and finally with water till free of acid. The fine part must now be removed by decantation. (Attempts to remove the fine asbestos by an elutriation process were not very successful.) The asbestos is suspended in a large volume of water, in a tall jar or cylinder, allowed to stand about five minutes, till the valuable coarser part is settled. The milky liquor in the upper $^2/_3$ of the jar is now siphoned off, the jar again filled with water and the asbestos stirred through it; after a few minutes the milky liquor is again drawn off. The fine asbestos in the liquor drawn off is of no value for filtering and if left with the coarse part, clogs the filter, making it very slow in operation. The decantation must be repeated five or six times till the liquor drawn off contains very little suspended matter. The remaining medium coarse asbestos is now ready for use. To make a quick-acting filter the fibers should be long and rather stiff so that the filtering bed will be somewhat springy and remain very porous under pressure. If the asbestos fiber is very soft and thread-like, the filter bed becomes compact and filters very slowly. After using in a determination, the asbestos may be recovered for using again, by washing with alkali, then acid and again decanting to remove fine material. The filtering tubes prepared with this asbestos are used much as the gooch crucible would be. With this apparatus and properly prepared asbestos, the operation of filtering and washing an ordinary P_2O_5 precipitation need not consume more than five minutes.

If an ordinary paper filter be used, there is danger of decomposition of the precipitate by the long washing necessary to remove all acid from the filter paper. This decomposition may be prevented by the presence of 2 per cent of potassium nitrate in the wash water. If paper is used, there is danger of reduction of the molybdate during the titration, after the solution becomes alkaline, thus producing a bluish color, which obscures the end point in the final titration back with acid. The ammonium phosphomolybdate precipitate packs very much during filtration by suction so that if there is much of the precipitate, it makes so deep a layer in the ordinary size of gooch crucible, that filtration and washing are slow. Besides, the gooch is not a convenient dish from which to transfer the precipitate and asbestos back to the precipitating flask. Both of these defects are avoided by use of the carbon filter tube of the size mentioned; besides, the tube has much greater capacity to hold liquid than the gooch, which is a great advantage when several are operated simultaneously.

The water used for washing the yellow precipitate must be neutral and free of organic matter, ammonia or CO_2 compounds.

C. EXPLANATION OF METHODS AND SOLUTIONS USED

Details of the method of operating are given under Section D.

For nearly all of the work here reported a solution of sodium phosphate was used, usually containing about three grams per liter. This makes about 20 mg. P_2O_5 in 25 cc., the amount usually taken for each test. For measuring the separate portions, a 25 cc. automatic overflow pipette was used. Its delivery was very constant and reliable. During the course of the work several different phosphate solutions were made and used. For this reason the actual P_2O_5 taken for each set of experiments was somewhat variable, and the correct amount is usually given at the beginning of each table. With some exceptions figures given are the result of two or more closely agreeing determinations; in many cases, numerous determinations were made. In some of the less important matters only the figures given were obtained.

The molybdate solution used was made up according to the method of the A. O. A. C., *Bulletin* 107, p. 4, Bureau of Chemistry, United States Department of Agriculture. One liter contained about 50 grams MoO_3 (85 per cent), 72 cc. ammonia (sp. gr. 0.90) and 250 cc. HNO_3 (sp. gr. 1.42). This was freshly filtered at time of using, and to each 100 cc., 5 cc. HNO_3 (sp. gr. 1.42) were added. In most cases 25 cc. of NH_4NO_3 (60 per cent solution) = 15 grams were used in each test.

In experimenting with the various substances, a concentrated solution of each was made and various amounts of it were added to the phosphate solution before making the volume up to 100 cc. with water. For convenience complete working details of the method are here given.

D. WORKING DETAILS OF THE VOLUMETRIC METHOD

For this process the solution may be prepared by any of the methods given in E 24, except by the use of sulfuric acid. For the precipitation, a wide mouthed Erlenmeyer flask of about 400 cc. capacity is convenient. Transfer to the flask, by means of a pipette, an aliquot of the phosphate solution such that it will contain 10 to 30 mg. phosphoric acid. It is desirable to have as nearly 20 mg. as convenient. Neutralize the aliquot taken by adding a slight excess of ammonia, then nitric acid to faint acidity; then add 25 cc. of ammonium nitrate, 60 per cent solution; then water to bring the total volume to about 100 cc. In case very small amounts of phosphoric acid are present, it is better not to increase the volume more than necessary, leaving it less than 100 cc. if convenient. Place the flask in the water bath at 65° C. and after a few minutes, when warm, add excess of ammonium molybdate solution, mix, and let stand at 65° for 15 minutes. (Temperature in the flask is usually 2 or 3 degrees lower than in the bath.) The amount of molybdate solution is varied in proportion to the phosphoric acid present.

The minimum amount to be used is 20 cc. and if a proper aliquot of the phosphate solution is taken, 40 cc. will be sufficient for almost any sample. The molybdate solution must be filtered immediately before using; then add to it 5 cc. of nitric acid for each 100 cc. of molybdate solution. In case there is very little phosphoric acid present, or, if the solution contains much silica, it is better to keep temperature at 50 to 55 instead of 65. It should never be higher than 65 on account of danger of precipitating molybdic acid, and the time should not be much over 15 minutes at this temperature. After expiration of the time, filter on asbestos in filter tube above described supported on a 12-ounce wide mouth bottle. Wash with pure water which must be neutral. By using 20 to 30 cc. of water for each washing, the precipitate is usually free of acid by the time the bottle is full. In order to test for freedom from acid, transfer the filter to a clean bottle in which collect some of the washings (20 to 30 cc.), add a few drops of phenolphthalein, then one drop of standard alkali. If the red color is persistent, the washing has been sufficient. Rinse off the outside of the filter tube with water. Invert it into the mouth of the flask and by means of the wire in the disk, push the precipitate out into the flask. Rinse out clean with water, into the flask. Now titrate with the standard alkali, NaOH or KOH with continual shaking, until the yellow precipitate has completely disappeared. This disappears gradually. Take care not to use a large excess of alkali. Two or three cc. excess is best. After *complete* disappearance of the yellow precipitate add $^1/_2$ cc. phenolphthalein solution and titrate back to colorless with standard nitric acid, which is usually of the same strength as alkali. The standard alkali used is of such strength that 1 cc. is equivalent to 1 mg. of P_2O_5 (32.38 normal). From this may be calculated the amount of phosphoric acid present.

E. DETAILED STUDY OF THE CHIEF CONDITIONS AND SUBSTANCES CONCERNED IN THE USE OF THE VOLUMETRIC METHOD

In general, except when otherwise stated, each test was conducted about as described under D.

1. Temperature

The yellow precipitate separates from the usual molybdate solution more or less rapidly, according to temperature. Hence, it is important to measure this effect at various temperatures.

TABLE I

A. 20.3 mg. P_2O_5 present			B. 21.3 mg. P_2O_5 present		
Time heated	Temperature °C.	Mg. P_2O_5 found	Time heated	Temperature °C.	Mg. P_2O_5 found
15	40	18.9(*a*)	15	50	20.6
15	50	20.2	30	50	20.8
15	60	20.1	60	50	21.0
15	65	20.3	120	50	21.3
15	70	20.8	60	65	21.6
..	..	....	15	65	21.3

(*a*) Very imperfect precipitation.

The precipitate formed at temperatures below 40° is very finely divided and difficult to filter properly, though it becomes fairly good if allowed to stand over night. Yet the result is low. A shows effects of variations in temperature for a fixed time. B shows effect of varied time at fixed temperature. High temperature promotes complete and rapid separation of yellow precipitate also of MoO_3. At low temperature MoO_3 does not separate so soon, but the yellow precipitate is also slow in forming, and too finely divided to filter well, so a medium point is selected at which the main evils are avoided and a reliable result obtained. For this work the official conditions seem as good as any, 15 minutes at 65° with 100 cc. volume, though it is quite possible that a different set of conditions would do as well if properly worked out. Thus, a higher temperature with shorter time would do very well, except that there is greater danger of separation of MoO_3 if temperature is not quickly lowered. Lower temperature with longer time is very frequently used, and is safer, the only objection being longer time necessary.

2. Time

Table I indicates that time has a very important effect on separation of MoO_3. This is better shown in Table II in which time is varied but temperature constant.

TABLE II

20.3 mg. P_2O_5 present

Time heated	Temperature °C	P_2O_5 found
1 min.	65	19.9
5 min.	65	20.1
15 min.	65	20.3
30 min.	65	20.4
60 min.	65	20.8
15 min.	65 then stood	....
24 hrs.	20	20.3

The last result shows that after the precipitation is properly completed at the elevated temperature, the result is not changed by allowing it to stand 24 hours at room temperature.

3. Volume or Concentration

The volume in which precipitation takes place has a very important effect on the character of the precipitate. In a concentrated solution of P_2O_5, the precipitate is too finely divided and does not filter and wash well. In a dilute solution the precipitate is slow in forming and is likely to be deficient in quantity. Table III indicates these effects.

TABLE III

A. 20.3 mg. P_2O_5 present		B. 4.07 mg. P_2O_5 present	
Volume Cc.	Mg. P_2O_5 found	Volume Cc.	Mg. P_2O_5 found
50	20.2	25	4.05
100	20.3	50	4.00
150	20.3	100	3.50
300	19.5	...	....

In this table all quantities were constant except volume. But if molybdenum is increased in proportion to total volume, the P_2O_5 found is nearly correct as is indicated in Table IV.

4. Proportion of Molybdenum

Whatever may be the composition of the yellow precipitate it is fully established by experience that much more molybdenum must be present in the solution than is necessary to combine with the P_2O_5 present. Twice as much is commonly used, often much more. This excess tends to separate from the solution at elevated temperatures and contaminate the yellow precipitate. Herein is perhaps the greatest inherent source of error in the volumetric method. Ammonium nitrate in the solution reduces the amount of molybdenum necessary for complete precipitation of P_2O_5, also, promotes separation of MoO_3. HNO_3 has the opposite effect. Hence, all these must be considered in adjusting the solution which is discussed under heading 9.

Table IV indicates effects of varying molybdenum, all other quantities remaining constant, except as indicated. In B the proportion of molybdenum to phosphoric acid is relatively high, and high results are shown. In C the opposite is true.

TABLE IV

A. 20.3 mg. P_2O_5 present			B. 4.07 mg. P_2O_5 present			C. 40.7 mg. P_2O_5		
Molybdate reagent used. Cc.	Total volume. Cc.	Mg. P_2O_5 found	Molybdate reagent used Vol.	Total volume. Cc.	Mg. P_2O_5 found	Molybdate reagent used. Vol.	Total volume. Cc.	Mg. P_2O_5 found.
15	100	19.6	5	100	3.90	30	100	39.6
20	100	20.1	10	100	4.35	40	100	39.9
25	100	20.2	15	100	4.40	50	100	40.0
30	100	20.3	20	100	4.40	75	125	40.2
40	100	20.3	..	...	....	100	125	40.1
60	100	20.5	..	...	....	...	...	....

5. Nitric Acid

Free acid must be present in order that the yellow precipitate may be formed as shown under *Effect of Free Acids* (E *8*). Nitric is the most suitable acid (E *25*). Contrary to the effect of NH_4NO_3 it tends to prevent separation of both the yellow precipitate and of MoO_3, *i. e.*, both are soluble in acid of sufficient concentration. As shown in Table VIII, less than the usual amount allows MoO_3 to separate, causing high results, while more than twice the usual amount has but little solvent effect on the precipitate.

6. Ammonium Nitrate

Ammonium nitrate, though formed in the reaction, is not necessary except to produce a desirable physical condition of the precipitate and render it less soluble in the liquid. It promotes the separation of MoO_3, thus causing high results, but if it is absent the precipitate is very finely divided, hence, difficult to filter, and result is low. Large excess of ammonium nitrate causes an amorphous precipitate, which passes through the filter during washing, yet results are high—due to co-precipitated MoO_3. Ammonium nitrate may be to some extent replaced by other salts which tend to have similar effects in promoting proper formation and separation to the precipitate. Thus in the presence of NaCl or $(NH_4)_2SO_4$, less NH_4NO_3 is required.

TABLE V

Substitution of NH_4NO_3

By NaCl			By $(NH_4)_2SO_4$		
NH_4NO_3 Cc.	NaCl Cc.	Mg. P_2O_5 found	NH_4NO_3 Cc.	$(NH_4)_2SO_4$ Cc.	MgP_2O_5 found
15	0	20.3	15	0	20.8
15	4	20.5	3	4	21.3
0	8	20.0	3	8	21.1
5	8	20.3	..	..	....
15	8	20.6	..	..	....
0	16	18.6	..	..	....
10	16	20.2	..	..	....

(This is complicated by action of SO_4 which usually tends to high results.) Therefore, if the solution contains much of some other salt, less NH_4NO_3 need be used. If the full usual amount is used in addition to the other salt present, the bad effects of an excess of the latter are apparent, while if less NH_4NO_3 were used the other substance would not interfere so much.

Besides its effects on the precipitate, ammonium nitrate prevents solution of the precipitate by the wash water during filtration, and partially offsets the bad effect of excessive soluble chlorides in some cases.

7. General Effect of Salts in Solution

Below 5 per cent most salts have but slight effect. Iron salts and sulfates are exceptions. Large quantities of all salts examined have similar general effect, though not to the same extent for all. Nitrates are least injurious. Large amounts of soluble salts increase solubility of yellow precipitate and tend to prevent its formation, also, cause it to run through the filter in washing. The only remedy is to decrease the concentration of the salt. Decomposition of the precipitate in washing is largely avoided by presence of 2 per cent of KNO_3 or NH_4NO_3 in the wash water. Molybdic solution or dilute HNO_3 is also effective, but is not permissible in the volumetric method.

8. Effect of Free Acids

The yellow precipitate is soluble in strong acids so that their general effect is to cause low results. But a certain amount of free acid is necessary to form the precipitate according to the equation:

$$CaH_4(PO_4)_2 + 24(NH_4)_2MoO_4 + 44HNO_3 = 2(NH_4)_3PO_4(MoO_3)_{12} + 42NH_4NO_3 + Ca(NO_3)_2 + 24H_2O.$$

This free acid may be either HCl, HNO_3, or H_2SO_4, though HNO_3 is preferable as shown under E *25*. Besides being necessary in the reaction, to form ammonium phosphomolybdate, free acid is necessary to prevent separation of MoO_3 and the quantity thus needed is variable depending on the amounts of salts, molybdenum, P_2O_5 and water in a given volume. Free acid is also needed to keep in solution certain bases, as Fe, Cu. The free acid usually present is commonly several times the amount needed in the reaction. According to the equation above, 1 part P_2O_5 requires 16.2 parts MoO_3 and 18.6 parts HNO_3. If the solution contains 0.02 per cent P_2O_5 this would need for the reaction 0.372 gram HNO_3. However, 30 cc. of the official molybdate solution used in this case would contain nearly seven grams HNO_3. The relation of these various substances may well be discussed under the heading:

9. Proportion between P_2O_5, HNO_3, NH_4NO_3, Molybdenum and Volume

Fifteen to thirty mg. P_2O_5 is the most convenient amount. There is no advantage in more P_2O_5 as sensitiveness of end point decreases in proportion as P_2O_5 increases, so that greater accuracy is not obtained by use of larger amounts of P_2O_5. This is one of the weakest points of the method and makes the result somewhat uncertain for high percentages of P_2O_5. For small amounts of P_2O_5, 15 mg. or less, it is better to keep the volume below 100 cc. in order to obtain rapid separation of yellow precipitate. In this case less NH_4NO_3 should be used. The relation between NH_4NO_3 and HNO_3 in the solution may be somewhat a matter of personal choice. It is shown by Hundeshagen (G 34) that at least 26 mol. HNO_3 to 1 PO_4 are necessary, and up to 80 do no harm; above that causes solubility of precipitate. But this was in the presence of but little NH_4NO_3. In my work, which is essentially according to the method of the Official Agricultural Chemists, 15 per cent NH_4NO_3 is used, in general, and with this about 7 per cent free HNO_3 (supplied by molybdate solution). This is about 3 times as much acid as Hundeshagen recommends. The purpose of NH_4NO_3 is to promote rapid and complete separation of precipitate but it also promotes easy separation of MoO_3 which tendency is counteracted by free HNO_3. This free acid which is contained in the molybdate solution helps preserve the reagent and tends to prevent separation of MoO_3 from this solution (molybdate) while standing before use, as well as after it is mixed with P_2O_5 solution. If less NH_4NO_3 is used, less HNO_3 should be used, to avoid solubility of precipitate.

In order to secure complete separation of the yellow precipitate in a short time, the amount of molybdenum used should be at least twice the amount necessary to combine with P_2O_5. NH_4NO_3 helps to reduce the amount of molybdenum thus needed. But the greater the excess of molybdenum present the greater is the danger of separation of free MoO_3: hence, the limit to 2 or 3 times the amount entering the precipitate.

In case of very small amounts of P_2O_5 results are usually high if large excess of molybdenum is used. In presence of more than ordinary amounts of P_2O_5 results are low unless molybdenum is correspondingly increased. In fact the proportion of all the other ingredients in the solution should be made to correspond to amount of P_2O_5 present. A good working proportion is this: 0.02 gram P_2O_5, 15 grams NH_4NO_3, volume 100 cc. and 30 cc. molybdate solution, containing 7 per cent free HNO_3.

10. *Chlorides*

TABLE VI

Mg. of P_2O_5 found with

Chloride added Percentage	NaCl	NH_4Cl	$MgCl_2$	$CaCl_2$	$FeCl_3$	HCl (Sp. gr.) 1.20)	$BaCl_2$
0	21.3	21.2	20.3	20.3	21.3	20.1	20.3
0.5	....	....	20.2	20.1	20.4	20.0	....
1	....	21.2	20.1	20.2	18.7	20.0	20.4
2	20.9	21.0	20.0	20.0	19.2	19.9	20.4
4	21.0	20.8	19.8	20.0	19.2	19.9	20.3
8	20.9	20.6	18.5	20.0	19.2	....	20.2
16	20.6	20.4	....	....	....	....	....

All chlorides examined tend to cause low results and solubility of yellow precipitate. Iron and magnesium chlorides are most injurious, calcium least. However, if HCl is used as the solvent in preparing the solution for analysis, then an aliquot is taken; the Cl present is not often sufficient to be perceptible in effect. The NH_4NO_3 used largely overcomes effect of Cl.

11. *Nitrates*

TABLE VII

Mg. P_2O_5 found with

Percentage added	HNO_3	$Cu(NO_3)_2$	$Fe(NO_3)_3$	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$NaNO_3$	Added	NH_4NO_3
0	20.3	20.8	20.8	20.8	20.2	20.2	..	20.3
0.5	no pptn.	....	....	....	....	....	0	20.0
1	20.5	....	20.2	20.9	20.2	20.2	3	20.1
2	21.1	20.7	19.6	20.9	20.2	20.2	6	20.3
4	21.0	20.8	19.6	20.9	20.2	20.2	12	20.5
8	20.3	21.0	15.6	21.1	20.2	20.3	24	20.7
16	20.0	21.1	....	21.8	20.3	20.4	48	21.3

$NaNO_3$ in addition to regular NH_4NO_3 has little effect up to 5 per cent. But if substituted for NH_4NO_3 in part or whole the precipitate is soluble, more or less. Hence, it is best to avoid large amounts of sodium salts. Nitrates in small quantity tend toward high results, but in large amounts modify the character of the precipitate greatly and cause low results, like any soluble salt in large amount.

12. *Sulfates*

TABLE VIII

Mg. P_2O_5 found with

Percentage added	H_2SO_4	H_2SO_4 (NH_4NO_3 absent)	$(NH_4)_2SO_4$	K_2SO_4	$CaSO_4$	$Fe_2(SO_4)_3$	$CuSO_4$	Hg_2SO_4
0	20.3	20.1	20.8	20.8	21.0	21.0	21.0	21.0
0.5	21.1	20.5	....	....	21.5	20.3	21.9	21.4
1	21.2	20.3	21.4	21.5	21.5	19.8	21.8	21.4
2	21.1	19.8	21.5	21.4	21.6	11.4	21.9	21.5
4	20.9	18.1	21.3	21.3	21.5	....	21.9	21.1
8	18.5	....	21.0	21.2	....	....	21.9	....
16	17.4	....	20.0	....	....	....	....	....

In presence of soluble copper compounds, a little Cu is contained in the precipitate and causes the asbestos to appear green in final titration. When more than 2 per cent H_2SO_4 is present it shows a strong solvent action on the precipitate. In absence of NH_4NO_3 this is much more apparent. Up to 2 or 3 per cent, soluble sulfates in general cause high results, above 3 per cent usually causes low results, with the bad effects of excess of any soluble salts.

13. *Removal of Soluble Sulfates from Solution*

High results, due to soluble sulfates, are avoided by precipitating SO_4 by $BaCl_2$. This should always be done in presence of considerable free acid in order to prevent separation of barium phosphate. The solution is then diluted to a suitable volume and an aliquot taken for determination of P_2O_5.

Examples of Removal of Sulfates

One hundred cc. phosphate solution placed in 200 cc. flask, added 5 grams K_2SO_4, 6 cc. HNO_3, boiled, added excess $BaCl_2$, neutralized with NH_3, cooled, filled to mark, filtered, took for determination, 50 cc. = 0.0208 P_2O_5, found, 0.0209. This shows that P_2O_5 is not carried down by $BaSO_4$ in acid solution.

14. *Examples of Effect of Soluble Sulfates*

Solutions of various fertilizers made by digestion with H_2SO_4 and K_2SO_4 as if for determination of nitrogen; no $BaCl_2$ added to remove SO_4: compared with solution of the same samples made by burning with MgO and dissolving in HCl, $BaCl_2$ added to remove SO_4.

TABLE IX

	Percentages P_2O_5 found with solution made by	
Material	Burning with MgO	Digestion with H_2SO_4
No. 70. Complete fertilizer...	12.50	12.95
	12.50	12.95
		12.95
No. 78 Bone meal..........	22.30	21.85
	22.30	22.45
		22.70
No. 86 Tankage............	12.55	13.20
No. 87. Complete fertilizer...	9.40	10.00

15. *Soluble Silica*

TABLE X—P_2O_5 FOUND WITH PERCENTAGE SiO_2 IN SOLUTION

0.0212	0.000
0.0212	0.005
0.0213	0.010
0.0218(a)	0.050
0.0217	0.100
0.0218	0.200

(a) After reprecipitating, this gave 0.0214.

If more than 0.05 per cent soluble SiO_2 was present it was precipitated by the acid phosphate solution before adding molybdenum, hence no higher results from larger amounts of SiO_2 present. The smaller amounts make the precipitate greenish yellow, flocculent, difficult to filter and very slow to dissolve in the KOH: results high. Reprecipitation removes most of the ill effects of soluble SiO_2 and brings result nearly correct.

16. Iron

Iron in solution as chloride, sulfate and nitrate causes low results, somewhat proportional to amount present (see Tables VI, VII, VIII). It always contaminates the yellow precipitate so that in final titration the end point is obscured by presence of ferric hydrate. This is somewhat prevented by presence of tartaric acid, or citric acid, in the molybdate solution, though enough tartaric acid to prevent separation of iron causes solubility of yellow precipitate and low results. Iron in the precipitate is avoided by double precipitation as given in E *18*.

Low results due to iron may be largely avoided by use of a large excess of molybdate solution. In the solution containing 20.8 mg. P_2O_5, presence of $FeCl_3$ = 8 per cent of Fe gave 13.2 mg. P_2O_5 when 30 cc. molybdate solution were used, but when 100 cc. molybdate were used, found 20.7 mg. P_2O_5.

TABLE XI—EFFECT OF INCREASED MO IN PRESENCE OF MUCH FE

Molybdate used Cc.	Percentage Fe as $FeCl_3$	Mg. P_2O_5 found
30	0	20.8
30	4	19.2
75	4	20.7
30	8	13.2
100	8	20.7

17. Effect of Oxidizing Agents

Bromine, below 2 per cent, no effect apparent: large amounts cause low results.

Chromic acid acts much the same as H_2SO_4, small amounts cause high results, large amounts, low results; 10 per cent completely prevented precipitation. A small amount of Cr was retained in the precipitate and gave a greenish tinge to final solution.

Potassium permanganate seems to cause somewhat high results, but this is uncertain because of the indefinite end point, especially with the larger amounts of $KMnO_4$, on account of the manganic oxide contained in the precipitate which masked the pink color in the final titration.

Results with these substances are shown in Table XII.

TABLE XII

Percentage substance added	Mg. P_2O_5 found with		
	$KMnO_4$	CrO_3	Bromine
0.0	20.1	20.1	20.1
0.1	20.1	20.4	20.0
0.5	20.3	20.5	20.0
1.0	20.4	20.1	20.1
2.0	20.5	19.7	19.8

18. Reprecipitation

In any case where the yellow precipitate is suspected of being impure, as from presence of MoO_3, Fe, SiO_2, or SO_4, it may be purified and a more nearly correct result obtained by dissolving in NH_3 and reprecipitation provided that the whole of the P_2O_5 is contained in the first precipitate. After precipitation is complete, and precipitate well settled, pour off through the filter as much as possible of the supernatant liquid, retaining precipitate in the flask. Add water and excess of NH_4OH to dissolve the precipitate in the flask, then HNO_3 till yellow precipitate begins to form, but keep a little alkaline. Now add 10 cc. NH_4NO_3 solution and water to make volume 100 cc., place in water bath at 65°, and when warm add 10 cc. molybdate solution with 5 cc. extra HNO_3 to re-form the yellow precipitate. After standing 15 minutes filter through original filter and treat as usual. The result is liable to be a little either high or low, but much better than if not reprecipitated. The slight amount of precipitate on the filter is not reprecipitated. The lack of exactness seems to be due to the difficulty in properly proportioning HNO_3, NH_4NO_3, Mo, and volume, as discussed in E *9*. Too little NH_4NO_3 or Mo, too much H_2O or HNO_3 cause low results; too much NH_4NO_3 or Mo, too little HNO_3 or H_2O, or too high temperature cause high results.

TABLE XIII—EXAMPLES OF REPRECIPITATION

From pure Na_2HPO_4	Mg. P_2O_5 found	
	Not reprecipitated	After reprecipitation
Amount present	20.1	....
No injurious substance present	20.1	19.9 20.2
1.5 grams $(NH_4)_2SO_4$	21.4	20.0 20.3
Heated 1 hour at 65°	20.5	20.1
Solution boiled	23.5	20.5

Solution of fertilizer No.	Percentages P_2O_5 found	
	Not precipitated	After reprecipitation
19	33.5	33.4
20	26.3	26.5
23	15.2	15.4
24	28.7	28.8
26	7.6	7.8

19. Organic Impurities

Some are injurious in small amounts, while several per cent of others is scarcely noticeable. Proteid substances are usually very bad in effect, but this may be much diminished by boiling with HNO_3. P_2O_5 in the acid soil extract, usually prepared for soil analysis, may well be determined without modification of the solution except when the soil contains much organic matter, when the latter must be decomposed by boiling with HNO_3. The organic matter in an acid solution of steamed bone meal does not interfere much in the determination of P_2O_5, but the solution from a tankage containing 5 per cent or more of N is not well suited for the determination. The organic matter in urine reduces the Mo, but after boiling with HNO_3 and HCl this difficulty is removed and P_2O_5 may be accurately determined in the solution without further treatment. Glue or gelatin forms an insoluble compound with the yellow precipitate, hence, is not admissible in the solution in which P_2O_5 is to be determined by the P. K. method. This fact is the basis of a titration method which has been worked out by A. Grete (G 41, 42) in which the boiling phosphate solution is titrated by a molybdate solution containing gelatin; the end point is that where no further precipitation occurs.

20. *Precipitation by Shaking without Heating*

Temperature used about 20° C., reagents, etc., same as in regular determination by heating, but time varied. Shaken by Wagner machine, same as used for determination of P_2O_5 in basic slag by Wagner citric acid method.

Table XIV—Mg. P_2O_5 Found by Shaking Method

Solution contained	20.9	
Found after shaking 15 min.	20.4	
Found after shaking 30 min.	20.4	
Found after shaking 60 min.	20.4	
Found, not shaken, 15 min.	20.3	Mixed and let stand at room temperature
Found, not shaken, 60 min.	20.3	
Found, shaken 30 minutes	20.5	Volume 200 cc. instead of 100 cc. Some MoO_3 precipitated
Found, shaken 30 minutes	21.3	Used 100 cc. Mo instead of 30

Time shaken has little effect; standing without shaking gives same results as if shaken. Increased volume, increased molybdate, or decreased HNO_3, cause separation of MoO_3, same as if heating method were used.

21. *Prevention of Separation of MoO_3 from Molybdate Solution on Heating*

On account of the difficulty caused by separation of molybdic acid from the molybdate solution used in determining P_2O_5, the following experiments were made with the hope of finding some feasible means of overcoming this defect in the method. So far nothing of the sort has been found, and these results are given to show what has been done, more for the guidance of any one who wishes to continue the investigation, than for the assistance of one who uses this method. Apparently the only way to avoid trouble from MoO_3 precipitated with ammonium phosphomolybdate is to avoid the conditions which cause it. These are discussed under headings *a*, *b*, *c*, etc.

a. Separation of MoO_3 from Solution by Heating with HNO_3

Solution contained MoO_3 about same as for ordinary determination, 1.65 grams $(NH_4)_2MoO_4$ in 100 cc., and varying NH_4NO_3 and HNO_3, heated at 65° C. In absence of free HNO_3, no separation of MoO_3 was caused by NH_4NO_3 from 0 to 15 per cent. When HNO_3 was added up to 1 per cent no MoO_3 was separated. From 2 to 10 per cent cause rapid separation of MoO_3 at 65°, most rapid with about 5 per cent HNO_3. Above 10 per cent HNO_3 causes solubility of MoO_3, and 16 per cent prevents separation entirely. With HNO_3, but NH_4NO_3 absent, separation of MoO_3 was very slight. With 15 per cent NH_4NO_3, 7 per cent HNO_3 and 3 per cent $(NH_4)_2SO_4$ there was no cloud after 2 hours' heating. This indicates that high results due to SO_4 are not because it tends to precipitate MoO_3 as had been supposed. Copper sulfate acted in the same way. $FeCl_3$, 2 per cent, delayed separation of MoO_3 for 45 minutes. $MgCl_2$, 10 per cent, and NH_4Cl, 10 per cent, had very little effect.

b. Effect of Ammonium Oxalate

Table XV

Time heated	Mg. P_2O_5 found
15 min. without oxalate	20.8 = correct amount
15 min. with 0.1 per cent oxalate	20.7
30 min. with 0.1 per cent oxalate	20.9
60 min. with 0.1 per cent oxalate	21.0

The oxalate has a solvent effect on yellow precipitate, also on MoO_3, hence, results are lower in its presence and the high results usually obtained after long heating are not so high in its presence. But as oxalic acid is a solvent for both MoO_3 and the yellow precipitate, the result is not reliable for it is due merely to a lowering of the amount of MoO_3 which would be separated by long heating. The effect of long heating is to precipitate MoO_3. This is partly balanced by the solvent effect of the oxalate and correctness of result is purely accidental.

c. Effect of Organic Matter

Table XVI—20.1 Mg. P_2O_5 Present

Reagent	Mg. P_2O_5 found	Reagent	Mg. P_2O_5 found
10 per cent alcohol	20.6	5 per cent cane sugar	20.0
10 drops anilin	20.1	Glycerine, 4 per cent	19.6
2 per cent anilin	19.6	Glycerine, 8 per cent	19.5
10 per cent cane sugar	19.9	Glycerine, 16 per cent	15.4

Anilin causes reduction of molybdate solution, produces a blue color and interferes seriously. Sugar hinders separation of MoO_3, also of yellow precipitate; hence, low results when much is used. Glycerine acts like sugar.

d. MoO_3 Precipitated by Heating Molybdate Reagent

Same solutions used as for regular P_2O_5 determination. 30 cc. molybdate and 15 grams NH_4NO_3 to 100 cc. total volume; heated at 65°, various time, filtered and titrated as usual, the MoO_3 being calculated as so much P_2O_5.

Table XVII

Time heated	P_2O_5 equivalent of precipitate
15 min. gave	0.0000
30 min. gave	0.0008
60 min. gave	0.0046
120 min. gave	0.0140

This indicates that heating 15 minutes at 65° will not cause much error due to precipitated MoO_3.

In another set of experiments solutions of same composition as above stated, were heated, one set 15 minutes, another set 60 minutes, filtered, washed and MoO_3 determined by three methods, titration with KOH; titration with $KMnO_4$, after reduction by Zn; and by drying and weighing. The amount separated by 15 minutes' heating was so small that duplicates did not agree well, but for 60 minutes' heating, results were fair.

Table XVIII

	Time heated	
	15 min.	60 min.
Mg. MoO_3 found by titration with KOH	6.6	88.8
Mg. MoO_3 found by titration with $KMnO_4$	8.2	89.0
Mg. MoO_3 found by weight of precipitate	4.2	93.7

Apparently the precipitate contains something else than MoO_3 as indicated by the higher result by weight after 60 minutes' heating. This may be $(NH_4)_2MoO_4$ or H_2MoO_4, etc.

e. Solvents for MoO_3 and Yellow Precipitate

MoO_3 obtained by heating regular molybdate reagent on steam bath till most of the molybdic acid was precipitated: strength of reagents 10 per cent, unless otherwise stated. Cold H_2SO_4, citric acid, HCl, HCl and H_2O_2, HCl and $KMnO_4$, HCl and $(NH_4)_2(SO_4)_2$ give very slight effect. Warmed HCl or HNO_3 dissolved precipitates readily. Oxalic acid and ammonium oxalate dissolve precipitates readily. Na_2SO_3 decomposes, and reduces molybdenum. In general, both are acted on about alike, but yellow precipitate is somewhat more soluble than MoO_3.

f. Prevention of Separation of MoO_3 on Heating Regular Molybdate Reagent Solution

Borax, sodium acetate, acetic acid, tartaric acid, alcohol, ether, toluol, phenol, CCl_4, no effect. H_2O_2, $KMnO_4$, CrO_3, iodin, 4 per cent glycerine, 10 per cent cane sugar, prevent separation of MoO_3.

22. *Effort to Improve End Point*

One weakness of the volumetric method is the lack of sharpness of the end point in the final titration. This is due to (*a*) phosphoric and molybdic acids being polybasic, and to their tendency to form two or more salts with the same base at the same time; and (*b*) the solution contains NH_3 for which phenolphthalein is not the best indicator. The latter is not of enough importance to merit much attention as ammonia may fairly well be titrated with this indicator provided it is dilute and cool as shown by Thomson (G 15). However, ammonia may be removed by boiling with excess of the standard fixed alkali, before titrating back with standard acid. This is the basis of Neumann's variation of the method (G 14).

b. The difficulty with polybasic phosphoric acid is avoided by removing it by means of neutral $BaCl_2$, thus leaving HCl in the solution for final titration. It was hoped that a similar plan could be followed with molybdic acid, but this did not succeed, although molybdic acid is precipitated by $BaCl_2$. After addition of $BaCl_2$, the end point was no sharper, in fact, was obscured by the large amount of white precipitate formed in the solution. Lead nitrate precipitates both phosphoric and molybdic acids. This was followed by excess of sodium sulfate to remove Pb. After this the end point was still less distinct, in presence of the large amount of white precipitates. Further efforts included, at various times, addition of sugar, glycerine, alcohol, ether, none of which was of any assistance. Among other indicators tried, rosolic acid was the only one at all suitable and it is not as good as phenolphthalein.

23. *Determination of Phosphoric Acid Equivalent of the Standard Alkali Used in the Volumetric Method*

One essential to the success of the volumetric method is that the strength of the standard alkali be accurately known in terms of P_2O_5. In theory this may be satisfactorily done by calculation from the equation $(NH_4)_3PO_4(MoO_3)_{12} + 23KOH = (NH_4)_2HPO_4 + 11K_2MoO_4 + 11H_2O + NH_4KMoO_4$. But as this equation and the exact composition of the yellow precipitate are matters of theory upon which all authorities do not agree, it seems best to depend on setting a standard by analysis of a compound of known P_2O_5 content. Many such have been proposed, and none of them are really satisfactory. The water-soluble crystalline phosphates contain water of crystallization, the amount of which is usually uncertain; hence their unreliability. Most of the insoluble phosphates are very difficult to prepare in a pure state, as they cannot be purified by recrystallization, and many of them are partly hydrolyzed by washing with water, so that their exact composition is not certain. My efforts to prepare $BaHPO_4$, $CaHPO_4$, $PbHPO_4$, $BiPO_4$, etc., did not succeed in making salts of constant composition. Silver phosphate was used as basis of atomic weight determinations by Baxter and Jones (G 32) and was prepared by them of perfectly definite composition. Dumas used it as a basis for standardizing the gravimetric method of P_2O_5 determination (G 31). In my experience the chief trouble with it is to prepare it in a pure state. This requires conditions which the ordinary laboratory does not possess, *e. g.*, a dark room and an abundance of sufficiently pure water. It is difficult to dry without reduction of the silver, but this does not seem to make much difference in the ratio of Ag to PO_4. I made several preparations of Ag_3PO_4. One was analyzed with the following results: Ag weighed as AgCl, P weighed as $Mg_2P_2O_7$.

		Found	Theory for Ag_3PO_4
Ag_2O	83.04	83.06	83.03
P_2O_5	16.96	17.01	16.97

This sample was used to set the strength of the standard alkali, NaOH.

Besides this, many comparisons of results by both gravimetric and volumetric methods on fertilizers, etc., have been made, and accuracy of the volumetric method thus established. For the purpose of this study a solution of 3 grams sodium phosphate in one liter of water was used. The phosphate was not recrystallized and had lost some of its water of crystallization, so that the P_2O_5 in it was not always the same in the numerous solutions that were used during the more than two years of investigation. In one of these solutions was found:

	Mg. P_2O_5	
By gravimetric method using 50 cc.	40.7	
By gravimetric method using 50 cc.	40.7	
By volumetric method using 25 cc.	20.3	= 40.7
By volumetric method using 25 cc.	20.4	

Assuming the formula of the yellow precipitate to be $(NH_4)_3PO_4(MoO_3)_{12}$ it would contain 3.78 per cent P_2O_5. The precipitate is easily dried and weighed, and using this factor P_2O_5 is found thus gravimetrically. Many have used this method successfully. My work with it has been little, but indicates that it is about as reliable as the volumetric method and in general subject to the same sources of error, the chief of which is due to contamination with molybdic acid. A few results are given.

TABLE XIX

P_2O_5 found by multiplying weight of yellow precipitate by 0.0378.
Mg. P_2O_5 in solution used, 21.1

Time heated in precipitating at 65° C.	Mg. yellow precipitate	Mg. P_2O_5
15 min.	565.5 × 0.0378	=21.4
	566.5	=21.4
60 min.	585.4	=22.1
	587.9	=22.2

The last illustrates the effect of long heating to precipitate MoO_3.

24. Methods of Making Solutions of Phosphates

The following methods of making the solution are used:

a. Dissolve in water.

b. Dissolve in HCl, HNO_3 or both.

c. If organic matter is present it may be removed by ignition either alone or with MgO or $MgNO_3$ or both, then dissolved in acid; or by wet combustion as in the Kjeldahl method for nitrogen; or sometimes by boiling with HNO_3.

Ignition with Magnesia.—This method is applicable to almost any organic material and the solution thus prepared is suitable for analysis by either the gravimetric or volumetric methods. It is the method mostly used in this laboratory. In a platinum or porcelain dish of 20–30 cc. capacity, place a layer of MgO, 2–3 mm. thick. On this place the sample, 2 grams mixed with an equal bulk of MgO. Cover the whole with a little MgO. If the substance is a liquid it may be mixed with MgO, and dried before ignition. Place in the muffle furnace, which should be cold. The muffle will heat so gradually that there is no danger of loss of the substance. It should finally be heated to bright red. If necessary to use a flame for the ignition, start with a very small flame and in course of 15–30 minutes increase to bright red. After cooling, wash contents of the dish into a flask (200, 250, or 500 cc. capacity) with water, add 20–30 cc. HCl and heat to boiling a few minutes. Be sure that there is an excess of acid present. When all is dissolved that is soluble, remove flask from the heat and *at once* add solution of $BaCl_2$ sufficient to throw down all soluble sulfates. Cool, fill to mark, mix. The solution may be filtered, or the flask allowed to stand a few hours, when the clear solution may be pipetted out, without filtering, for the analysis.

I have used this method for five years and found it very satisfactory. A similar plan was recently proposed (G 38). Although I have not experimented much on this point, my work indicates that some phosphorus may be lost from volatile organic substances containing it when ignited with magnesia. Presence of $Mg(NO_3)_2$ guards against this loss. About 5 cc. of the official solution is mixed with the sample in a platinum dish, then some MgO added, the whole dried, then ignited as above. The MgO prevents loss of substance by deflagration which occurs when organic matter is ignited with $Mg(NO_3)_2$ in absence of added MgO. Avoid excess of Mg as it tends to cause low results (see Table VI).

25. Use of HCl or H_2SO_4, etc., instead of HNO_3 for Acidifying Ammonium Molybdate Solution

To 30 cc. neutral ammonium molybdate, of same strength as used for regular P_2O_5 determination, added 10 grams NH_4Cl, 2 cc. HCl and water to make total volume 100 cc. After a few minutes a flocculent precipitate formed and dissolved on heating at 65° C.; after 10 minutes precipitate formed again and would not dissolve by boiling. Dissolved in excess of NH_3 acidified with HCl it formed a clear solution which gradually became cloudy on standing at 65°, by separation of MoO_3 much the same as if the usual molybdate solution made up with nitrates instead of chlorides, were used. When the experiment was repeated, but using 4 cc. HCl instead of 2 cc. as at first, the precipitate did not form so soon, but otherwise acted about the same. Hence, it is inferred that HCl and its salts do not serve well instead of HNO_3 and its salts to make the molybdate solution for determination of P_2O_5, although MoO_3 does not separate as quickly from this solution as from the nitrate solution.

When this chloride solution of MoO_3 was used to determine P_2O_5 the usual yellow precipitate was formed, but not so well as if the nitrate solution were used. Substituting H_2SO_4 and $(NH_4)_2SO_4$ in the molybdate solution instead of nitrate gave similar effects, but better than with chlorides. When acetic acid was used there was no precipitate formed, hence, it is unable to take the place of nitric acid. A certain amount of free acid is necessary to cause formation of the yellow precipitate. In these experiments it was observed that a larger volume of HNO_3 than H_2SO_4 is needed, and more HCl than HNO_3, which is to be expected, considering the relative amount of acid in a given volume of each.

TABLE XX—MG. P_2O_5 FOUND BY USE OF HCl, H_2SO_4, C_2H_3OOH INSTEAD OF HNO_3 IN MOLYBDATE SOLUTION

Cc. acid	HCl	H_2SO_4	Acetic acid
1..........	13.5	22.1	No precipitate
2..........	6.0	21.8	....
4..........	21.7	21.6	....
P_2O_5 present.	21.0	21.0	....

26. Composition of the Yellow Precipitate

Many investigators have analyzed ammonium phosphomolybdate, and with somewhat various results, though it is ordinarily accepted that its formula is $(NH_4)_3PO_4(MoO_3)_{12}$. My work indicates that the most probable cause of variable results is the contamination of the yellow precipitate with MoO_3 or other compounds of molybdenum, most frequently caused by too high temperature of too long heating at moderate temperature. When the precipitate, formed in a not too concentrated solution at high temperature, is examined by the microscope it is found to contain two very distinct kinds of crystals, the yellow rhombohedrons of ammonium phosphomolybdate often united into beautiful stars, and long, slender, colorless needles of molybdic acid. A number of different preparations of the yellow precipitate made under conditions known to favor separation of MoO_3 were found by the microscope to contain crystals of MoO_3 while if these conditions were avoided the MoO_3 could not be seen. All my efforts to separate the two compounds after they are formed together were unsuccessful, as indicated in *21*. My theory is that the yellow precipitate is as definite in composition as $BaSO_4$ or AgCl, even though formed under very different conditions of precipitation. This was stated by Hundeshagen in 1888.[1] The following experiments are given to support this theory. The fact that avoidance of conditions known to cause separation of MoO_3 in actual analytical

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[1] *Z. anal. Chem.*, **28**, 141.

work leads to correct results, while the opposite is nearly sure to cause incorrect results, is also in support of this theory.

A quantity of yellow precipitate was made, well washed and dried at 120° C. Portions of this were dissolved and reprecipitated under various conditions as given below, filtered, washed and dried as before. From these, and also from the original, portions of 0.5 gram were weighed out and titrated with KOH as if for a regular determination. Uniformity of the results, as shown by constant acidity, indicates that the precipitate is of definite and constant composition even though formed under quite varied conditions.

TABLE XXI

Conditions of reprecipitation	KOH used Cc.
15 min. at 65°	18.6
60 min. at 65°	18.6
15 min. at 65° and 3 per cent $(NH_4)_2SO_4$	18.5
15 min. at 65° and 10 per cent $MgCl_2$	18.5
15 min. at 65° and 1 per cent $FeCl_3$	18.5
Boiled	18.7
Original preparation	18.6
Original preparation	18.6

The reprecipitation was effected by HNO_3, no more MoO_3 being added, hence the MoO_3 usually separated by adverse conditions, from the usual excess present, did not appear, but in each case precipitation was incomplete as shown by formation of more yellow precipitate on addition of molybdate solution to the filtrate. (This illustrates the need of an excess of Mo in order to secure complete separation of P_2O_5.)

F. SUMMARY

Working details of the Pemberton-Kilgore method for determination of phosphoric acid are given.

Great rapidity and fair accuracy of the method are shown.

A satisfactory method of preparing asbestos for filtration is given. In the detailed study of conditions affecting the method it is shown that:

High temperature causes high results; too low temperature causes low results: but in both cases this is much modified by time. Below about 40° C., temperature has not much effect, regardless of time: higher temperature than this is desirable in order to secure a desirable quality of precipitate. The longer the precipitate is heated and the higher the temperature the higher the result: 15 minutes at 65° gives best results (E *1* and *2*).

In too concentrated solution precipitate is finely divided and difficult to filter. In too dilute solution separation is incomplete in reasonable time. A suitable concentration is 20 mg. P_2O_5 in 100 cc. (E *3*).

Too little molybdate solution gives low results; too much tends to high results, due to its tendency to separate MoO_3 on heating (E *4*).

Nitric acid is necessary to the reaction but too much causes solubility of precipitate (E *5*).

This is counteracted by ammonium nitrate which tends to precipitate MoO_3 (E *6*). Hence, HNO_3 and NH_4NO_3 should be properly proportioned as shown in E *9*. Volume, P_2O_5, and molybdate solution must also be considered here.

Chlorides, in general, cause solubility of yellow precipitate and low results, partially avoided by use of NH_4NO_3 (E *10*).

Nitrates in general cause high results, by causing separation of MoO_3 (E *11*).

Sulfates cause high results (E *12*), remedied by reprecipitation (E *18*).

Soluble silica in small amount is negligible; in larger amount, causes high results (E *15*), avoided by reprecipitation (E *18*).

Iron tends to cause low results, remedied by larger excess of molybdate solution (E *16*).

Oxidizing agents as such have no specific effect (E *17*).

When the yellow precipitate is contaminated from any cause, it may be purified and made nearly correct by reprecipitation (E *18*).

Organic matter tends to cause low results and difficulty in manipulation (E *19*), hence, should be removed by burning (E *24c*).

Shaking in cold instead of heating to form yellow precipitate tends to low results, is of no advantage to avoid separation of MoO_3, and is not so convenient as the method using heat (E *20*).

There is no suitable method to avoid high results caused by MoO_3 separated with the yellow precipitate except reprecipitation. It is much better to avoid its separation in first place (E *21*).

Effort to improve end point of titration failed (E *22*).

Ag_3PO_4 is a suitable substance for setting the strength of the volumetric solution used (E *23*).

A simple and convenient method of removing organic matter by ignition with MgO is explained (E *24*).

The idea that some other than the nitrate solution of MoO_3 may be used for precipitating P_2O_5 is found erroneous. It was thought that separation of MoO_3 would be less in some other than the nitrate solution (E *25*).

Variable composition of the yellow precipitate as indicated in the literature is probably due to MoO_3 separated with it but not in any proper sense a part of the yellow precipitate (E *26*).

G. BIBLIOGRAPHY

1. Pemberton's Original Method. J. Am. Chem. Soc., **15**, 382 (1893). Also in Chemical News, **46**, 4,
2. Pemberton's Later Method. J. Am. Chem. Soc., **16**, 278 (1894).
3. Kilgore's Method. U. S. D. A., Division of Chemistry, Bulletin **43**, 68–104 (1894).
4. Work on Kilgore's Method by A. O. A. C. U. S. D. A., Bureau of Chemistry, Bulletin **47**, 70 (1896); **49**, 60 (1897); **56**, 76 (1899); **57**, 69 (1899); **62**, 35 (1901); **67**, 22 (1902); **81**, 164 (1904).
5. Kilgore's Work on Proper Washing of Yellow Precipitate. Use 200 cc. H_2O, Wash by Suction. J. Am. Chem. Soc. **19**, 703 (1897).
6. Time to Separate Yellow Precipitate. De Roode. J. Am. Chem. Soc., **17**, 43 (1895).
7. Williams Shaking Method. J. Am. Chem. Soc., **23**, 8 (1901). With description of filter tube, etc., as used in California Fertilizer Control.
8. Investigation of Pemberton-Kilgore Volumetric Method by Veitch. J. Am. Chem. Soc., **18**, 389 (1896).
9. Determination of P_2O_5 in Presence of Colloidal Silica; Washing with H_2O_2, etc. Chem. Abstracts, **6**, 1416 (1912), June 10. From Compt. rend., **154**, 775.
10. Removal of Soluble Silica Precipitated with Yellow Precipitate by Washing with Water. Z. anal. Chem., **26**, 584.
11. Solubility of MoO_3 and Yellow Precipitate in Washing Solutions. U. S. D. A., Bureau of Chemistry, Bulletin **47**, 72–73. Same subject in Z. anal. Chem., **3**, 446 (1864).

12. Effect of Soluble Sulfates. Richardson, J. Am. Chem. Soc., 1314 (1907).
13. Use of Tartaric Acid to Prevent Separation of Fe and Mo, by Juptner, Chem. Centralblatt, **2**, 1813 (1894).
14. Neumann's Method. Z. phys. Chem., **37**, 115 (1902). (Boils yellow precipitate with KOH to remove NH_3, then cools and titrates back with acid.)
15. Reaction of Phenolphthalein with P_2O_5. Thompson, Chemical News, **47**, 127, 186 (1883).
16. Amount of Phenolphthalein Necessary to Use. Long, Am. Chem. J., **11**, 84 (1889).
17. Direct Weighing of Yellow Precipitate. Gladding, J. Am. Chem. Soc., **18**, 23 (1896); U. S. D. A., Div. of Chemistry, Bulletin **51**, 47 (1898); **49**, 60 (1897).
18. Purification of Yellow Precipitate by Double Precipitation and Estimation of P_2O_5 by Weight of Yellow Precipitate, with Study of Effect of Iron and Various Substances. Woy, Chem. Ztg., **21**, 442 (1897). Translation in Treadwell & Hall, Anal. Chem., II, 344.
19. Finkner's Method. Berichte, **11**, 1640 (1878). Well washed and dried at 160–180, factor, 0.3794. Hundeshagen's factor for same is 0.3753.
20. Estimation of P_2O_5 by Weight of Yellow Precipitate, Wash with Acetone Dry in Vac. Lorenz method, Chem. Abstracts, May 20, 1912, 1266. Original in Z. anal. Chem., **51**, 161–175. First paper *Ibid.*, **46**, 193.
21. Estimation of P_2O_5 by Weight of Yellow Precipitate. Chem. Abst., **6**, 584 (1912), March 10. Original in Oesterr. Chem. Ztschr., **14**, 1–5 and abstract in J. Chem. Soc., **100–11**, II, 1028.
22. Lorenz Method Direct Weighing of Yellow Precipitate after Drying. Landw. Vers.-Stat., **55**, 183.
23. Ignition of Yellow Precipitate to P_2O_5 $(MoO_3)_{24}$, Effect of Various Salts and Adding Mo Solution Gradually. Sherman & Hyde, J. Am. Chem. Soc., **22**, 652 (1900).
24. This is essentially Woy's method. Chem. Ztg., **21**, 441, 469 (1897).
25. Precipitate Ignited below Red Heat and Weighed. Factor = 0.3946 for P_2O_5 $(MoO_3)_{24}$. Berichte, **11**, 1640 (1878).
26. Estimation of P_2O_5 by Weight of Yellow Precipitate, after Heating till Blue. Factor, 0.0396. Double Precipitation Used to Get Pure Precipitate. Auld, Analyst, **37**, 130 (1912).
27. Use of $BaCl_2$ to Get Correct End Point in Titration. THIS JOURNAL, July, 1912, p. 520.
28. Volumetric Determination of P_2O_5, Use of $BaCl_2$, to Improve End Point. Chem. Abst., May 20, 1912, p. 1265. Original in J. Wash. Acad. Sci., **2**, p. 114.
29. Colorimetric Determination of P_2O_5. Chem. Abstracts, March 10, 1912, p. 662.
30. Colorimetric Determination of P_2O_5. Prep. Sodium Molybdate, Etc. Expt. Station Record, **26**, 406 (1912, April).
31. Silver Phosphate as Standard for P_2O_5. Dumas, Chem. Eng., **11**, 185 (1910).
32. Preparation of Pure Ag_3PO_4. Baxter and Jones, J. Am. Chem. Soc., **32**, 298 (1910).
33. $NaNH_4HPO_4{,}H_2O$ as Standard Phosphate. Jorgensen, Z. anal. Chem., **45**, 273 (1906).
34. Hundeshagen's Work on Yellow Precipitate, Etc. Z. anal. Chem., **28**, 141. Trans. in Chemical News, **60**, 168, 177, 188, 201, 215.
35. Comparison of Several Methods for P_2O_5 Determination by D. J. Hissink. Chem. Weekblad, **115**, (1905).
36. Influence of Al, Mg, Ca on P_2O_5 Determination. Neubauer, Landw. Vers.-Stat., **63**, 141 (1905–6).
37. Citric Acid to Prevent Contamination of $MgNH_4PO_4$ with MgO. Lorenz, Z. anal. Chem., **32**, 64 (1893).
38. Use of MgO for Incinerating Material for P_2O_5 Determination. Chem. Abstracts, **6**, 1416 (1912, June). From Z. physiol. Chem., **76**, 426.
39. Same subject in Experiment Station Record, **28**, 20 (1913, Jan.).
40. Loss of P_2O_5 in Burning Wheat. Leavitt and LeClerc, J. Am. Chem. Soc., **30**, 391, 617 (1908).
41. Direct Titration of Phosphate Solution by Molybdate Solution Containing Gelatin. By A. Grete, in Koenig, Unters. Landw. and Gewerblich Stoff.
42. Same subject in Experiment Station Record, [3] **28**, 203 (1913).
43. Neumann's Method for P_2O_5, Use of Formaldehyde. Experiment Station Record, **26**, 406 (1912, April).
44. Loss of Phosphorus on Ignition of $Mg_2P_2O_7$. Neubauer, J. Am. Chem. Soc., **16**, 289 (1894).
45. Composition of Yellow Precipitate, Etc. By Baxter, Am. Chem. J., **28**, 298 (1902).
46. Same by Baxter and Griffin, Am. Chem. J., **34**, 204 (1905).
47. Use of H_2SO_4 to Obtain Constant Results. By Lagers, Z. anal. Chem., **47**, 561 (1908).

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THE COMPOSITION OF SEDIMENTS FROM THE POTOMAC AND SHENANDOAH RIVERS

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This investigation was undertaken to ascertain whether or not the sediments from the two rivers showed any marked chemical and mineralogical differences, with a view to using the results in the study of soil erosion. Samples of water were collected by the Weather Bureau in five-gallon lots, at various times during an interval of two years. The sediments were allowed to settle, the water siphoned off and the residues dried. In most cases the amount of sediment was so small that a chemical analysis was impossible. Mineralogical examinations, however, were made of each sample. The particles, generally, were of extremely small size; and were very much weathered and coated with iron oxides, hydroxides, organic matter, and possibly other material. Consequently, the character of the larger percentage of the grains was wholly indeterminable. The mineralogical analyses represent simply that part of the material which was in large enough particles and fresh enough for determination. This determinable matter probably never amounted to more than ten per cent of the total sample. It is not to be concluded that the minerals cited in the following tables were the only ones present. They are the more prominent ones which could be positively identified, and it is quite probable that other mineral species were present which defied identification.

The lithology of the two river basins seems to be very similar as will be seen from the following résumé:

The Potomac River above Cumberland comes into contact with sandstones, shales, limestones, etc. From Cumberland to Harper's Ferry it flows over or in close proximity to sandstones, shales, limestone, and unconsolidated sands and clays.[2]

The Shenandoah River above Riverton flows over limestone-shale and sandstone-shale formations. The headwaters rise in a sandstone-shale-limestone formation, and flow over a narrow band of sandstone-shale. Below Riverton it flows over limestone and shale, and touches a sandstone-shale-quartzite formation.[3]

DETAILED MINERALOGICAL ANALYSES (W. H. FRY, ANALYST)

SEDIMENTS FROM CUMBERLAND, MD. (POTOMAC RIVER)

No. 1. Hornblende, biotite, quartz, feldspar [labradorite(?)], orthoclase. The doubtful labradorite showed twin structure and the determination was made by the extinction of the twins in conjunction with the refractive index. However, the particle was very small; but it is certainly one of the plagioclase group. There were present very small fragments of what appear to be silicious tests of spicules of some form of microscopic animal or plant life.

No. 2. Quartz, biotite, animal or vegetal spicules, plagioclase, a doubly refracting grain with a high index of refraction which may be zircon (the small size of the particle prohibited its determination), hornblende(?), small amount of magnetic particles.

No. 3. One rather large grain of what appears to be a glass. It is isotropic with an index or refraction very near 1.54. It is probable that this is a fragment broken from a glass vessel. Magnetic particles, quartz, hornblende.

No. 4. Magnetic particles, muscovite, quartz, isotropic particles with index of refraction near 1.54, plagioclase.

No. 5. Largely organic matter. The organic material masks the mineral constituents so as to make them indeterminable.

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[1] Scientists in Soil Laboratory Investigations, Bureau of Soils, U. S. Department of Agriculture.

[2] *Maryland Geological Survey*, **3**, Pl. 6 (1899).

[3] T. L. Watson, "A Geological Map of Virginia," Va. Geol. Survey.

No. 6. Quartz, some indeterminable ferromagnesian mineral, hornblende, animal or vegetable tests.

No. 7. Muscovite, biotite, quartz, animal or vegetable tests, hornblende.

No. 21. Magnetic particles, quartz, muscovite, plagioclase, animal or vegetable tests, biotite, microcline.

No. 29. Magnetic particles, quartz, muscovite, hornblende, biotite, animal or vegetable tests, orthoclase.

No. 34. Quartz, hornblende, biotite. All of the particles in this sample are of very small dimensions.

No. 36. Slight amount of magnetic particles, quartz, orthoclase, hornblende, mica(?).

No. 39. Magnetic particles, quartz, muscovite, biotite, hornblende, animal or vegetable tests.

No. 41. Magnetic particles, quartz, hornblende, muscovite, orthoclase, biotite. Very much vegetable matter present.

No. 43. Slight amount of magnetic particles, quartz, biotite, hornblende.

Sediments from Riverton, Va. (Shenandoah River)

No. 14. Quartz, garnet, muscovite, biotite, orthoclase.

No. 15. Magnetic particles, quartz, biotite, orthoclase.

No. 16. Quartz, muscovite, animal or vegetable tests, biotite.

No. 20. Quartz, muscovite, biotite, plagioclase (?), garnet, hornblende.

No. 27. Quartz, plagioclase. This material is extremely fine and is very much coagulated.

No. 31. Slight amount of magnetic particles, quartz, biotite, orthoclase, hornblende.

No. 32. Isotropic particles with index of refraction about 1.54, probably glass, quartz, orthoclase, biotite, hornblende.

No. 37. Quartz, calcite. This material is extremely fine.

No. 38. Quartz, hornblende, mica(?). Material is very fine.

Sediments from Harper's Ferry (Potomac River)

No. 8. Quartz, biotite, muscovite, labradorite, orthoclase, few vegetable or animal tests, chlorite(?).

No. 9. Quartz, hornblende, biotite, plagioclase, muscovite.

No. 10. Quartz, muscovite, particles deeply coated and impregnated with some coloring matter, probably iron oxides.

No. 11. Magnetic particles, quartz, hornblende, muscovite, animal or vegetable spicules, biotite, plagioclase.

No. 12. Magnetic particles, quartz, zircon, hornblende, calcite plentiful, tourmaline, biotite, orthoclase, muscovite.

No. 13. Magnetic particles, quartz, very much altered biotite, plagioclase, hornblende, muscovite.

No. 18. Magnetic particles, quartz, muscovite, garnet, biotite, orthoclase.

No. 19. Magnetic particles, quartz, biotite, garnet, hornblende, plagioclase, orthoclase.

No. 22. Magnetic particles, quartz, biotite, muscovite, microcline, plagioclase, orthoclase, hornblende. A fair amount of this material consists of grains of about the dimension of very fine sands, thus differing from the usual silty or clayey character of the sediments. These large grains are mainly quartz.

No. 23. Very small amount of magnetic particles, quartz, biotite, small amount of animal or vegetable tests, labradorite, some ferromagnesian mineral, muscovite, orthoclase. Practically all the particles are very small.

No. 24. Quartz, animal or vegetable tests, microcline, labradorite, biotite, muscovite, orthoclase, hornblende, calcite.

No. 25. Small amount of magnetic particles, quartz, plagioclase, biotite, muscovite, hornblende, orthoclase.

No. 26. Magnetic particles, quartz, muscovite, tourmaline, orthoclase, plagioclase, biotite, hornblende.

No. 28. Quartz, biotite, animal or vegetable tests, rutile, garnet, muscovite, hornblende.

No. 30. Very slight amount of magnetic particles, quartz, biotite, orthoclase, plagioclase, rutile, microcline, muscovite, shell fragments which effervesce with hydrochloric acid.

No. 33. Very slight amount of magnetic particles, quartz, muscovite, hornblende, biotite.

No. 35. Very slight amount of magnetic particles, quartz, hornblende, biotite, orthoclase, plagioclase(?), muscovite.

No. 40. Quartz, orthoclase, biotite, hornblende, muscovite, plagioclase.

No. 42. Magnetic particles, quartz, microcline, biotite, muscovite, calcite, plagioclase.

No. 44. Magnetic particles, quartz, labradorite, biotite, muscovite, orthoclase.

No. 45. Small amount of magnetic particles, quartz, muscovite, biotite, hornblende.

No. 46. Small amount of magnetic particles, quartz, hornblende, some mineral which appears to be an amphibole other than hornblende, muscovite, biotite.

No. 47. Magnetic particles, quartz, hornblende, muscovite, plagioclase, biotite.

No. 48. Quartz, muscovite, biotite(?), calcite(?).

No. 49. Quartz, hornblende. Particles extremely fine.

Table I—Summary of the Minerals Found in the Sediments from the Different Stations

Cumberland	Riverton	Harper's Ferry
Hornblende	Hornblende	Hornblende
Biotite	Biotite	Biotite
Quartz	Quartz	Quartz
Orthoclase	Orthoclase	Orthoclase
Plagioclase	Plagioclase	Plagioclase
Magnetite	Magnetite	Magnetite
Muscovite	Muscovite	Muscovite
Labradorite(?)	........:	Labradorite
Zircon(?)	....	Zircon
Microcline	....	Microcline
Femic mineral(?)	....	Femic mineral(?)
....	Garnet	Garnet
....	Calcite	Calcite
....	....	Tourmaline
....	....	Rutile
....	....	Chlorite(?)

As can be seen from Table I, the sediments from Riverton do not show the presence of microcline, the doubtful femic mineral, labradorite, and zircon, which are present in the sediments from Cumberland, while the Riverton sediments contain garnet and calcite in addition to the minerals found in the Cumberland sediments. The sediments from Harper's Ferry, where the two rivers join, contain all of the minerals found in the sediments from the other two stations, and tourmaline, rutile, and doubtful chlorite in addition. However, it should be remembered that only a relatively small proportion of the minerals were determinable and that the composition of the indeterminable material, were it known, might or might not considerably modify this table.

Table II—Chemical Analyses of Sediments from Cumberland

C. F. Miller, Analyst

No.	SiO_2	$Al_2O_3 + Fe_2O_3$	CaO	MgO	P_2O_5	Na_2O	K_2O
1	52.03	27.78	0.65	1.70	0.30	1.92	3.28
6	48.97	24.88	1.15	1.16	0.40	1.41	2.36
34	55.23	25.50	1.07	1.37	0.24	0.67	2.91

Table III—Chemical Analyses of Sediments from Riverton

R. F. Gardiner, Analyst

No.	SiO_2	$Al_2O_3 + Fe_2O_3$	CaO	MgO	P_2O_5	Na_2O	K_2O
14	63.00	22.56	0.48	0.90	0.52	0.72	1.36
27	67.07	21.06	0.46	1.12	0.34	0.90	2.42
38	50.51	27.34	0.63	1.27	0.63	....	....

Table IV—Chemical Analyses of Sediments from Harper's Ferry

Average of Duplicate Analyses by R. F. Gardiner and C. F. Miller

No.	SiO_2	$Al_2O_3 + Fe_2O_3$	CaO	MgO	P_2O_5	Na_2O	K_2O
12	58.91	22.70	1.33	0.94	0.43	0.76	1.93
22	67.05	18.05	0.50	0.91	0.46	....	....
23	63.33	20.95	0.71	1.00	0.30	1.70	2.18
28	64.73	20.54	0.86	1.07	0.28	0.78	2.26
35	62.53	21.08	1.12	1.23	0.29	0.48	2.05
48	53.73	25.00	1.07	1.44	0.31	0.90	2.16

The soda and potash determinations were made by the J. Lawrence Smith method, the others by fusion with sodium carbonate. Samples 22 from Harper's Ferry and 38 from Riverton were so small that only a partial analysis could be reliably made.

The analyses do not show any definite relation between chemical composition and the amount of sediment carried in the streams when the samples of water were taken. This was to be expected, since unequal rainfall over the varying geological formations of these large river basins would carry into the streams material of varying composition.

The results are in harmony with the well-known fact that the finer particles of soils such as would be carried by stream waters are high in potash, phosphoric acid, lime, organic matter, etc.

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ESTIMATION OF THE LIME REQUIREMENT OF SOILS[1]

By J. A. Bizzell and T. L. Lyon

Several methods have been proposed for the estimation of soil acidity, but none is entirely satisfactory. The difficulty is that the true nature of the acidity is not understood. The problem is further complicated by the fact that lime may be beneficial to a soil in other ways than by simply correcting an acid condition. The nearest approach to a quantitative determination of the lime requirement of a soil, therefore, would seem to be an estimation of the total absorptive power of that soil for lime. This is the principle upon which the well-known method proposed by Veitch[2] is based. The most serious objection to this method from the analyst's standpoint is the large number of determinations which must frequently be made before the alkaline point is reached. The writers have also frequently found it difficult and sometimes almost impossible to determine the saturation point. This is true particularly of soils containing a large quantity of organic matter yielding highly colored extracts, and of those containing a large percentage of clay. Many clay soils will not settle sufficiently, even after very long standing, and the clay particles in such cases are so fine as to defy filtration by the ordinary methods.

With a view to overcoming these difficulties the writers have examined a method described by R. Albert[3] and propose certain modifications which seem to render it suitable for estimating the lime requirement of soils.

In brief, the method as proposed by Albert is as follows: To 25 grams of air-dried soil add 200 cc. boiled distilled water, 50 cc. of a standard solution of barium hydroxide, and 5 grams solid ammonium chloride. Distil the mixture, collecting the ammonia formed in tenth-normal acid. The amount of ammonia found in the distillate is assumed to be proportional to the free barium hydroxide not required to saturate the soil. Barium hydroxide was found preferable to calcium hydroxide, since the latter seems to form with the soil certain easily decomposed compounds which effect decomposition of ammonium chloride.

Table I—Lime Requirement Calculated as CaO. Parts per Million Dry Soil

Lab. No.	Veitch method	Albert method	Lab. No.	Veitch method	Albert method
2333	1500	930	2626	0	0
2619	1100	67	3749	900	0
2620	1100	24	3750	0	0
2621	700	0	3751	0	0
2622	0	0	3752	900	134
2623	1100	156	3753	1400	560
2624	1000	201	3754	1000	0
2625	900	0	3755	500	0

This method was compared with the Veitch method on a number of samples of soil and subsoil of the Dunkirk clay loam type, obtained from the experiment field. The results are given in Table I.

The results by the two methods were widely different, and in view of the field results obtained by the use of lime on this soil, indicated that the figures obtained by the Albert method were much too low. This discrepancy appears to be due chiefly to two factors which apparently were not recognized by the author.

In the first place solid ammonium chloride undergoes slight decomposition when boiled with water, and appreciable quantities of ammonia are given off. When boiled with some soils ammonium chloride gives up enough ammonia to very materially affect the results, rendering the figures for acidity much too low. The amount of ammonia given off was different for each soil. Twenty-five samples were examined and the ammonia formed expressed in equivalent of tenth-normal acid varied from 0.4 cc. to 5.6 cc. It becomes necessary, therefore, to determine this factor for each soil and to make a correction accordingly.

The second error consists in assuming that the absorption of barium hydroxide is immediate. This assumption was found to be incorrect. It was found that fixation of barium hydroxide by a soil was complete when the mixture was heated in a water bath for one hour at the temperature of boiling water.

The effect of this treatment is shown in the following table:

Table II—Barium Hydroxide Absorbed Expressed as Lime (CaO). Parts per Million Dry Soil

Lab. No.	Absorbed immediately	Absorbed during one-hour standing in boiling water	Lab. No.	Absorbed immediately	Absorbed during one-hour standing in boiling water
2619	425	963	3749	313	694
2620	425	940	3752	515	1209
2623	403	1187	3754	268	985
2624	425	896	3755	224	761

The higher figures obtained by the longer contact of the barium hydroxide and soil might be ascribed to the removal of the base from solution by the carbon dioxide of the air, in which case the longer exposure would introduce an error. To test this point 50 cc. of the standard barium hydroxide solution and 50 cc. of water were placed in a 500 cc. Kjeldahl flask. The unstoppered flask was then placed in a water bath maintained at the boiling temperature and allowed to remain one hour. The flask was then removed, 150 cc. water and 5 grams solid ammonium chloride added, and the mixture distilled in the ordinary Kjeldahl apparatus with the following results:

	Ammonia expressed in equivalent of $N/10$ acid Cc.
50 cc. barium hydroxide + 5 grams ammonium chloride....	51.4
5 grams ammonium chloride..............................	1.6
Formed by barium hydroxide.............................	49.8

As direct titration of 50 cc. barium hydroxide un-

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[1] Paper presented at the 48th meeting of the A. C. S., Rochester, September 8–12, 1913.

[2] *J. Am. Chem. Soc.*, **24**, 1120.

[3] *Z. angew. Chem.*, **1**, 533.

exposed required 50 cc. of the tenth-normal acid, it is evident that the one-hour exposure does not introduce an appreciable error.

In view of the foregoing results, the writers propose the following modification of the Albert method:

The air-dried soil is prepared according to the method of the Association of Official Agricultural Chemists.[1]

Place 25 grams of the soil in a Jena Kjeldahl flask. Cover with 50 cc. boiled distilled water and add 50 cc. tenth-normal hydroxide solution. Digest in a briskly boiling water bath for one hour with occasional shaking. Remove from the water bath, add 150 cc. distilled water and 5 grams solid ammonium chloride. Connect the flask with a nitrogen distillation apparatus, and distil. Collect the distillate (150 cc.) in tenth-normal acid and titrate, using methyl orange as indicator. The strength of the barium hydroxide is determined by titrating directly 50 cc. of the solution, using methyl orange as indicator. The difference between the two titrations, therefore, represents the amount of barium hydroxide absorbed by the soil.

The soil has a slight decomposition effect on the ammonium chloride. It is necessary to correct for this in each case by distillation of 25 grams of soil with 5 grams ammonium chloride, omitting the barium hydroxide solution. The ordinary Kjeldahl apparatus may be used, but care must be taken that stoppers and connections are free from alkali, which may have been left from previous use in the ordinary Kjeldahl distillations.

This method has been compared with the Veitch method on several samples of different types of soil and the results are given in the following table:

TABLE III—LIME REQUIREMENT CALCULATED AS CaO. PARTS PER MILLION DRY SOIL

Lab. No.	Description of soil	Veitch	Modified Albert
2619	Dunkirk clay loam	1100	963
2620	Dunkirk clay loam	1100	940
2621	Dunkirk clay loam	700	694
2623	Dunkirk clay loam	1100	1187
2624	Dunkirk clay loam	1000	896
2625	Dunkirk clay loam	900	694
3749	Dunkirk clay loam	900	694
3752	Dunkirk clay loam	900	1290
3754	Dunkirk clay loam	1000	985
3755	Dunkirk clay loam	500	761
15405	Volusia loam	1912	1836
15407	Volusia loam	1434	1321
15409	Volusia loam	1434	1749
15413	Volusia loam	1434	1344
15425	Volusia silt loam	1912	2531
15427	Volusia silt loam	2390	2620
15430	Volusia silt loam	1673	2307
15432	Volusia silt loam	2629	2352
15443	Dunkirk clay loam	1673	1768
15445	Dunkirk clay loam	717	1232
15449	Dunkirk clay loam	1195	1456
13151	Volusia silt loam	1195	1344

The results obtained by the new method agree very well with those obtained by the Veitch method, and since there is no apparent method of standardizing either, it may be assumed to be just as correct.

The new method possesses the great advantage of rapidity, and if the details are carefully observed, it is very easy to obtain concordant results.

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[1] U. S. Dept. of Agric., Bureau of Chemistry, *Bull.* **107,** 14.

AN INTERESTING SOIL WATER QUESTION IN BRITISH GUIANA

By MAURICE BIRD[1]

Received September 15, 1913

Some years ago, Harrison[2] first called attention to the markedly alkaline condition of the soil water underlying the sugar estates fringing the coast of British Guiana, and its pernicious effect upon the growth of the sugar cane; and since this interesting problem is one to be very appropriately recorded in the pages of THIS JOURNAL, the writer has prepared the following brief account of it.

The appended analyses are typical of the sugar soils of British Guiana, and indicate their wonderful fertility from a standpoint of plant food. The yield and quality, however, of the cane grown upon them is very often disappointing, and this is due to the fact that, many of these lands lying below sea level, deep and thorough drainage is well nigh impracticable, with the results that as the soil slowly and continuously decomposes, the surrounding and underlying water becomes charged with alkaline mineral matter, the product of this decomposition, and this alkaline material entering through the roots, acts in a very deleterious manner upon the juice of the cane.

	Soil from Pln. Albion, Berbice (Coastal estate)	Soil from Pln. Friends, Berbice (River estate)	Soil from Pln. Hampton Court, Essequibo (Coastal estate)
Water and volatile matter	18.050	19.660	14.503
Insoluble matter	66.250	65.609	66.915
Iron and aluminum oxides	13.780	14.503	17.496
Lime	0.345	0.134	0.316
Magnesia	0.629	0.431	0.504
Potash	0.458	0.495	0.501
Soda	0.148	0.110	0.112
Phosphoric acid	0.248	0.256	0.224
Nitrogen	0.172	0.351	0.196

NOTE—Though weighed as ferric oxide some of the iron in these soils is in the ferrous form.

The excess of magnesia over lime in the above is very noticeable, and this appears to be the case throughout in the alluvial soils of the colony.

Coming now to the soil waters, the writer examined a great many under varying conditions of rainfall etc., finding the alkali, as determined by titrating with decinormal sulfuric acid, to range from a trace to 480 parts per million of water, when calculated as sodium carbonate; while the total mineral matter, determined by evaporation of the water rose to over one per cent of the water. This saline material entering the roots of the growing cane was found to produce from three to five times the quantity of ash in the juice that is found in the juice of cane grown on well drained soils. This ash, or mineral matter, of the juice concentrating in the molasses from the process of the sugar factory was found (as so lucidly described by Geerligs)[3] to form uncrystallizable compounds with the sucrose, whereby much sugar is lost. In order to break up these compounds and render the sugar available it becomes necessary to employ some

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[1] Chemist to the New Colonial Co., Ltd.

[2] *West Indian Bulletin,* **9,** I, 1–39.

[3] "Cane Sugar and its Manufacture," by H. C. Prinsen Geerligs.

such method, as osmosis or the Steffen process, as is in use in the beet sugar industry.

Since the soil water contains a large proportion of magnesia, which in the cane juice exercises an especially deleterious effect in restraining the crystallization of sugar, the experiment suggested itself to the writer of precipitating the magnesia from the soil water with a solution of hydrate of lime. As this proved highly successful, large quantities of lime (from two to three tons per acre) were applied to a large tract of sugar lands, with the result that the juice of the subsequently grown cane was very markedly improved.

SUMMARY

One of the chief obstacles to profitable sugar production in British Guiana is the highly saline character of the soil water, to overcome which every effort should be made to achieve deep and thorough drainage, which can be most advantageously supplemented by heavy applications of slaked lime to the land. Where these remedies are not practised a large loss of sugar in the factory can be obviated only by employing a special process, such as either of those indicated above, to separate the sugar from the abnormal quantity of mineral matter present.

Pln. Albion, Berbice
British Guiana

MICROÖRGANISMS IN COMMERCIAL LIME-SULFUR[1]

By C. A. Peters and A. W. Brooks

Received October 13, 1913

Manufacturers of commercial lime-sulfur have been troubled for some time by the occasional thickening of their product when stored in barrels. As far as can be ascertained second-hand, wooden barrels of about 50 gallons' capacity are used in handling the product, and of a large number of barrels filled at the same time with the same material only an occasional one will develop the thickened material.

The nature of the thickened product has not been understood. In consistency it resembles a thin ketchup. In color it is nearly white, although seeming to be tinted red by the lime-sulfur mother liquor. The solid matter of the mixture remains in suspension settling but slightly if at all.

A qualitative examination, made by the writers, of a sample of this thickened material revealed a number of things which may be listed as follows: (1) When such lime-sulfur ketchup was filtered and dried the residue was largely sulfur soluble in carbon disulfid. (2) No sulfids, sulfites, or thiosulfates were present in the washed residue. (3) When thickened lime-sulfur containing the suspended material was heated, a clear solution was obtained which was evidently the original concentrated lime-sulfur solution. These results indicated that the precipitate was largely, if not entirely, sulfur. This idea was confirmed by the approximate quantitative conversion of the residue from portions of the thickened lime-sulfur mixture into barium sulfate. Such residues filtered on asbestos or paper were washed with water until the filtrate was colorless and either dried about 15 hours in an electrically heated oven at 65–70°, and weighed, or converted into barium sulfate and weighed. The results are given in Table I.

Table I—Conversion of Residual Sulfur into $BaSO_4$

No.	Weight of residue on asbestos Gram	Sulfur calculated from $BaSO_4$ Gram	Difference Gram
1	0.0365	0.0384	+0.0019
2	0.0431	0.0474	+0.0033

The amount of sulfur registered in Experiment 1, 0.0365 gram, was transferred to a beaker with the asbestos on which it was filtered. The whole mass was boiled 15 minutes with 50 cc. of a 10 per cent solution of caustic potash, and the sulfur oxidized by 50 cc. of ordinary 3 per cent solution of hydrogen peroxide. The mixture was then made acidic with hydrochloric acid, filtered through paper and washed, a solution of barium chloride added to the filtrate, and the precipitate of barium sulfate dried, heated, and weighed.

In Experiment 2, a 5 cc. portion of the thickened lime-sulfur mixture was filtered on asbestos, the residue was washed until the filtrate was colorless, dried about 15 hours at 65–70° and weighed. A duplicate portion was filtered on hardened paper, the washed residue separated from the paper was treated in a beaker with caustic potash, and precipitated and weighed as barium sulfate, as just described. The figures as given are multiplied by two before insertion in the table so that they may be compared directly with those of Experiment 1. The results are vitiated by the occlusion of potassium salts by the barium sulfate, and in Experiment 1, in addition, probably, by the silica from the asbestos, but they show an approximately quantitative conversion of the sulfur into barium sulfate.

It seeming to be established that the precipitate in the lime-sulfur ketchup was due to a mass of suspended sulfur, ineffective attempts were made to reproduce this characteristic ketchup substance by heating various lime-sulfur solutions until precipitation took place. None of the concentrated mixtures resulting resembled at all the original ketchup substance and microscopical examination of the residues showed masses of crystals which could have been only sulfur.

When, however, the original ketchup mixture was examined under the microscope the first real light was shed on the problem. The material consisted of masses of long threads, and motil rods were in abundance. The threads separated from the lime-sulfur liquid by filtering and washing, and, viewed in a water medium magnified 480 x, developed in a few minutes cross striations, and in the course of an hour or so some of the threads divided at the cross lines. In a few hours, after further changes, in place of the threads only spherical cells remained, the position of some of the threads being definitely marked on the microscope slide by a row of these spherical bodies. This description indicates that the solid matter in this lime-sulfur ketchup is due to microorganisms of a group closely allied to *Beggiatoa*.

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[1] Material and funds for this work were furnished by the Bowker Insecticide Company of Boston, Mass.

This identification was confirmed by Dr. van Suchtelen of the Department of Microbiology.

The source of the infection by the microörganism is not known but the facts outlined in the first paragraph that only one barrel out of a possible hundred develops the organism and that the barrels used are necessarily second-hand, point to the previously inoculated barrel as the source of the trouble.

As it appears unusual that these microörganisms should appear in quantities in lime-sulfur concentrates data regarding the mixture may be of interest.

Density.—The densities of the ketchup mixture, the filtrate from it and of other lime-sulfur solutions were taken in an ordinary specific gravity bottle of 25 cc. capacity, with an open capillary tube, at room temperature which was 25°. The results are recorded in the following table:

TABLE II

No.	MATERIAL	Observed density	B. ° from commercial scale	REMARKS
1	Water	0.9966	....	Check
2	Lime-sulfur ketchup	1.3047	34.0	
3	Lime-sulfur solution	1.2996	33.6	Filtrate from Expt. 2
4	Lime-sulfur solution	1.3020	33.7	Ketchup heated until solution resulted and loss of volume made up
5	Lime-sulfur solution	1.2992	33.6	Duplicate of No. 4
6	Lime-sulfur solution	1.3214	35.3	Ketchup heated until solution resulted and loss of volume not made up
7	Lime-sulfur solution	1.3078	34.2	Same as No. 6 except heated with air condenser
8	Lime-sulfur solution	1.3072	34.2	Same as No. 6 except heated under return water condenser

An examination of the data in Experiments 7 and 8 shows that the original lime-sulfur solution in which the microörganisms developed was of the maximum density, 1.3075 (34° B.), for commercial preparations, and Experiment 3, that the filtrate from the ketchup was of a density of 1.2996 (33.6° B.), which is still slightly stronger than necessary for the trade. It is further seen, Experiments 2, 7 and 8, that the density of the clear liquid is only slightly altered (—0.008) by the withdrawal of sulfur by the microorganisms. Experiment 6 as compared with 7 and 8 shows how the density of these concentrated solutions is changed (+0.015) by the withdrawal of a small amount of water—less than $^1/_{25}$–$^1/_{50}$ of the total volume in this case.

Sulfur in Suspension.—The amount of sulfur per cubic centimeter in suspension in the bodies of the microörganisms in the ketchup is 0.0043 gram as obtained from Experiment 2 in Table I.

SUMMARY

Microörganisms of *Beggiatoa*, or a closely related group, have been found to be the cause of an apparent precipitate of sulfur occurring in commercial lime-sulfur concentrates, making the whole mass of the consistency of thin ketchup. Some data regarding this thickened lime-sulfur is given.

The further study of the microörganisms, their identification, the sources of infection, and means of prevention are being investigated.

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THE ASSAY OF INDIVIDUAL PLANTS OF DATURA STRAMONIUM L., DATURA TATULA L. AND OTHER SPECIES AND VARIETIES[1]

By F. A. MILLER AND J. W. MEADER

It has been stated in a recent communication[2] that the examination of individual plants of the daturas for their total alkaloidal content has been undertaken as a means of following the effects of prolonged cultivation upon the percentage of alkaloids, and as a means of selecting high-yielding individual plants for breeding purposes. The present discussion is a continuation of this investigation, together with additional data upon other species and varieties not heretofore included. A review of the literature on stramonium was given in the original communication. This was followed by the assays of several individual plants of *Datura stramonium* L. and *Datura tatula* L. Seeds were collected from all the assayed plants and those from the individuals containing the highest and lowest percentages of alkaloids from each of the two species were planted May 30, 1912. The results obtained from these plantings are considered in the present discussion.

The conditions of growth were practically the same as those under which the parent plants were produced. The soil, a stiff clay loam though not identical, was that of an adjacent field and of a similar physical character. The plot was fairly uniform except for an excess of sand and gravel at one end. The plants growing at this point were smaller and less vigorous than the others. When about three inches high they were thinned to four feet in the row. Cultivation was begun at this time and continued throughout the growing season.

Eight plantings were made, four of *Datura stramonium* L. and four of *Datura tatula* L. These were made from the highest and lowest yielding individuals from each of the two species, as given in the original communication. The plants indicating these extremes assayed 0.55 per cent and 0.46 per cent in *Datura stramonium* L. and 0.65 per cent and 0.47 per cent in *Datura tatula* L. Four of the above plots received an application of normal commercial fertilizer at the rate of six hundred pounds per acre. This was applied when the plants were about one foot high.

The collection of samples of leaves for assay from individual plants of each of the eight plots was made early in September. These samples were dried at room temperature, granulated and sealed in amber bottles until assayed. Following are the results obtained from nineteen selections of individual plants from *Datura stramonium* L. Ten of these were from the high- and nine from the low-yielding parent.

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[1] Paper presented at the 47th meeting of the A. C. S., Milwaukee, March, 1913.

[2] *8th Int. Cong. App. Chemistry*, **17**, 57.

TABLE I—*Datura stramonium* L.

Highest plant originally assayed 0.55 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B- 980	Parent plant	0.55	B- 980	Parent plant	0.55
B-1349	Selection	0.50	B-1360	Selection	0.67
B-1351	Selection	0.56	B-1361	Selection	0.66
B-1352	Selection	0.50	B-1362	Selection	0.62
B-1353	Selection	0.54	B-1363	Selection	0.65
B-1354	Selection	0.42	B-1364	Selection	0.48
	Average,	0.50		Average,	0.61

Lowest plant originally assayed 0.46 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B- 982	Parent plant	0.46	B- 982	Parent plant	0.46
B-1355	Selection	0.58	B-1357	Selection	0.64
B-1356	Selection	0.57	B-1368	Selection	0.68
B-1365	Selection	0.58	B-1369	Selection	0.58
B-1366	Selection	0.65	B-1370	Selection	0.71
B-1367	Selection	0.63			
	Average,	0.60		Average,	0.64

The *Datura tatula* L. selections, of which there were ten each from the high- and low-yielding parents, gave the following results:

TABLE II—*Datura tatula* L.

Highest plant originally assayed 0.65 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B- 984	Parent plant	0.65	B- 984	Parent plant	0.65
B-1344	Selection	0.53	B-1378	Selection	0.72
B-1348	Selection	0.56	B-1379	Selection	0.75
B-1376	Selection	0.77	B-1380	Selection	0.69
B-1377	Selection	0.59	B-1381	Selection	0.73
B-1383	Selection	0.64	B-1382	Selection	0.44
	Average	0.62		Average,	0.68

Lowest plant originally assayed 0.47 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B- 985	Parent plant	0.47	B- 985	Parent plant	0.47
B-1341	Selection	0.47	B-1371	Selection	0.66
B-1342	Selection	0.45	B-1372	Selection	0.50
B-1343	Selection	0.52	B-1373	Selection	0.48
B-1346	Selection	0.45	B-1374	Selection	0.53
B-1347	Selection	0.57	B-1375	Selection	0.54
	Average,	0.49		Average,	0.54

A small plot of *Datura ferox* L. was grown from seed obtained from Haag & Schmidt, of Erfort, Germany. Four selections were made and samples of leaves from these selected plants assayed as follows:

TABLE III

No.	Source	Assay Per cent
B-1345	*Datura ferox*	0.53
B-1350	*Datura ferox*	0.62
B-1358	*Datura ferox*	0.70
B-1359	*Datura ferox*	0.66

A small planting of *Datura humulus flava* was made of seed from the above source. A mixed sample of leaves assayed 0.42 per cent. Individual selections could not be made on account of the failure of the plants to produce seed. This was due to the late planting and injury from early frost. The plants did not flower until September and were extremely sensitive to frost.

The foregoing figures indicate a considerable range of variations in the percentage of alkaloids as found in the individual plants. This variation in the progeny of both the *Datura stramonium* L. and *Datura tatula* L. selections is greater than that of the two parent plants. In the species stramonium this is 0.09 per cent in the parents, while in the progeny it is 0.23 per cent for the selections from both the fertilized and non-fertilized plots. The highest yielding plant was produced by the low parent upon a fertilized plot while the lowest yielding plant was produced by the high parent upon a non-fertilized plot. Contrary to expectations the higher averages were obtained upon the fertilized and non-fertilized plots from the low-yielding parent. For the fertilized plots these averages are 0.64 per cent from the low parent and 0.61 per cent from the high parent. For the non-fertilized plots they are 0.60 per cent from the low parent and 0.50 per cent from the high parent.

In the species tatula the variation of the two parent plants is 0.18 per cent while in the progeny it is 0.31 per cent and 0.32 per cent upon the fertilized and non-fertilized plots, respectively. The highest yielding plant was produced by the high parent upon a non-fertilized plot, while the lowest yielding plant was also produced by the high-yielding parent but upon a fertilized plot. The latter was an abnormal plant producing few leaves and for this reason might be expected to give a low yield. The next lowest appears, according to expectation, in the progeny of the low parent and upon a non-fertilized plot. The averages in this case are the reverse of what was noted for the species stramonium and are according to expectations. The higher averages are obtained from the progeny of the high parent and from the fertilized plots. For the fertilized plots these averages are 0.68 per cent from the high parent and 0.54 per cent from the low parent. For the non-fertilized plots they are 0.62 per cent from the high parent and 0.49 per cent from the low parent.

Table IV shows extremes as noted in the parents and offsprings and the variations as found upon fertilized and non-fertilized soils.

The greater range of variations in individual plant yield as found in these second generation plants is probably due to the fact that the parent plants represented mixed strains. Such mixed strains resulting from promiscuous pollination might produce plants giving altogether different yields from the parents. When the original selections were made no precautions were taken to prevent cross pollination. This precaution is necessary with the daturas if known parentage is desired. It has not been conclusively shown that the property of a plant to produce a definite percentage of alkaloids is uniformly transmitted to the offsprings. Inbreeding or close pollination of all selected plants is necessary in the study of the transmission of such a character. The results so far obtained indicate that the seeds from open pollinated plants are either of composite parentage or that the character under consideration is not uniformly inherited. The results seem to point toward the former supposition with certain exceptions. Some degree of uniformity is to be noted in the assays of these second generation plants. There is more uniformity among the individuals within the groups assayed than there is between these individuals and the parent plants. Considering only the non-fertilized plots in this respect the progeny of the high-yielding stramonium is most uniform. The parent assayed 0.55 per cent and the progeny 0.50 per cent, 0.56 per cent, 0.54 per cent and 0.42 per cent. This uniformity within the groups is greatest in the tatula selections and is sufficient to maintain the averages in the order expected. Taking the average assay of the progeny of the low-yielding parent from the non-fertilized plot as a unit, the averages from the other plots of this species follow in their expected order, *i. e.*, 1.00 : 1.10 : 1.26 : 1.38. In the species stramonium, however, the uniformity within the groups is not sufficient to maintain this order. In this case the order is 1.00 : 1.06 : 0.82 : 1.01.

TABLE IV

Datura stramonium

	Assay Highest yielding plant Per cent	Assay Lowest yielding plant Per cent	Variations Per cent
Parent plant	0.55	0.46	0.09
Non-fertilized	0.65	0.42	0.23
Fertilized	0.71	0.48	0.23
Datura tatula			
Parent plant	0.65	0.47	0.18
Non-fertilized	0.77	0.45	0.32
Fertilized	0.75	0.44	0.31

Greater extremes in the alkaloidal yield of the individual plants have been located than were found in the original investigations. This is doubtless due to the small number of plants originally assayed. It is believed that such extremes can be determined immediately by the examination of a sufficiently large number of individual plants produced under uniform conditions. Whether or not the greatest extremes in the two forms under discussion have been reached can be determined only by further study. The location of the highest extremes is the principal object. The possibility of the fixation of this high-yielding property must then be determined by inbreeding. If such a procedure is possible, high-yielding strains or races of the alkaloidal producing plants can be developed for commercial purposes. With four exceptions all of the forty-three assayed plants have been inbred and mature seeds obtained from them for planting. Twenty crosses (hybridizations) have also been made between various individuals of the three species studied. A few reciprocal crosses have been made. The alkaloidal yield of these hybrid forms will be studied in comparison with the yield of the inbred parents and their progeny. Perfect uniformity in the behavior of any character cannot be expected in the first generation from inbred plants. This is due to latent tendencies, the elimination of which may require two or more generations by inbreeding.

It has already been stated that another object of this investigation was to follow the effects of prolonged cultivation upon the yield of alkaloids. The idea that cultivation causes a decrease in the value of medicinal plants has been current for many years, but apparently without foundation. The results obtained are contrary to this belief and are an indication of what may be accomplished through cultivation and improvement. All plants in the experimental plots have been under cultivation two years. The original source of the seed from which the cultivated strains were started is known absolutely in the case of *Datura tatula* L., as wild plants a few inches high were transplanted from a vacant lot in Indianapolis to the experimental plot. Thus two years under cultivation is known to be correct for this species. This is not true, however, with *Datura stramonium* L. The seeds from which the original planting was made were obtained in the London market and may or may not have been gathered from wild plants. Mixed samples were collected for comparison from wild plants found growing adjacent to the experimental plots. Following is a table of the average assays of the wild and cultivated plants:

TABLE V—AVERAGE ASSAYS (PERCENTAGES)

Datura stramonium

Source	1910	1912	1912
Original plants	0.50	Fertilized	Non-fertilized
High-yielding plant	....	0.61	0.50
Low-yielding plant	....	0.64	0.60
Wild plants	....	....	0.28
Datura tatula			
Original plants	0.58	Fertilized	Non-fertilized
High-yielding plant	....	0.68	0.62
Low-yielding plant	....	0.54	0.49
Wild plants	....	....	0.35

These averages indicate the beneficial effect of cultivation both with and without fertilizer. In most cases these averages are higher in the second year than in the first. The general averages of all the selected plants assayed this year is greater in each case than the averages of the plants originally assayed. The exceptions are most marked in the averages of the progeny from the low-yielding parent. In *Datura stramonium* the averages are equal to or greater than the original average.

These forms will be continued under cultivation. Seed from the highest yielding individuals will again be planted and the resulting plants assayed in the same manner as those previously examined. In addition to the original objects of the investigation, *i. e.*, the effects of cultivation and selection upon yield of alkaloids, the influence of hybridization upon this yield will also be noted. Other species and varieties will be included as seed supplies become available.

DEPARTMENTS OF BOTANY AND ANALYTICAL CHEMISTRY
ELI LILLY & COMPANY, INDIANAPOLIS

LABORATORY AND PLANT

DETERMINATION OF NITROGEN BY THE NITROMETER

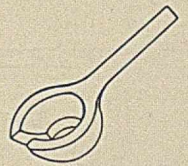
By C. M. Joyce and Harry La Tourette

Received October 20, 1913

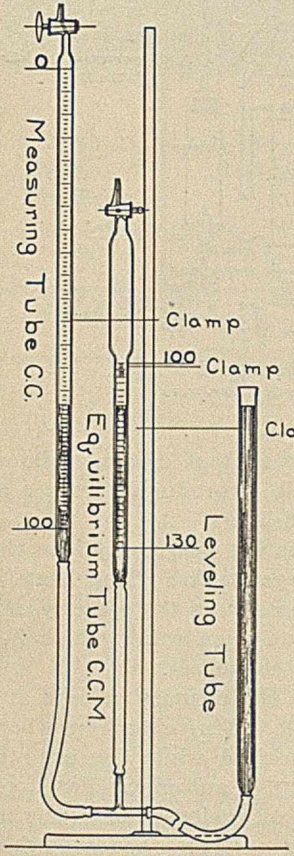
The nitrometer consists of a gas generating bulb fitted at the top with a two-way cock leading to a dissolving cup and a gas exit tube, and which has at the bottom a connection for a rubber tube leading to a leveling tube, the whole being filled with mercury to a level just below the upper cock; a cylindrical glass measuring tube graduated from 0–100 cc. connected to a leveling tube through a T tube leading to an equilibrium tube. The latter is shaped like an inverted 100 cc. pipette graduated downward below the bulb from 100–130 cc. The whole system is filled with mercury so that the measuring tube may be completely discharged by raising the leveling tube.

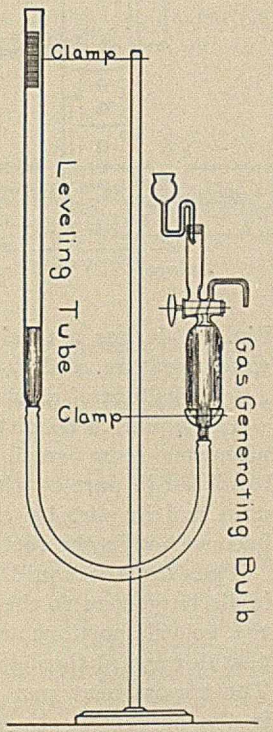
ADJUSTING THE EQUILIBRIUM TUBE

The volume of 100 cc. of dry air at 0° C. and 760 mm. under the temperature and barometric conditions prevailing at the time is calculated, three drops of 98 per cent sulfuric acid are drawn into the tube and the level of the mercury fixed in accordance with the calculation. The cock of the tube is then closed and sealed with melted paraffin. The volume in this tube may be confirmed at any time by opening the measuring tube and adjusting the leveling tube so that the level is the same in the three tubes. The volume of gas in the equilibrium tube is then read and compared with the calculated volume at the time, a correction in the subsequent gas readings in the measuring tube being made accordingly.



Holder for Gas Generating Bulb





NITROGEN IN POTASSIUM NITRATE

Approximately 0.4 gram potassium nitrate is placed in a weighing tube, dried two hours at 110° C., desiccated 24 hours over sulfuric acid and weighed exactly by difference into the cup of the gas generating bulb. This is dissolved in 9 cc. 95 per cent sulfuric acid added through a siphon thistle tube, entering the top of the dissolving cup through a tight-fitting rubber stopper. When the salt is dissolved it is drawn into the gas generating bulb and followed by two washings 1.5 cc. each of 95 per cent acid. The bulb is then shaken with a motion normal to its long dimension until the volume of gas determined by a rough paper scale pasted on the leveling tube becomes constant, this operation taking from 3 to 5 minutes.

The gas is passed into the measuring tube and after standing 5 minutes the leveling and measuring tubes are so adjusted that the level in the equilibrium tube reads 100 cc. and is the same as the level in the measuring tube. The reading of the latter is then taken. As the temperature and barometric conditions, in so far as they affect the measured volume of the gas, are automatically compensated by the equilibrium tube, and as the gas is washed with sulfuric acid and is, therefore, dry, the percentage of nitrogen may be calculated directly, correcting only for the calibration of the equilibrium and measuring tubes. Seventeen determinations made when the room temperature ranged from 20–28° gave 13.71 per cent nitrogen, the theoretical being 13.84 per cent.

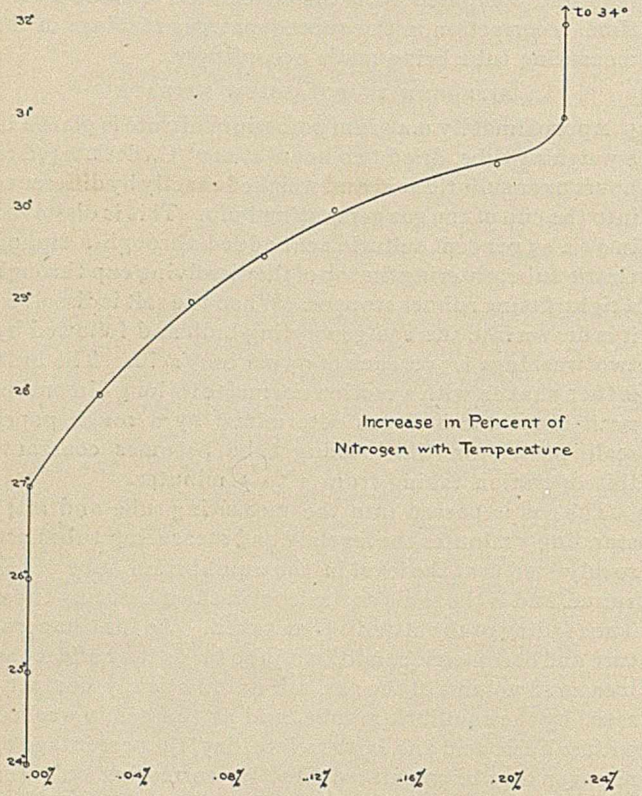
EFFECT OF ROOM TEMPERATURE

It was noted that the nitrogen determinations of pyroxylin when the room temperature was over 30° C. appeared abnormally high. Determinations of potassium nitrate were accordingly made at temperatures of 31–35° when the theoretical percentage was obtained. This would indicate that the solubility of nitric oxide in 95 per cent sulfuric acid diminishes practically to zero under these conditions. Nitrogen determinations of a well pulped sample of nitrocellulose were made at room temperatures ranging from 25° to 35° C. with the result that the apparent percentage increased beginning at 27° C., being 0.03 higher at 28°, 0.07 at 29°, 0.10 at 29.5°, 0.13 at 30°, 0.20 at 30.5°, and 0.23 from 31.0° to 35.0°.

The results on nitrocellulose had been previously corrected for solubility of nitric oxide in sulfuric acid, the correction being based on the difference between the found and calculated values for potassium nitrate. This correction amounted to approximately 0.10 per cent and would account for about half the difference observed when nitrocellulose was determined at the temperatures before cited.

The greater apparent increase in nitrogen in pyroxylin over potassium nitrate with rise of temperature can be accounted for only by the partial breaking up of the cellulose into carbon monoxide and carbon dioxide.

The formation of carbon dioxide has been partially investigated, the contents of the measuring tube from determinations made when the temperature was over 30° C., having been passed through an absorption tube filled with barium hydrate solution. This method offers some difficulties, owing to the small quantity of carbon dioxide, the presence of which has been determined only qualitatively thus far. The exact measurement of this gas and the formation of carbon monoxide will be investigated later.



Duplicate Kjeldahl determinations of the sample of nitrocellulose determined at varying temperatures were 0.09 per cent below the figure obtained with the nitrometer between 20° and 28°. This difference is within the limit of error of the two methods.

LIMITATIONS OF NITROMETER

The nitrometer gives results reliable within 0.02 per cent on nitrate nitrogen, using 0.4 to 0.5 gram sample. It is not available for the determination of nitrogen in celluloid or other substances containing carbon ring compounds which appear to prevent the complete liberation of nitric oxide in the presence of sulfuric acid and mercury.

SUMMARY

Besides the corrections for calibration and standardization of the nitrometer in accordance with temperature and barometer, the gas readings should be corrected for solubility of nitric oxide, which diminishes when the temperature goes above 28° C., and the formation of other gases by the breaking up of the cellulose molecule which increases.

The following table gives the algebraic sum of these two corrections for temperatures ranging from 20° to 35° C.:

Temp.	Cc.	Temp.	Cc.
20.0–27.5	+0.90	30.0	—0.14
28.0	+0.74	30.5	—0.70
29.0	+0.34	31.0–35.0	—0.94
29.5	+0.10		

ARLINGTON CO., ARLINGTON, N. J.

LABORATORY COLUMN STILL

By H. K. BENSON

Received September 22, 1913

In the description[1] of the equipment of the chemical engineering laboratory of the University of Washington, Fig. 9 of Plate 1 shows the location of an alcohol still. During the last year, through the kindness of a local manufacturer, a working model of a continuous column still has been installed, which has given excellent results in operation.

The still, which is made of copper, consists essentially of a preheater, primary column and rectifying column. The general plan of construction is shown in the sectional drawing, Fig. 1, and photo of the installation, Fig. 2. It has a total cubic content of 9.24 gallons, water measure, and is capable of producing from 2 to 4 proof gallons of alcohol in 8 hours.

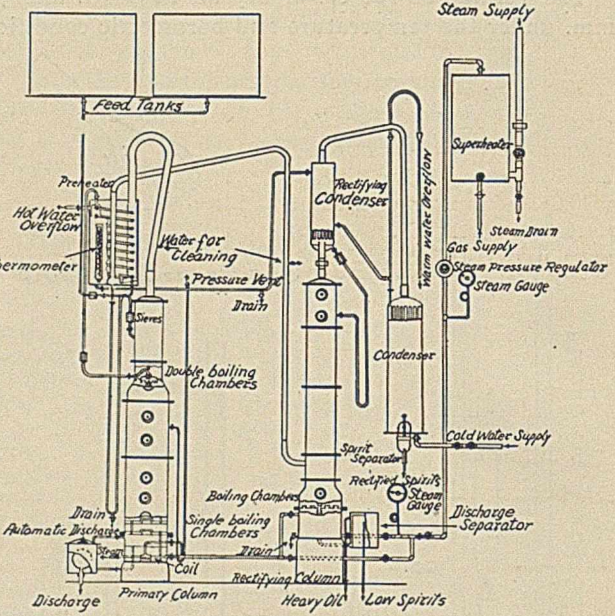


FIG. 1

The liquid to be distilled is fed by gravity into the preheater from small storage tanks. The heat is furnished in part by the vapors from the primary column and in part by radiation from water which has become hot in the rectifying condenser.

Thus the hot liquid enters the primary column and is discharged on to the double boiling chambers where the volatile portions are vaporized while the residues pass downward through a trap, or automatic discharge. The vapors next pass into an enclosed annular ring in the preheater, the heavier portions condense while the lighter pass over into the rectifying chamber, are subjected to repeated condensation and vaporization and finally constitute the high proof alcohol.

Steam is drawn from the heating system, passes through a superheater and thence into a pressure

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[1] THIS JOURNAL, 4, 609 (1912).

regulator. For experimental work dealing with the production of ethyl alcohol from sulfite waste liquor and of methyl alcohol mixtures suitable for denaturing purposes, a steam pressure of less than 5 pounds was found efficient.

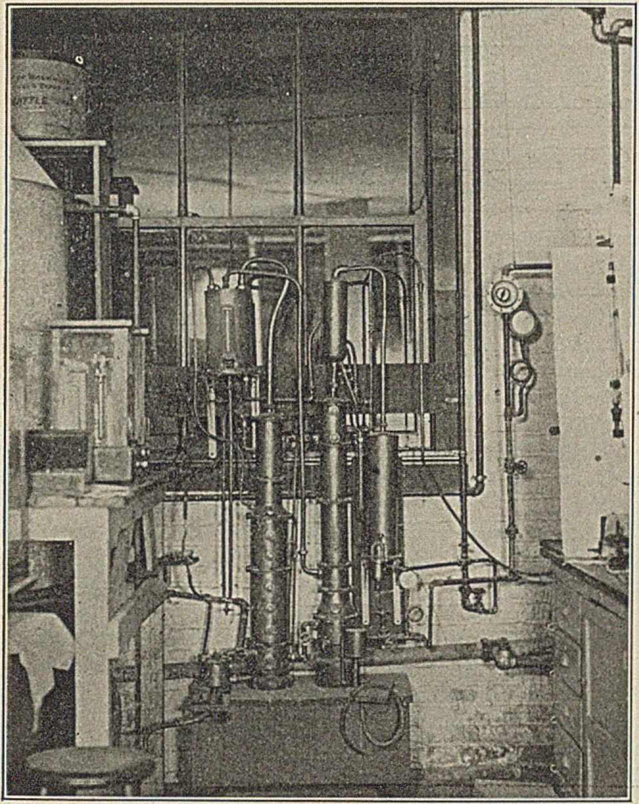


Fig. 2

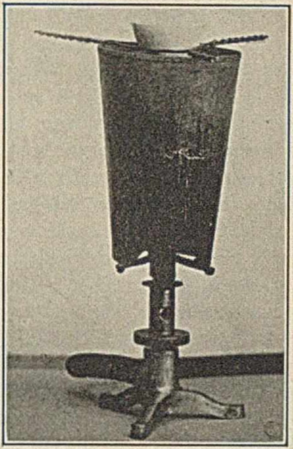
Laboratory of Industrial Chemistry
University of Washington, Seattle

AN IMPROVED LABORATORY BURNER

By Chas. P. Fox

Received September 16, 1913

In laboratories where air currents are troublesome, a cylindrical wind shield, independent of the burner, is often employed. For use with any of the common types of laboratory burners, the attachment shown in the accompanying photograph is much more convenient.



It consists of an inverted sheet metal cone 5 inches long, 2 inches in diameter at bottom, and 3 inches at top, and supported by a 3-armed frame attached to the burner tube.

By making the support sufficiently rigid the triangle holding the crucible in ash determinations and the gauze when heating small beakers may be placed directly across the top of the shield.

Any tinsmith can fashion and attach the shield, using for the 3-armed frame an ordinary chimney support (E. & A., No. 2613 or Sargent, No. 1080).

This type of burner, as improved, has been found very useful in light laboratory work. The improvement has been in use several years and, as far as known, is original.

Akron, Ohio

ADDRESSES

BIOCHEMISTRY[1]

By Carl L. Alsberg

I did not come to Rochester with the intention of making a speech, but find—I am sorry to say—that Prof. Chambers expects me to talk. He made the request—or, shall I say, demand—as we came to this room. I find that I am driven to the usual refuge of those who have to speak when they would rather be silent—that is, I will take refuge in the history of my subject.

This subject has, I think, some general interest because originally no very definite distinction was made between biochemistry and any other kind of chemistry. One of the first real biochemists was Lavoisier, whom all matter, whether living or dead, interested. He performed the first calorimetric experiments. He was the inventor of the ice calorimeter, and showed that animal heat was the result of oxidation. All the chemists of that generation, and the immediately succeeding one did biochemical work. I need only cite Liebig, who is perhaps in some ways the greatest of all biochemists. Unfortunately, about the latter part of Liebig's life chemists lost interest in biochemistry. This was due very largely to the sudden and tremendous development of organic chemistry, which was brought about by the discoveries of men like Hofmann and Kekulé. It was so easy to make new synthetic substances, and thereby gain a sort of immortality, even though the main result of putting a chlorine atom here and a bromine atom there was to fill up Beilstein. In consequence, thoroughly trained chemists did not busy themselves with subjects that were really important in the elucidation of that matter which is found in living organisms, and which forms the physiological basis of life. The scientists in biology and medicine needed such information. The chemists did not give it to them. Consequently, physicians and physiologists who were ill-equipped for chemical research were forced to carry forward the work of biochemistry. Though the net result of their work made decidedly for progress, only too often it created confusion and artificial difficulties. Even the best biochemists of those days make us wonder why they did not pursue their chemical investigations as far as the chemical methods of that day would permit. The answer is, I think in many cases, that they were not real chemists but physiologists with a chemical veneer. Fortunately, this has been changing during the past decade, largely owing to the work of Emil Fischer. While we recognize in him a master of chemical technique, we may be certain that in a measure, at any rate, the preëminent position which he occupies

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[1] Chairman's address, Biological Chemistry Section, 48th meeting, A. C. S., Rochester, September 8–12, 1913.

among the chemists of his time is due to his clear conception of the really most important work in organic chemistry along biochemical lines. Fortunately, more and more organic chemists are following in his footsteps, and are devoting their attention to substances which occur in living things. I wish here to make a plea for more of this sort of work in America. I believe that the rewards and recognition for knowledge of chemistry applied in biochemistry are great, because the work of the biochemist will be applauded not merely by chemists, but also by zoölogists, botanists and physicians. A biochemist has a wider audience because his work presents a more general appeal than the work of organic chemists upon such subjects as dyestuffs and the like. Further, I wish to point out the value of instruction in allied subjects. Not every organic chemist can successfully attack all biochemical problems. Besides his organic chemistry, other experience in physiology, and above all, experience in dealing with substances which do not crystallize is necessary. In many cases it is difficult to conduct biochemical research because the biochemist must very frequently begin with the smears, which the organic chemist consigns preferably to the slop jar. While the things which will not crystallize interest the organic chemist less, they are the very classes of substances with which the biochemist must deal. Great care, great patience and a knowledge of colloids are required of the organic chemist who wishes to work in biochemistry, but I feel confident that the reward for such men is great, not merely in pure science, but also in the industries and in the arts.

The history of biochemistry in America is similar to that abroad. In America it developed first in the seventies and eighties in the medical schools of the country; and, at that time, it was controlled by physicians and physiologists abroad. The subject was narrowed to the consideration of biochemistry as affecting the life of man; that is to say, the chemical side of physiological processes of the human body together with such considerations of bacteriological chemistry as affect man in health and in disease. This phase of biochemistry is cared for very adequately and acceptably by the American Society of Biological Chemists, the first biochemical society to be formed in America.

The phases of biochemistry which the American Chemical Society can very naturally expect to encourage are quite distinct from the aims of the American Society of Biological Chemists. Our usefulness will include the biochemistry affecting agriculture, phytochemistry in particular, and such industrial processes as are based upon biochemical reactions. For example, the more exact study of the chemical composition of fruits, grains, and food products. It must be admitted that, at present, we know only those chemical substances occurring in considerable amounts in such important grains as wheat and corn. The minor constituents in grains of much importance have not been identified with exactness. If we consider grains of less importance even this degree of knowledge can not be claimed.

Some of our most important modern industries, like those dealing with starch, artificial fabrics, leather tanning materials, glue and gelatin, meat packing and the flour milling industry require biochemists, and we are now training men to deal with such practical problems.

If our society confines itself to the activities already mentioned, there still remains a wide field of biochemistry uncared for, the biochemistry of the lower animals. This part of the biochemical work will become a part of the work in the zoölogical societies of the country. My view is that three societies of biological chemistry can well exist in America without competing in any way, each one caring for a specific need. These would include the biochemistry of the higher animals and its application to medicine; the biochemistry of the lower animals; and biochemistry in its application to plants, agriculture, and the industries.

Bureau of Chemistry
Washington

THE PROGRAMS FOR THE SECTIONAL MEETINGS OF THE AMERICAN CHEMICAL SOCIETY
A SUGGESTION[1]

By Bernhard C. Hesse

Suddenly confronted with the major responsibility for the programs for the nine meetings of the New York Section of the American Chemical Society for the current session, the question as to what results are to be aimed at took sharp and definite form in my mind.

The answer to that question, as nearly as it can be arrived at by observation of members of the audiences at these meetings and by interrogation of a number of them, can never be anything but a generalization or a number of generalizations, which appear to be about as follows:

1. We come to these meetings to hear a good, lively discussion and not to listen to a catalog of analytical results or numerical constants or detailed experiments. Final, conclusive and generalized results are what we are after.
2. Discussion, in order to be lively, should be prepared in advance and every one should have an opportunity to become acquainted with the general trend of the papers prior to the meeting.
3. Extemporaneous discussion too often leads very far afield and the real points of the paper read and in issue are not touched upon.
4. The meetings are too long and of too uncertain duration.

That these generalizations have a foundation in fact became evident by a number of walks through the various rooms of this building during meetings of this and of other societies. It is a safe estimate that, in general, there were quite as many men in the foyer, in the social room and in the restaurant as there were in the audience in Rumford Hall. Those on the outside frequently comprised a number of men who were eminently fitted to discuss the papers presented; on inquiry as to why they were not in Rumford Hall the general answer was to the effect that they were waiting for the conclusions to be stated and then they might have something to say; no sitting through the reading of the dry details for them! Following up some of these individuals, it turned out that although they were present when the final conclusions of the papers were stated yet they said nothing in the discussion and the explanation given was that while they did not agree with the conclusions stated yet they had not their material in such condition as to use it with convincing effect; generally they indulged in disparaging remarks of what little discussion had taken place; in not a few cases some have remarked that if they had only known the day before what so-and-so was going to say they'd have loaded for bear, and shot so-and-so's conclusions as full of holes as a sieve. Making due allowance for a little braggadocio they probably meant that under those circumstances they might have made a creditable opposition showing. The crucial question, however, is: "Would they?"

It is a fact thay many of our members reside at a distance and it is imperative for them to leave the Chemists' Building before a definite time, say 10.30 P.M., in order that they may not be unduly delayed in their arrival home. Everybody knows that once a commuter's mind is on his train his mind is not on much else and particularly not on the subject matter of the paper; the fact is that he is anxious to have the matter over with so that he can have a moment's chat with some particular person in the audience and as likely as not, that particular person is not at that time in any particular hurry to leave and communication with him in the meeting-room is, to say the least, awkward and embarrassing, if not unfeasible. The unavoidable result needs no further portrayal here. We have probably each and all of us been through that experience.

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[1] Chairman's address at the October 10th Meeting of the New York Section of the A. C. S., The Chemists' Club, New York.

This is not a complete statement of the problem nor of the facts but it probably contains the essentials and the salient points of both and will answer for a working basis for the consideration of a plan of action which may be capable of overcoming some of the defects just noted.

It is becoming more and more the practice at the large meetings of a number of technical and scientific societies to have the papers to be read at those meetings printed and distributed to the members in advance of the meetings. This plan tends to minimize these defects, at any rate. If now, the author were to be limited to a few moments to recapitulate in a few words the most important essentials and the debatable points in lieu of reading the entire paper and if one or more members could be induced to prepare a set and carefully worded discussion of such papers as lend themselves thereto also in advance of the meeting, the way seems to be open to complete overcoming of the foregoing defects if only the auditors will then do their part and critically think the subject matter over and properly fortify and equip themselves in advance of the meeting. If discussions under those circumstances be not lively and short and to the point as well as interesting and useful such failure must then lie in and be inherent to the subject matter, itself.

Of course, for sectional meetings the expense of printing the papers in advance is prohibitive; to base the program upon articles appearing in our own journals and of fairly recent date seems as though it should be feasible; at any rate, that is the suggestion I am now making, that sectional meetings could, with profit to all, be based, in part at any rate, upon one or more papers in recent numbers of our own journals and that one or more persons be invited to prepare a set discussion of such papers as lend themselves thereto, but in all cases such discussion is to be opened and closed in the briefest manner possible by the author or perhaps by some one the author might choose to designate. All who attend will have had opportunity to acquaint themselves in advance with the nature of the communication and its main points, conclusions and contentions.

Making this plan effective will put a greater share of responsibility on the audience and in view of the lethargy of the human being the all-important question is: "Will the audience do its share?"

For a time I was tempted to try this plan out during the present session, but having only recently had considerable and weighty proof of the enormous inertia of the human mind in the acceptance of a new order of things, I have refrained from such attempt and have contented myself with bringing my thought to your attention in this manner in the belief that if it corresponds in any degree to any real existing need that this Section can be depended upon to take such action in the premises as the merits seem to warrant.

90 William Street
New York City

EMPIRICAL REQUIREMENTS IN ASPHALT SPECIFICATIONS

By Leroy M. Law

Received October 1, 1913

INTRODUCTION

The purchase of materials under specifications is a practice that is daily becoming more general. It is a natural outgrowth of the systematic study of one's requirements and the scientific development of products to meet them. The practice has reached its present broad application and usefulness largely through the aid of the chemist and it is in the interest of chemists engaged in bituminous work that this paper is primarily written.

Under ideal conditions, purchasing under specifications is beneficial to both consumer and producer. The former is enabled to state in precise terms his exact requirements in the way of material needs. This establishes quality and, as a result, all competitors are placed upon an equal footing and competition resolves itself into the real objective, competition in price alone. To a producer, it means first of all that he is given an equal chance with others in the trade, and as all deliveries are to be rigidly inspected, he feels safe that another dealer cannot submit a profitless price in the hope of furnishing an inferior article.

The mutual understanding or, to use the definition of contract, the "meeting of minds," is brought about through the agency of the specification proper and it is, therefore, highly important that this feature should receive serious consideration. Its prime object is to define the requirements in terms which permit of ready interpretation, avoiding all possible uncertainties which may give rise to disputes under the contract. This point is vital and really forms the foundation of this great system, yet even in some of our most elaborate specifications its importance is frequently neglected. In many of the early types we have seen such requirements as "The material must be A. B. C. brand or equal thereto" and "the material shall have given satisfactory service under similar conditions for such a period of time." With such crude clauses specifications fail of their purpose for the actual requirements are at best but vaguely stated and the producer has no way of ascertaining if his wares are "equal to" or have "given satisfactory service" in the judgment of the person who reviews the bids and makes the award.

Such conditions especially unfair to the manufacturer are rapidly disappearing, yet to-day in many of the so-called scientific specifications, the adoption of requirements based on arbitrary methods of analysis has placed the honest producer in an equally uncertain and embarrassing position. It is to three such requirements which have gained and still hold surprising popularity in many current bituminous specifications that I now invite your attention.

DISCUSSION

The first stipulation of this character to be mentioned is that limiting the so-called "fixed carbon" and it is indeed difficult to understand just how this requirement even secured a foothold in asphalt specifications.

Fixed carbon is a test stolen from fuel chemistry, where it serves to indicate the coke remaining after the gaseous constituents have been removed by heating the material, with exclusion of air, under prescribed conditions. Those who have had any experience in fuel work whatever know full well that this test is purely empirical and that the variations among different operators, especially in different laboratories, is often considerable.

A committee of the American Chemical Society gave considerable study to the matter some years ago and in 1899 recommended the procedure[1] that is now followed in conducting this determination. It is to be understood however that this method is not applicable even to some fuels like the lignites which are very prone to spark. How much more inapplicable then will the method be to softer materials like the asphalts and road oils which have also the disagreeable tendency of foaming out of the crucible at certain stages of the heating?

Chemists should know that city illuminating gas, the source of heat, varies in different localities; in fact in some cities the composition is entirely different from that in others, hence a variation in heat, to say nothing of the difference in type and the condition of burners employed. It has also been found that the degree to which the platinum crucible is polished has also an effect on fixed carbon results and there are doubtless other sources of variation not as yet discovered.

The point is that asphalt chemists who advocate such requirements in their specifications, fail to realize these features

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[1] *J. Am. Chem. Soc.*, **21**, 1116.

and their resulting effect on the limitations of accuracy. Fieldner,[1] of the U. S. Bureau of Mines, in speaking of the fixed carbon test, makes the following statement in regard to coal and what he says in regard to coal is equally applicable to the fixed carbon in asphalts for the same procedure is used with both materials:

"The volatile matter and fixed carbon represent the relative proportions of gaseous and solid combustible matter that may be obtained from the coal by heating it in a closed vessel. This is done by heating a finely powdered sample in a small, covered platinum crucible, in the flame of a Bunsen burner or Méker, burner for exactly seven minutes. The volatile matter consists mainly of the combustible gases—hydrogen, carbon monoxide, methane, and other hydrocarbons and some non-combustible gases such as carbon dioxide and water vapor. The volatile matter does not include water present in the coal as moisture at 105° C. (221° F.).

"The residue of coke left in the crucible after deducting the ash is reported as 'fixed carbon.' The 'fixed carbon' does not represent the total carbon in the coal, as a portion of this element is driven out in combination with hydrogen in the volatile matter; furthermore, 'fixed carbon' is not pure carbon, but still contains several tenths per cent each of carbon, hydrogen, and oxygen; from 0.4 to 1.0 per cent nitrogen; and about half the sulfur that was in the coal. It should be clearly understood that the terms 'volatile matter' or 'volatile combustible matter' and 'fixed carbon' do not represent any definite compounds which existed in the coal before heating. The method of determination is purely arbitrary and variations of temperature and rate of heating will cause variations amounting to several per cent; even with a strict adherence to the method recommended by the American Chemical Society, variations of three and four per cent in both the volatile matter and fixed carbon may occur in different laboratories. One of the most prominent factors in causing variations is the temperature at which the crucible is heated."

"It is especially pronounced in anthracite and semi-bituminous coal. It is not improbable for one laboratory to report 4 per cent and another 7 per cent volatile matter on the same sample of anthracite, or 14 per cent and 17 per cent, respectively on the same sample of Pocahontas coal. The different percentages of volatile matter were actually produced by different conditions of heat treatment. Caution must, therefore, be observed in making comparisons of the volatile matter and 'fixed carbon' in proximate analyses made in different laboratories. Even determinations made at the same laboratory by the same analyst may vary to the extent of 0.5 per cent."

If such wide variations do occur with coals what, then, should we expect when the method is applied to soft asphalts and even oils?

As a chemist of one of the large asphalt companies, I have observed this fixed carbon requirement enforced to extremes and yet to no purpose or benefit to the consumer. The yield of fixed carbon cannot be controlled in the process of manufacture, unless through gross carelessness in coking material. In this case, the defects will be shown far more accurately by increased insoluble matter in the various reagents employed in bitumen analysis.

Results on Fixed Carbon (Percentages)

Sample No.	213	215
Laboratory A	12.00	17.4
Laboratory B	13.62	16.85
Laboratory C	10.91	13.13
Laboratory D	12.52	17.54
Laboratory E	12.63	17.20
Laboratory F	17.10	22.00

Some weeks ago the writer prepared two samples of bituminous material of different consistencies, dividing each sample into several portions. These were sent to several laboratories to make the fixed carbon tests. The operators selected were not those of the usual commercial laboratories, but chemists who are especially qualified and equipped for asphalt work, and regarded as our foremost experts in this branch of the profession. The tabulated results of their work are shown in the accompanying table.

Inspection of the figures shows a variation in fixed carbon on the same samples of over 6 per cent in one case and nearly 9 per cent in the other. When experienced operators such as the above differ by these amounts on identical samples, is there any wonder that with chemists generally, the variations are even greater? It is to be regretted that chemists do not study the value of these tests before incorporating them in their specifications and extend to good materials and their honest manufacturers a just consideration. If fixed carbon in Baltimore is different from fixed carbon in Pittsburgh and, if in any one place the results are to vary from day to day, what possible value can the test have as indicating the value of a material? Furthermore, how is the manufacturer to test his products in every consumer's laboratory, to ascertain conditions prevailing in each of them?

Some days back it was our misfortune to have a shipment of asphalt rejected, because the fixed carbon as determined in the customer's laboratory ran from one-tenth to three-tenths in excess of the prescribed limit. I had previously tested the batch from which this shipment was made, and found the fixed carbon considerably below the requirements of the specifications. Think of a scientist holding up a material on such a narrow margin as this, when even the most precise chemical methods are seldom within this limit of accuracy, especially as carried out in ordinary commercial testing! An absurd feature of the case is that another carload from the same batch was accepted as meeting the requirements, the inspecting chemist doubtless being unconscious of the variation he was experiencing in his own laboratory.

But I leave the subject of fixed carbon to pass to another empirical requirement of still greater uncertainty, *i. e.*, the so-called paraffin determination.

This procedure is supposed to show the amount of hard or "scale" paraffin present in the material and is, therefore, considered to be an index as to its liability to crack in cold weather or granulate with age. The general procedure employed in this determination is doubtless familiar, consisting of distilling the material rapidly down to dry coke and collecting the distillate. The latter is then weighed, an aliquot portion removed, dissolved in alcohol-ether, chilled and the crystallized scale filtered off, dried and weighed. Many specifications prescribe that the scale shall not exceed a certain figure, yet few of them prescribe their modifications in detail. The results are that each customer performs the test in the manner most agreeable or convenient to himself, and the manufacturer has to stand for the whims and modifications introduced.

Usually the test is conducted in a glass retort, yet some operators substitute in its stead an iron one. That this may influence results matters little, so the manufacturing chemist must visit all these laboratories to become familiar with each chemist's details, return and endeavor to duplicate conditions.

Dow and Smith,[1] using an iron vessel, show the effects of different rates of heating, type of condenser, etc., and furthermore, express the belief that at certain heats soft paraffins may be converted into the scale form. In the face of these experiments and opinions we have chemists who insist that the higher the paraffin scale obtained the more accurate the method, their

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[1] This Journal, **5**, 270.

[1] *Engineering News*, June 8, 1911.

claim being that "you can not get out more than there is in it."

In an effort to learn something as to the paraffin test as generally applied, the six laboratories who replied to the fixed carbon inquiry were also asked to determine paraffin scale in the same samples. They did so with the exception of one laboratory which for reasons not stated, declined to make the determinations. I trust that laboratory E realizes the unscientific status of the paraffine scale test and it was this realization that prompted them to decline to report on the subject.

Results on Paraffin Scale (Percentages)

Sample No.	213	215
Laboratory A	3.6	2.8
Laboratory B	0.10[1]	1.58
Laboratory C	2.7	1.49
Laboratory D	1.21	1.25
Laboratory E	....	....
Laboratory F	4.13	3.04

[1] Material foamed considerably. Analyst is of opinion that there is no accurate method and results are only approximate.

The above results tend to make a laughing stock of the profession and are printed only with the hope that asphalt chemists may soon get together and study or eliminate these embarrassing subjects.

Our company is furnishing a certain material to one customer who limits paraffin to one per cent. From him we have had no complaint whatever, yet the same material is ineligible under another specification having been reported to contain paraffin in excess of four per cent. I ask you candidly which chemist is right, and what is the manufacturer to do under such conflicting evidence?

Turning now to a third requirement of questionable scientific value, and non-indicative of either quality or service results, I call attention to a requirement in many road oils and binder specifications which states that the material at, say, 50 penetration, shall have a specified minimum ductility. The idea is that the bitumen shall possess adhesiveness, a quality best shown by the ductility test and by concentrating to 50-penetration, the standard consistency for this ductility test, all materials are brought to a uniform basis of comparison.

Thus far, the idea is sound but the method of concentration, the all-important feature, is sadly and ignorantly neglected. Some chemists in a blind attempt at conserving ductility, stipulate that during concentration, the temperature shall not exceed, say 400° or 500° Fahrenheit. Others provide for "occasional" stirring, but generally they neglect the essential feature in asphalt treatment, namely the agitation. In hardening the softer asphalts, agitation plays if anything, a far more important role toward conserving ductility than does the mere restriction of temperatures. My interviews with inspecting chemists relative to this test, show that they are uniform only in following "no regular procedure."

Some of them use heat test residues which by accident have just reached 50 penetration or again this residue treated to a further heating on a hot plate or in an oven to obtain the desired consistency. Others concentrate the material from an oily state to asphaltic consistency in a single operation, either on a hot plate or in an oven, with or without agitation as suits their fancy and the manufacturer must ascertain and duplicate in his laboratory all of these eccentricities to find out the chance his material has of passing a so-called scientific specification.

On one occasion the writer submitted to a prospective customer a series of asphalt products varying in consistency from a maltha down to an asphalt cement. These were tested by the inspecting chemist who passed the harder materials, but rejected the softer ones, as absolutely lacking in ductility when reduced to 50 penetration.

The chemist allowed me to look over his results, and I observed that with the material requiring the least concentrations he had secured the highest ductility and in case of the fluid material requiring the greatest concentration to reduce it to 50 penetration, practically no ductility was obtained. All of the products were from the same primary material, the maltha, the harder ones being produced by refinery operation which neither he nor any one else could duplicate in the evaporation tins of the asphalt laboratory.

In the instance cited, the chemist's process was undoubtedly one destructive to ductility for the longer the heating required to reach 50 penetration the lower the ductility of the product. The individual in question avoided the issue by deciding that to his mind the test represented service conditions where no agitation of the material took place. And so I might go on with a number of other requirements without theoretical or practical significance, but why take up time or space?

Suffice it to say that such clauses as fixed carbon, paraffin scale, etc., in their present empirical state and coupled with a narrow and rigid interpretation are not only a discredit to the profession, but destroy the value of a sincere specification.

It has just been stated that the principle object of the specification is to lay before the manufacturer in a clear, concise manner the requirements that are to be met. When he is unable to interpret these with a reasonable and standard equipment, the purpose of the specification fails.

CONCLUSION

The rapid developments in bituminous highway work during recent years has been accompanied by an accumulation of inspection methods, desirable and questionable ones springing up together and the many young chemists in this field of work doubtless look upon them as methods of established, scientific value. Other chemists with only time for routine work of testing become advocates of such requirements as they might otherwise suppress. Furthermore specifications of one city or municipality are frequently copied from those of another which presumingly from a longer experience in bituminous work is looked upon as a criterion in such matters.

And so by these and other unstudied procedures our asphalt specifications have been brought to this present empirical condition, and the time is at hand for chemists in this branch of the science to coöperate in weeding out the tangled field of laboratory methods.

No one chemist should, and no true scientist will, decide that check results in his own laboratory establish the reliability of a test or method of analysis. Such is at least to be expected. A true scientist will endeavor to ascertain what the procedure shows in the hands of others, presuming, of course, average qualifications in experience and skill.

If as a result of such study fixed carbon, paraffin, etc., are found to be of value, then it will be of interest to all concerned to adopt definite procedures and agree on the limitations of accuracy. If they cannot be developed into real scientific methods, capable of yielding concordant results in the hands of all qualified chemists, then they should, by mutual consent, be abandoned. In their present empirical condition they can not be of any possible assistance in determining the quality or even the uniformity of a product, but on the other hand, their employment frequently works injustice to valuable materials.

Until the status of these tests is better established would it be any more than fair to the manufacturer to omit such requirements from bituminous material specifications?

Laboratory U. S. Asphalt Refining Co.
East Brooklyn, Baltimore, Md.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

SULFITE WASTE LIQUOR PROBLEMS

Paper for November 12, 1913 reports that in the manufacture of chemical woodpulp by the sulfite process, half of every cord so treated is dissolved by the liquor in which the wood is boiled, and is discharged into the adjacent rivers as waste liquor. According to the latest bulletin on pulpwood, issued by the Forestry Branch, Ottawa, the amount of pulpwood subjected to this chemical treatment in 1912 was almost 290,000 cords. Half of this amount was absolute waste. The average price of a cord of pulpwood is six dollars, so that this waste, reduced to its money equivalent, represents a loss to Canada of over $800,000. Nor is this the only loss, for by this process 140 pounds of sulfur are required to dissolve the waste materials out of each cord of wood. Some of the gases generated in the process are recovered, but most of the sulfur passes off in the waste liquor, and no method has yet been found to recover it for use a second time. Sulfur costs twenty-five dollars a ton, and the loss in this particular is equivalent to a money loss of over half a million dollars on the total amount wasted.

In view of the fact that each year more and more pulpwood is being manufactured into pulp by this process in Canada, the utilization of this waste liquor becomes an important problem. Even the most practicable method so far devised does not recover enough valuable products to make it pay.

The waste liquor contains many materials, such as oxalic acid, tannin extracts, dyestuffs and alcohol constituents which, if they could be easily recovered, would make the liquor of great commercial value; but in spite of the tremendous amount of work has been done on the subject, especially in Europe, the problem still remains for the most part unsolved. As the liquor also contains carbohydrates, it should be possible to obtain turpentine, and eventually it may be possible to obtain rubber from it. In furthering the solution of such problems and in eliminating other forms of wood waste, the new Forest Products Laboratories being established by the Dominion Government at McGill University will doubtless play an important part.

One use of the waste liquor mentioned above, that has been tried at Grand' Mère, Quebec, where the Laurentide Company has large pulp and paper mills, consists in its utilization for street-watering. Experience has shown it to be as efficacious in keeping down dust as oil is, while the objectionable odor of oil is absent.

NICKEL A BY-PRODUCT IN THE UNITED STATES

The Geological Survey reports that there are no producing nickel mines in the United States. The output of nickel from domestic ores is merely a by-product from electrolytes of the copper refineries. Salts and metal equivalent to 328 short tons of metallic nickel were saved in domestic refineries in 1912 from both foreign and domestic ores. Nickel ore, "imported for consumption," is mostly from the Canadian deposits.

PRACTICAL CONSIDERATIONS AFFECTING CHOICE OF THERMOMETERS IN INDUSTRIAL PLANTS

In *The Institution of Mechanical Engineers*, Whipple points out that questions of first cost, up-keep, etc., must be considered in the selection of thermometers for either high or low temperatures.

As a rule the temperatures found throughout a steam plant may be taken with mercury thermometers, sockets, or mercury cups being placed in the steam pipes into which the mercury thermometers are placed. On the other hand, it is frequently troublesome to read the important thermometers in the plant, and they often go unread. The thermometer at the foot of the smoke stack, and the one on each side of the economizer, although giving valuable information as to the efficiency of the plant, are frequently unnoticed. For this reason it is advisable to install resistance thermometers, which can be easily read on a galvanometer mounted in the boiler or engine house. When dealing with high superheater temperatures, a recorder or an alarm thermometer will be found of service.

Mercury thermometers are generally employed in cold storage work, but experience has shown that in the case of large stores —say ten rooms or over—it pays to install resistance thermometers. A great deal of time is spent in reading mercury thermometers throughout a large building which necessitates the opening and shutting of a number of doors, and which, in addition to the labor cost, is wasteful of power and tends to destroy the uniformity of temperature in the various rooms. The applications of pyrometers in works for the treatment of metals are very varied. One of the most important is the measurement of the temperature of the air in the hot air main of a blast furnace. If prime cost is not an overwhelming consideration, then resistance thermometers should be used connected to a Callendar recorder. Thermocouples may be used, but if an accuracy comparable to that of the resistance thermometers is desired, a scale control board, and various precautions with regard to cold junctions, etc., must be adopted.

Unfortunately, although the temperature at which a metal is cast is admitted to be of such great importance, yet there is no really satisfactory way of determining the temperature of the molten metal. The conditions, especially where a large crucible is used, make it practically impossible to insert a pyrometer into the metal, and the readings obtained with radiation or optical pyrometers are not consistent, owing to variations in the quality and quantity of the slag and the frequently great divergence from black-body conditions.

The closed-tube radiation pyrometer can be safely used when small crucibles are employed; the thermocouple also, if protected by an outer salamander tube, may be employed for molten brass.

The greatest field for the application of pyrometers lies in the heat treatment of metals, where the success of a pyrometer installation depends almost entirely on the mounting. Experience shows that, in the case of large furnaces, it is advisable to put the thermometer in the floor of the furnace in the following way: A slot is chopped into the furnace floor and into this a fire-clay tube is grouted, the space surrounding the tube being filled in with fire-clay flush with the bottom of the furnace. The pyrometer is slipped into the tube through the side of the furnace. The weight of the head of the pyrometer is taken by a flanged socket, which is screwed into the protective plating of the furnace, the pyrometer being held to the socket by means of readily removable bolts and nuts. Thus the pyrometer can be introduced between the gas ports of the furnace.

In practically all porcelain works Seger cones are employed to control the firing. Although the information given by them is extremely valuable as showing the maximum temperature attained, yet they fail to show the rate at which a kiln is being heated, and this is frequently of fundamental importance. Thermocouples are best employed for the measurement of the lower or preliminary temperature and radiation pyrometers for higher or finishing temperatures.

THE SALT INDUSTRY OF RUSSIA

It is pointed out in *The Times Russian Supplement*, August 11, 1913, p. 8, that there is a great discrepancy between Russia's salt production and her resources in this respect.

Geological investigation proved long ago that there are in various parts of the Russian Empire untouched deposits of salt, that there are lakes in the Astrakhan province and in Siberia which possess a considerable salt capacity, and that mineral salt can be found in large amounts in the Caucasus and in the Ural Mountains. Vast areas that are suspected to be salt-bearing have up to the present time not yet been surveyed. Oil borings in the Ural Caspian district have within recent years disclosed the presence of hundreds of millions of tons of rock salt in the Gouriev and Emba districts. A recent calculation estimates the salt resources of Russia to be capable of supplying the whole world for centuries with this indispensable commodity. In spite of this fact, the production of salt in Russia hardly covers the comparatively moderate consumption of the Empire.

In 1880, Russia produced no more than 750,000 tons of salt. In 1900, the production had increased to two million tons, and in 1912, the output reached $2^1/_4$ millions.

Nearly half of the Russian salt output is obtained in the lakes of Baskunchak and of the Crimea. Although the lake-salt production is the cheapest, the irregularity of its output induces those engaged in the industry to take a special interest in the product obtainable by boiling and in rock salt.

Salt-boiling is principally applied in the Perm and Slaviansk districts.

It is interesting to note that the Siberian dairy farms are using the Slaviansk and not the Perm salt, which, though nearer the Siberian consumer and obtained by the same process of boiling, is inferior in quality.

The most advanced and promising branch of the Russian salt industry is rock salt, of which 85 per cent is produced in the Bakhmut district, in Southern Russia. The average yearly salt output in Bakhmut was for 1901–5, 500,000 tons and for 1906–10, 560,000 tons, while in 1912, it reached over 600,000 tons. The production of rock salt is less expensive than preparation by the boiling process.

Russia's production is limited by the internal demand, which is increasing slowly. The use of salt in cattle food is practically unknown to the Russian peasantry, and the chemical industries using it as a raw material are not sufficiently developed.

The salt industry depends much on the State, which is the owner of one-half of the salt-producing areas and a producer of several hundred thousand tons. The State gives leases against a certain royalty of extracted salt, and is entitled to force the firms to sell their whole output to the Government at a fixed price. The rise of the price of salt was the object of special investigation by a Commission in 1911, but up to the present moment the State has not used its right of compulsory pre-emption.

The Amur district, a great fishery centre, and consequently an important consumer of salt, is importing this commodity from Japan, China, and especially from Germany, to the amount of over 500,000 tons.

The salt industry being closely connected with the general industrial development of the country, progress in agriculture and chemical production, as well as the betterment of the economic standard of the population, will necessarily lead to an increased output.

CHEMICAL TRADE OF GERMANY

Consul-General Harris, of Frankfort on the Main, summarizing a number of German authorities, discusses the progress of the chemical trade of Germany during the past few months and throughout 1912. In connection with the statement made by Mr. Harris as to the progress of Germany's chemical trade, statistics show that the exports of raw chemical products during the first half of 1913, compared with 1912, record an increase of more than $10,000,000 worth, and reach a total of $47,000,000. Of colors and dyestuffs, an increase of about $6,000,000 is noted, the total for the first six months of the present year being $36,000,000. Of varnish, lac and putty, the exports amount to nearly $739,000, and really declined during the six months period. Of ethers, alcohol, etc., the total exports for the first six months of 1913 were over $5,000,000 worth, a gain of $1,500,000. Exports of artificial fertilizers show a decline of about $300,000 in a total exportation of the first six months of $6,143,000 worth. Of pharmaceutical products, a gain of more than $2,000,000 is noted for the first six months, the total being $11,963,000.

Giving some details as to the more important items in Germany's trade with the United States and other countries, and calling particular attention to the trade in fertilizers and explosives, Mr. Harris says:

The items of chief importance in the export trade are chemical raw products and colors and dyestuffs, forming together about three-fourths of the total value. Exports of raw materials during the first half of 1913 showed a gain of about 30 per cent over the corresponding period in 1912, 32 per cent over the January-June portion of 1911, and 110 per cent over the first semester of 1908.

A marked increase was shown also in the various salts, such as chloride of potassium, etc. Belgium, France and Austria-Hungary are the principal countries of destination of these shipments, while for salts to be used for fertilizers, which are also included in the export figures, the United States, Sweden, Russia and Austria-Hungary are the chief customers. The import trade of these salts is so small as to be insignificant.

As purchasers of German aniline and other coal-tar colors, China, England and the United States lead. The total shipments of these colors in the first half of 1913 reached in value $16,855,000, against $15,726,000 last year. Imports of dyestuffs, with figures much lower than the exports, include certain specialties.

Germany's shipments of artificial fertilizers, while showing a falling off from those of 1912, advanced during the past six years by about 150 per cent. Thomas meal (exports, first half of 1912, $2,762,000; 1913, $2,703,000) and superphosphate (exports, first half 1912, $3,205,000; 1913, $2,995,000), as by-products of the rapidly increasing mining industries of Germany, furnish the principal items of these exports, which go chiefly to Austria-Hungary, the Netherlands, Russia and Denmark. Imports of artificial fertilizers during the first six months of 1913 amounted to 60 per cent of the exports and came chiefly from Belgium and France.

IMPRESSIONS OF EUROPEAN SEWAGE-TREATMENT METHODS

As Philadelphia's representative, Mr. George E. Datesman, principal assistant engineer of the Bureau of Surveys, visited Europe and made studies of the systems of sewage treatment in cities of Germany, Austria, Holland, Belgium, France and England. The principal conclusions of his report follow:

1. The establishment of government rivers boards to supervise sanitary conditions and works proposed is essential to proper results. The art of sewage disposal apparently has stopped at percolating filters, but an adequate and less costly substitute is anticipated. It is practicable to obtain from properly designed and operated sewage works a clear, odorless, sparkling and non-putrescent effluent from a sewage of extreme concentration, even if it has become septic.

2. Sludge resulting from sewage treatment can be rendered innocuous, practically inodorous and wholly unobjectionable and can be disposed of without nuisance, sometimes profitably. By certain combinations of treatment desired results may be secured at a fraction of the cost of other recognized scientific methods of treatment in satisfactory operation.

3. In the conservation of a water supply, sewage-disposal

systems should bear only their proportion of the cost of treatment. The construction of a properly designed, economical and sanitary collection system is the first essential in sewage disposal.

4. The use of the separate system of sewer conduits has been abandoned as inadequate for urban districts. Polluted streams can be made pure by a system of interceptors to prevent sewage from reaching the streams.

5. Rivers may be made clean and nuisances to sight and smell may be prevented by simple screening or by screening and tankage treatment, provided the diluting volume of river flows and its velocity are sufficient to prevent deposits. Where not used as a water supply the extent to which a river may be used as an oxidizing agent thus offers a problem to be determined.

6. At the present stage of the art there is no process that gives better or cheaper results than the form of tank used at the works of the Emscher Genossenschaft in Germany. Should screening be desired, the so-called Reinsch screens as used at Dresden, Germany, are the most cleanly and efficient of any observed. Experience has proved that adequate tankage treatment is more effective and less costly than the operation of fine screens.

7. Of the bacterial treatments, the percolating filter furnishes the best results both in oxidizing the organic matter and in the removal of putrescibility. The speed of operation is greater than by any other system, with consequent reduced first cost for land areas.

8. When sufficient fats are present in the sewage, they may be profitably recovered from sludge. Drying for fertilizer and fuel use has also proved profitable in some cases.

9. Submerged outlets from disposal works are essential for proper dilution. Disinfection with hypochlorite of lime as a final treatment is not in use either in England or Germany. In the conditions of the rivers in the former country it would not be effective in removing pollution.

ACTION OF ALKALI AND SEA WATER ON CEMENTS

The United States Bureau of Standards has investigated the above subject and has published the results of its investigations in *Bulletin* **12**. Since the physical test covered a period of exposure of not to exceed 3$^1/_2$ years, the following conclusions drawn should be considered somewhat tentative:

Portland cement mortar or concrete, if porous, can be disintegrated by the mechanical forces exerted by the crystallization of almost any salt in its pores, if a sufficient amount of it is permitted to accumulate and a rapid formation of crystals is brought about by drying; as larger crystals are formed by slow crystallization, the same results would be obtained on a larger scale, but in greater time if the drying were slow. Porous stone, brick and other structural materials are disintegrated in the same manner. Hence, in alkali regions where a concentration of salts is possible, a dense non-porous surface is essential.

While in the laboratory a hydraulic cement is readily decomposed if intimately exposed to the chemical action of various sulfate and chloride solutions, field inspection indicates that in service these reactions are much retarded if not entirely suspended in most cases, due probably to the carbonization of the lime of the cement near the surface or the formation of an impervious skin or protective coating by saline deposits.

Properly made Portland cement concrete, when totally immersed, is apparently not subject to decomposition by the chemical action of sea water.

It is not yet possible to state whether the resistance of cement to chemical disintegration by sea water is due to the superficial formation of an impervious skin or coating, which is subsequently assisted by the deposition of shells and moss forming a protective coating, or by the chemical reaction of the sea salts with the cement forming a more stable compound without disintegration of the concrete, or by a combination of both of these phenomena.

Marine construction, in so far as the concrete placed below the surface of the water is concerned, would appear to be a problem of method rather than materials, as the concrete sets and permanently hardens as satisfactorily in sea water as in fresh water or in the atmosphere, if it can be placed in the forms without undue exposure to the sea water while being deposited.

Contrary to the opinion of many, there is no apparent relation between the chemical composition of a cement and the rapidity with which it reacts with sea water when brought into intimate contact.

In the presence of sea water or similar sulfate-chloride solutions, the most soluble element of the cement is the lime. If the lime of the cement is carbonated it is practically insoluble. The quantity of alumina, iron or silica present in the cement does not affect its solubility. The magnesia present in the cement is practically inert.

The change which takes place in sea water when brought into intimate contact with the cement is as follows: The magnesia is precipitated from the sea water in direct proportion to the solubility of the lime of the cement. The sulfates are the most active constituents of the sea water, and are taken up by the cement. Their action is accelerated in the presence of chlorides. No definite sulfate compound was established. The quantity of chlorine and sodium taken up by the cement is so small that no statement can be made as to the existence of any definite chloride or sodium compound formed with the cement.

Metal reinforcement is not subject to corrosion if embedded to a depth of 2 inches or more from the surface of well-made concrete.

ALLOYS OF ALUMINUM

C. H. Ivinson, in the *Mechanical Engineer*, discusses the alloys of aluminum with the common and rare metals.

An alloy of 4 per cent nickel has been shown to disintegrate in a very short time after being cast, but the introduction of copper is an advantage. Phosphide of copper added in quantitites of 1.5 per cent to a zinc-aluminum alloy containing from 12.5 to 15 per cent zinc gives fluidity to the molten metal. Phosphide of zinc containing 25 per cent phosphorus may be substituted in the proportion of 0.05 per cent. This is one of the best fluxing and cleansing agents the writer knows for all aluminum alloys, and should be added to the molten alloy for a few minutes before pouring by wrapping in paper and plunging to the bottom of the crucible by means of tongs and stirring briskly.

Magnesium-aluminum alloys containing 1 to 10 per cent magnesium are much improved by the addition of 5 per cent zinc, as this addition imparts better wearing properties to the metal and aids in producing homogeneous castings. By the addition of 1 per cent phosphide of copper less oxidation of the metal takes place during the melting operations.

During the last few years metallurgists have been experimenting with some of the rarer metals, and this part of the subject is most interesting. The writer has alloyed aluminum with almost all the rarer metallic elements, such as cerium, neodymium, lanthanum, tantalum, zirconium, and beryllium, and some of these alloys gave most remarkable results even in quantities of only 1 per cent and under. Cerium and beryllium alloys are particularly interesting. An addition of 0.5 per cent of cerium raises the tensile strength of the metal from 4.5 tons per square inch to 10.3 tons per square inch, and gives an elongation of 8.5 per cent on 2 inches. This alloy was placed in sea water and boiled for 60 hours; the sample was carefully weighed before and after the boiling process, and there was no loss in weight. One side of the metal was polished and, after the boiling, was found to be untarnished. An alloy of 2 per cent beryllium gave a tensile strength of 11.8 tons per square inch with an elongation of 10 per cent on 2 inches. It was of a beautiful silver-white color, and could be hammered out cold into leaf; it also withstood the action of sea water perfectly.

Manganese, titanium, chromium, molybdenum, tungsten, etc., form a very interesting series of alloys, either when alloyed by themselves or in the presence of copper. Titanium and chromium alloys are both affected by sea water and ordinary atmospheric conditions. The former alloy, when polished in the presence of sea water, develops white spots on the metal which, when removed, show deep pit marks on the surface of the metal; this applies to the alloys of chromium as well.

Tungsten has been recommended as being a suitable metal to alloy with aluminum to resist corrosion, but the writer did not find this very satisfactory. An alloy containing 2 per cent copper and 0.5 per cent tungsten rapidly disintegrated under ordinary atmospheric conditions. At least 100 different samples of this alloy were prepared in the varying proportions of 0.2 to 5 per cent pure tungsten alloyed by itself with the aluminum, and also in conjunction with nickel, manganese, copper, etc. The results of some of these were disappointing.

The alloy of zinc and nickel containing 3 per cent nickel and 0.75 per cent zirconium gave extraordinary results as far as tensile strength was concerned, having 12.2 tons per square inch, with elongation 9 per cent on 2 inches. Its behavior in sea water was very extraordinary; it was boiled for 72 hours in sea water, and when tested, after the boiling process, showed only 4 tons per square inch tensile strength. Its fracture was very crystalline, and it was also very brittle. Zirconium 0.75 per cent, when alloyed with aluminum without the presence of nickel, gave the same tensile strength after the boiling process as before, namely, 9.3 tons per square inch.

Molybdenum, when alloyed with aluminum, had the opposite result. An alloy was made containing 1.5 per cent molybdenum with aluminum which, after being boiled in salt water, gave a lower tensile strength than before the boiling; but when the molybdenum was alloyed with the aluminum in the presence of copper in the proportions of molybdenum 1.5 per cent and copper 1.5 per cent, the tensile strength of the metal after the boiling process was the same as originally.

WATERPROOFING OF CONCRETE STRUCTURES

CONCLUSIONS OF COMMITTEE ON WATERPROOFING MATERIALS OF THE AMERICAN SOCIETY OF TESTING MATERIALS

While the committee has not arrived at sufficient conclusions to formulate definite specifications for making concrete structures waterproof, certain results have been reached which may be of assistance in securing impermeable concrete.

In the laboratory and under test conditions using properly graded and sized coarse and fine aggregates, in mixtures ranging from 1 cement, 2 sand and 4 stone to 1 cement, 3 sand and 6 stone, impermeable concrete can invariably be produced. But the reverse often obtains in actual construction, permeable concretes being found even with 1 cement, 2 sand and 4 stone mixtures and these are of frequent occurrence where the quantity of the aggregate is increased. This the committee attributes to defective workmanship, to use of imperfectly sized and graded aggregates, use of excessive water and lack of proper provision to take care of expansion and contraction.

Properly graded sands and coarse aggregates are rarely, if ever, found in nature in sufficient quantities to be available for large construction, and the effect of poorly graded aggregates in producing permeable concrete is aggravated by poor and inefficient field work; it is seemingly a commercial impossibility on large construction to obtain workmanship even approximating that found in laboratory work. In consequence of these conditions substances calculated to make the concrete more impermeable—either incorporated in the cement or added to the concrete during mixing—are often used.

The committee has investigated a sufficient number of these special waterproofing compounds as well as certain very finely divided mineral products, to form a general idea of the different types.

The majority of patented and proprietary compounds tested have little or no immediate or permanent effect on the permeability of concrete and some are even injurious. The permanent effect of such additions, if dependent on the action of organic compounds, is very doubtful. In view of their possible effect upon the early strength and durability of concrete after considerable periods, no integral waterproofing material should be used unless it has been subjected to long-time practical tests under proper observation to demonstrate its value, and unless its ingredients and the proportion in which they are present are known. In general, more desirable results are obtainable from inert compounds acting mechanically than from active chemical compounds whose efficiency depends on change of form through chemical action after addition to the concrete.

Assuming average quality as to size of aggregates and reasonably good workmanship in the mixing and placing of the concretes, the addition of from 10 to 20 per cent of very finely divided void-filling mineral substances may be expected to result in the production of concrete which under ordinary conditions of exposure will be found impermeable, provided the work joints are properly bonded and cracks do not develop on drying, or through change in volume due to atmospheric changes, or by settlement.

In large construction, no matter how carefully the concrete itself has been made, cracks are apt to develop, due to shrinkage in drying out, expansion and contraction under change of temperature and moisture content and through settlement. Hence, it is often advisable on important construction to anticipate and provide for the possible occurrence of such cracks by external treatment with protective coatings. Such coating must be sufficiently elastic and cohesive to prevent the cracks extending through the coating itself. The application of merely penetrative void-filling liquid washes will not prevent the passage of water due to cracking of the concrete.

While some penetrative washes may be efficient in rendering concrete waterproof for limited periods, their efficiency may decrease with time and it may be necessary to repeat such treatment. The first effort, therefore, should be made to secure a concrete that is impermeable in itself, and penetrative, void-filling washes should be resorted to only as a corrective measure.

While protective extraneous bituminous or asphaltic coatings are unnecessary, so far as the major portion of the concrete surface is concerned, provided the concrete is impermeable, they are valuable as a protection where cracks develop in a structure. It is therefore recommended that a combination of inert void-filling substances and extraneous waterproofing be adopted in especially difficult or important work of any nature. Protective bituminous or asphaltic coatings are often subject to more or less deterioration with time, and may be attacked by injurious vapors or deleterious substances in solution in the water coming in contact with them. The most effective method for applying such protection is either the setting of a course of impervious brick dipped in bituminous material into a solid bed of bituminous material or the application of a sufficient number of layers of satisfactory membranous material cemented together with hot bitumen.

Their durability and efficiency are very largely dependent on the care with which they are applied. Such care refers particularly to proper cleaning and preparation of the concrete to insure as dry a surface as possible before application of the protective covering, the lapping of all joints of the membranous layers, and their thorough coating with the protective material.

The use of this method of protection is further desirable because proper bituminous coverings offer resistance to stray electrical currents.

Of course, no addition of waterproofing compounds or substances can be relied upon to counteract completely the effect of bad workmanship, and the production of impermeable concrete can be hoped for only where there is determined insistence at all times on good workmanship on all structures.

FULLER'S EARTH

The United States Bureau of Mines has just issued a pamphlet (Bulletin No. 21) by Charles L. Parsons, on Fuller's Earth.

Dr. Parsons states that "The United States produces all of the fuller's earth used for refining petroleum within its borders. On the other hand, most of the fuller's earth used in bleaching edible oils has been imported from England. Recently a few of the refiners of cottonseed oil have begun to utilize domestic fuller's earth, whereas others have been unable to substitute it successfully for English earth in their practice. Many samples of American earth distinctly superior in bleaching powder to the English earth have come to the attention of the Bureau of Mines. For these reasons an investigation of the mining, preparation, and use of fuller's earth in this country, especially in its application to edible oils, was conducted in order to ascertain why our own raw material has been deemed inapplicable to our needs.

"During the calendar year 1912, according to figures of the United States Geological Survey, there were imported into the United States 1,970 tons of unground fuller's earth, valued at $11,619, and 17,139 tons of ground fuller's earth, valued at $133,718, these values being based on the wholesale market price at the port of origin. The addition of transportation charges, commissions, etc., make the price to the American refiner $14.50 to $16 per ton. According to the latest figures compiled by the United States Geological Survey, the United States in 1912 produced 32,715 tons of fuller's earth, valued at $305,522 or $9.34 per ton, at the mine. Most of this domestic production was from three plants in Florida and one in southwestern Georgia and was used almost wholly for decolorizing petroleum. A small amount from other localities was used in the refining of edible oils. No figures definitely differentiating fuller's earth from other clays are kept in regard to our exports, but it is certain that several thousand tons of domestic earth were exported to Germany, and it is also true that German refiners of edible oils have used and are using large quantities of American fuller's earth and have a higher appreciation of its merits than our own refiners.

"As a result of the investigations made, the Bureau of Mines believes that the United States has fuller's earth far better suited for refining edible oils than any imported, and that to assure the almost universal use of this earth by American refiners there is required only a careful and intelligent technical control of the preparation of the output and its application to the bleaching of oils."

NEW CHEMICAL PROCESS FOR FIBER

A new process of manufacturing cellulose has been worked out by Dr. J. König: Balsam, fir, pine, spruce, beech and oak woods, as well as spun fibers, may be transformed into a very fine, easily bleachable cellulose, with a cattle feed substance residue, and the elimination at the same time of the waste liquor troubles. The *Journal of the Society of Chemical Industry* (Oct. 15, 1913, p. 939) states that the disintegrated wood or other fibrous material is steamed with four to five times its weight of a 3 to 5 per cent solution of ammonia under a pressure of 2 to 3 atmospheres for five or six hours. The liquor is removed by pressing and the residue is washed with boiling water, the ammonia being recovered by distillation of the liquors, with the addition of lime, if necessary; resins and tannins are obtained from the residue from distillation. The digested material is next steamed in a similar manner with 4–5 times its weight of 0.4 to 0.6 per cent sulfuric acid for 6–8 hours under a pressure of 1 to 2 atmospheres. The liquors from this treatment contain sugars, the products of the hydrolysis of hemicelluloses and pentosans. These liquors are neutralized either with the lime employed for the recovery of the ammonia or else with powdered limestone and evaporated. The syrup obtained is separated from the calcium sulfate and mixed with dry fodder, chopped hay, brewers' grains, bran, etc., and fed to cattle.

An alternative process consists in steaming with sodium carbonate solution instead of ammonia in the first stage and with hydrochloric acid in the second stage, and mixing the waste liquors from each process so that they neutralize each other; the sodium chloride thus formed is not injurious to the use of the evaporated syrup as a fodder. The exhaustive alkaline and acid treatments do not remove the lignin from the wood, and the residue still contains over 25 per cent of lignin. This, however, is in a form which is readily oxidizable by hypochlorite bleach liquor and the fiber is treated in stages, preferably with dilute sodium hypochlorite, until a residue of bleached cellulose is obtained. It is estimated that 200 pounds of wood yield six pounds of resin (or two to four pounds of tannic acid), fifty pounds of fodder extract rich in sugars and sixty-two to eighty-two pounds of bleached cellulose.

SEWAGE DISPOSAL IN NEW YORK

Number 6 of the *Preliminary Reports* of the Metropolitan Sewerage Commission of New York is the presentment of a study of the collection and disposal of the sewage of the lower Hudson, lower East River and Bay division. Number 7, in the same series, includes the critical reports of G. J. Fowler, of Manchester, England, and J. D. Watson, of Birmingham, England, on the projects of the Commission. These experts agree in advocating the construction of main drainage channels to carry off the sewage of lower New York into the Atlantic Ocean.

EXHAUSTING LAMP BULBS AT HIGH TEMPERATURE

According to *Scientific American* (Oct. 18, 1913), a new method is used for making a vacuum in incandescent lamps or other glass vessels. Heretofore, to eliminate the last traces of moisture and expel air bubbles which adhere to the side of the glass, the lamps have been heated in a special furnace lined with asbestos to equalize the heat to a temperature of 250 or 350° C. But all the air bubbles do not detach even at this heat, and a greater heat cannot be used for fear of softening the glass, when the air pressure would collapse the bulbs. Quite lately the Berlin Allgemeine Company used a vacuum process which permits heating to a higher point and even softening the glass while the lamps are on the air pumps. This is done by placing the lamps in an electric furnace in which a vacuum is made, so that there is scarcely any external pressure on the lamps and they can be heated as high as 500° C. Larger end tubes can be used on the lamps which is better for the vacuum process, but it is a hard matter to fuse off such large tubes for closing, when they have a vacuum inside, as collapsing may occur. An original method is used for this, and a spiral wire electric heater surrounds the tube so that it is softened and can be drawn out while still inside the furnace; the closing off of the lamp is thus effected without air pressure on the outside. Then the surface is allowed to cool down to 350° C. before opening and putting on the atmospheric pressure.

CADMIUM STORAGE BATTERY PLATES

Scientific American (Oct. 18, 1913) reports that Förseke and Aschenback use a new process for making cadmium electrode plates for alkaline accumulators. They use cadmium obtained in finely divided form as a spongy precipitate from a solution of cadmium salt. They add zinc powder to a solution of cadmium chloride; the precipitated spongy cadmium, mixed with zinc powder and a small amount of oxide of mercury, is spread upon suitable supports for making the battery plates. Such porous cadmium electrodes are used in a caustic soda or potash bath against a nickel electrode. At the first charging by current, the mercury oxide is reduced to the metallic state and the mercury then envelops the particles of cadmium and zinc. On discharging the battery, the zinc dissolves out, while the cadmium becomes oxidized and the mercury remains in the same state and is not affected. The zinc thus remains only temporarily in the mass, and aids in rendering it porous.

FRENCH ALCOHOL PRODUCTION AND USES

Consul General Frank H. Mason, Paris, reports that the French Ministry of Finance has just published some very interesting statistics concerning the production and use of alcohol in France. The total production in 1912 was 87,440,420 United States gallons, as compared with 63,797,165 gallons in 1911. In spite of this enormous production, France received from foreign countries 4,913,571 gallons of pure alcohol and liqueurs. There was a total export trade of 8,321,370 gallons: 40,044,517 gallons were beverages, a small quantity was used for perfume manufacture, and 17,994,896 gallons were denatured. About 2,306,130 gallons were employed for mixing with wine, and 1,490,106 gallons were used in the manufacture of vinegar. Out of the quantity taxed for consumption, 21,905,701 gallons took the form of "eau de vie," or brandy, 5,776,457 gallons were used for absinthe, and 282,557 gallons were used for making perfumery. The remainder was employed in the manufacture of different liquors. Of the 17,994,896 gallons of denatured alcohol 12,662,483 gallons were used for heating and lighting, while 4,113,504 gallons were employed for the manufacture of explosives.

NATURAL GAS USED

According to B. Hill, of the United States Geological Survey, the total estimated consumption of natural gas in the United States in 1912 was 562,203,452,000 cubic feet, valued at $84,563,957, an average price of 15.04 cents a thousand cubic feet, compared with 512,993,021,000 cu. ft., valued at $74,621,534, an average price of 14.55 cents, in 1911. The number of domestic consumers supplied with gas in the United States in 1912 was 1,621,557 and the value of gas consumed for domestic purposes amounted to $50,960,883, while the number of industrial consumers was 15,936 and the value of gas consumed for industrial purposes was $33,603,074. On the assumption that 28,000 cubic feet of gas equals in heating power 1 ton of coal, the fuel displaced by gas consumed in 1912 was equivalent to approximately 20,000,000 tons of coal.

One feature of particular interest in the year 1912 was the completion of the pipe line which is to convey natural gas from the Buena Vista Hills, of Kern County, Cal., to consumers in the city of Los Angeles and the surrounding towns.

West Virginia produced 215,785,027,000 cubic feet, valued at $29,064,968. Pennsylvania was the largest consumer of gas, herself producing to the value of $22,823,725, but consuming $26,486,302 worth of gas. West Virginia, on the other hand, consumed only about one-fourth of her output, the balance being piped into other States.

GOLD AND PLATINUM BY THE TON

The production of pig iron in 1912 was 33,802,685 tons of 2,000 pounds each; that of platinum was 1.3 tons. The value of the iron per ton was $12.44 as against $1,328,391 per ton for the platinum.

For the sake of convenient comparison and because in commercial practice the various ores and metals are measured by a variety of units such as the long, short and metric ton, flask, avoirdupois pound and troy ounce, the United States Geological Survey has issued a short summary of the "Production of Metals and Metallic Ores in 1911 and 1912," stated in terms of the short ton of 2,000 lbs., considerable of which, however, is derived from imported ores, bullion, etc. A comparison of the production of some of the better known metals may be of interest.

	Short tons	Value
Platinum	1.304	$1,732,221
Gold	188.108	113,415,510
Silver	4,471.4	80,187,317
Aluminum	32,803.0	15,089,380
Quicksilver	939.9	1,057,180
Nickel	22,421.0	17,936,800
Tin	8.4	8,850
Copper	734,052.0	242,337,160

PRODUCTION OF PLATINUM

Platinum is now worth $46 an ounce, against $20 five years ago. Increased prospecting last year in the United States, however, resulted in a total output of only 721 ounces of crude metal. The world's output is estimated by the Geological Survey in troy ounces as follows:

	Ounces		
Country	1910	1911	1912
Russia	275,000	300,000	300,000
Canada	30	30	30
New South Wales	332	470	500
Colombia	10,000	12,000	12,000
United States, domestic crude	390	628	721
United States, from foreign and domestic matte and bullion	1,000	1,200	1,300
Borneo and Sumatra and other	209	...	200
Total	286,961	314,328	314,751

Imports of platinum into the United States in 1912 aggregated $4,503,682 in value.

NOTES AND CORRESPONDENCE

SYRIAN AUTOBURNING LIMESTONE[1]

Several months ago, U. S. Consul Whiting, Jerusalem, Palestine, reported (*Daily Consular Reports*, July 21, 1911) upon the self-burning limestone found in the district of Hauran in Syria.

Hauran is a volcanic region lying to the south of Damascus and east of the Upper Jordan. Its surface consists of an elevated plateau made up of fertile plains and barren lava hills. The rich plains are wheat-producing lands.

A railroad running from Damascus taps this section. Mr. Whiting, who visited this locality and inspected the industry, gives this description:

"The formation occurs in beds, 20 by 30 feet thick, between layers of ordinary limestone. The rock being soft and full of crevices is easily quarried with primitive tools. When freshly quarried the material is black and has a slight odor of petroleum. The rock is broken into small pieces, piled against the quarry wall and then enclosed on 3 sides with a rough wall of the same material, making a rectangular heap 10 feet long by 10 feet wide with a height of 2 feet in front and 6 feet in rear. Small holes or flues are left in the wall for draft. The fire, kindled

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[1] Paper presented at the 48th meeting of the A. C. S., Rochester, September 8-12, 1913.

by flint and steel is started by a small sheaf of straw. After 12 hours' burning, during which much black and strong smelling smoke is given off, the rock is converted into a lime, white in color, suitable for strong plaster and in every way superior to brush burned lime, and is sold, on account of its low cost of production, at much lower figure. Samples of this rock and its lime were loaned for inspection by the Bureau of Trade, Department of Commerce.

"Another sample of the original rock was procured through the kindness of the U. S. Consul at Jerusalem.

"This Syrian autoburning limestone probably belongs to the asphaltic limestone series of Nebi Musa. These are dark gray, bituminous limestones containing phosphoric acid and holding fossil fish, in layers alternating with variegated red, yellow and white marl" (*Baedeker*, 48, Syria: Geology).

An examination of the samples shows these characteristics: Grayish brown color; no definite odor; soft, resembling hard pressed and dry mud; breaks with a slight conchoidal fracture; specific gravity, 1.74; ignites easily and burns with a smoky flame; can be easily reduced to lime by using a crucible and Bunsen flame. A partial analysis shows:

Loss, drying at 100° C.	0.12%
Silicious matter	2.97%
Iron and alumina oxide and phosphate	7.35%
Calcium carbonate	67.46%
Magnesium oxide	trace
Organic matter	21.87%
Total determined	99.77%
Sulfur, original limestone	1.94%
Nitrogen, original limestone	0.68%
Phosphoric oxide, original limestone	1.38%

The powdered rock when extracted with chloroform yields 5.37 per cent of a thick brown extract, medium soft, tough and of slight asphaltic odor. When dry-distilled the rock yields 5.28 per cent of a thick, yellowish oil, and alkaline liquor and much foetid-smelling gas. Total loss on distillation is 19.53 per cent.

The heavy, black evil-smelling smoke mentioned by Consul Whiting, and the results of our own small scale experiments suggests the use of a modern kiln whereby valuable by-products (unburned hydrocarbon and ammonia) may be saved.

The original limestone when burned in a calorimeter develops 3220 B. t. u. per pound or a heating value of approximately $^1/_4$ that of Ohio coal. (Calculations by Chas. E. Kohler, Akron, Ohio.) The softness of the rock together with its proportion of organic matter, phosphoric acid and nitrogen should render it an important soil builder. To such an origin may be due the reason why the Mukra wheat plains of Hauran are regarded as the granaries of Syria.

The rock when finely ground and bolted through a 100-mesh screen gives a *compounding material* suitable for use in black rubber goods. For the purpose indicated it is of value on account of its *mill deportment* and velvety rich colored compound (Ridgway: Color Nomenclature; Plate III, No. 2, deep clove-brown) produced.

CHAS. P. FOX

AKRON, OHIO

OBITUARY—JULES OGIER

In the death, at the age of sixty, of Jules Ogier, past president of the Société de Chimie and a member of the Comité Consultatif d'Hygiène Publique de France, France has lost one of her most celebrated forensic and sanitary chemists. After serving as assistant in chemistry at the École supérieure de Pharmacie de Paris, Ogier became assistant to Berthelot at the Collège de France; and in 1883 he was appointed director of the toxicologic laboratory in the medico-legal service of the Paris prefecture of police.

Ogier is best known for his work in public hygiene, which included investigations pertaining to the introduction of water into a number of the large cities of France, the purification of water, the disposal of the sewage of Paris, and the substitution of zinc white for white lead. He was the author of thirty volumes of judicial reports and of the well-known "Traité de Chimie Toxicologique," which appeared in 1899.

W. A. HAMOR

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

SIXTH ANNUAL MEETING, NEW YORK, DECEMBER 10–13, 1913

PROGRAM OF PAPERS

Meetings to be held at The Chemists' Club.

Presidential Address. DR. T. B. WAGNER.

Sanitary Control of the City of New York. ERNST J. LEDERLE.

A Practical Road to the Standard Catalogue. W. M. GROSVENOR.

The Commercial Applications of Ozone. A. VOSMAER.

The Sweetland Filter Press (Lantern Slides and Small Working Model). E. J. SWEETLAND.

A New Filter Press. ALFRED BURGER.

Other papers to be presented—titles not given.

Members will attend the joint meeting of the American Chemical Society, the Society of Chemical Industry and the American Electrochemical Society at the Chemists' Club. Topic of meeting: "The Welfare of Employees in Factories."

EXCURSIONS

Barber Asphalt Paving Company, Maurer, N. J.

Balback Smelting and Refining Company, Newark, N. J.

Sanitary Utilization Company at Barren Island.

Willard Parker Hospital Group of Laboratories, Department of Health of New York City.

Hanson & Van Winkle Company.

Electro-plating and Experimental Plant, Newark, N. J.

Crucible Steel Company of America, Atha Works, Newark, N. J.

Chemical Engineering Laboratories at Columbia University.

Johns Manville Asbestos Company Plant, South Amboy, N. J.

ORTHO-TOLIDINE AS A REAGENT FOR THE COLORIMETRIC ESTIMATION OF SMALL QUANTITIES OF FREE CHLORINE—A CORRECTION

In the article under the above title, THIS JOURNAL, 5, 915, in the table at the top of p. 917, only the third or final color in each case refers to a precipitate, the other colors referring to clear solutions.

S. J. HAUSER

NOVEMBER, 14, 1913

BOOK REVIEWS

Industrial and Manufacturing Chemistry: Organic. By GOEFFREY MARTIN (assisted by fourteen specialists). New York, D. Appleton & Co., 1913. Large octavo, xx + 726 pp.

Martin states in his preface that this book embraces both British and American practice and that his aim as editor has been to cover the whole range of subjects with which the industrial chemist and manufacturer are usually concerned, and to make a book which will serve either as a text-book or as a work of reference.

The book is divided into twenty-three sections as follows: The Oil, Fat, Varnish and Soap Industry, 139 pages; The Sugar

Industry, 35 pages; The Starch Industry, 12 pages; The Cellulose Industry, 32 pages; Fermentation Industries, 104 pages; The Charcoal and Wood Distilling Industries, 14 pages; The Turpentine and Rosin Industry, 8 pages; Industrial Gums and Resins, 8 pages; The Rubber Industry, 16 pages; The Industry of Aliphatic Chemicals, 20 pages; The Illuminating Gas Industry, 26 pages; Industry of Coal Tar and Coal Tar Products, 24 pages; Industry of the Synthetic Coloring Matters, 44 pages; The Industry of Natural Dyestuffs, 6 pages; The Ink Industry, 8 pages; The Paint and Pigment Industry, 18 pages; Textile Fiber, Bleaching and Water-Proofing Industry, 16 pages; The Dyeing and Color-printing Industry, 34 pages; The Leather and Tanning Industry, 28 pages; Glue, Gelatine and Albumen Industry, 8 pages; The Industry of Modern Synthetic and Other Drugs, 18 pages; The Modern Explosives Industry, 34 pages; The Industry of Photographic Chemicals, 10 pages.

Milk, cheese, condensed milk and milk powders are discussed in the section on the fat industries. Except for incidental mention in connection with fats and gelatin, no account is given of the industry of slaughtering and meat packing, which, according to the U. S. Census, is the largest manufacturing industry in this country. Except for sugar and fat the food industries, generally, are inadequately treated, the author apparently not realizing to what extent these industries are now coming under chemical control.

As is to be expected in a work consisting of a collection of chapters written by different persons, the text is of uneven quality. Some of the chapters are well written and give a good conception of the industries described; others are little more than catalogues of the materials and products of the industry. At the beginning of each chapter is given a short bibliography, usually confined to book titles and not extending to periodical literature. In those sections in which manufacturing processes are described there are numerous good cuts, and among these it is a pleasure to find several which appear to be new.

On the whole, the work does not seem to be sufficiently well-balanced or well-digested to make a satisfactory text-book, but it appears well worthy of a place on the reference shelf.

H. C. Sherman

Chemistry of the Oil Industries. By J. E. Southcombe, M.Sc., chief chemist of the Henry Wells Oil Co., Salford; lecturer on oils and fats, Royal Salford Technical Institute, etc. (Van Nostrand, 1913.)

This book seems destined to be popular as its two hundred pages run nearly the whole gamut of the oil industry, embracing petroleum, shale oil, waxes, animal and vegetable oils and their products, coal tar oils receiving little mention.

Our main utterance is not against, but because of this book. In the past twelve months or so a number of text-books on oils have appeared, such as the 1913 edition of Holde, *Untersuchung der Kohlenwasserstofföle und Fette,* which covers in a somewhat more comprehensive manner the field treated by Southcombe. Then there is a little book by Gurwitsch, *Wissenschaftliche Grundlagen der Erdölbearbeitung,* treating the subject of petroleum in an admirable way. These with Rakusin and several others afford plenty of publications from the German or Russian standpoint. Through an American publisher, two English writers, Bolton and Revis, have just issued a book on Fatty Foods. A recent book by Simmons and Mitchell on Edible Oils and Fats is also a terse contribution to the subject.

In short, we have plenty of text-books or manuals from authors on the other side, who are largely unfamiliar with the practice in this country and often do not attempt any description of American methods. Practically no books treating of American practice in a satisfactory and comprehensive way exist and one must hunt up chapters in various treatises in order to secure the rather meagre material available. The appearance of another American publication by a writer from abroad, leads us to plead for a book on the oil industry written by American experts. A treatise in the style of Rodger's Industrial Chemistry, but devoted solely to petroleum, coal tar, animal and vegetable oils and waxes, prepared in collaboration by American chemists would be most welcome and American publishers undoubtedly would be assured of much better sales for such a book than for those from English writers.

But to return to Southcombe, the first chapter entitled Introductory Organic Chemistry, although giving one a "Cook's Tour" through the subject, is really admirably written. The chapters on mineral and shale oils are rather brief, but give a general notion of present-day theory and practice. Benzene is described as having a boiling point of 85° C. In the preface, Southcombe intimates that colloid chemistry is one of the important considerations involved in the present study of oils, but it appears that he has not discussed this phase of the subject to a sufficient extent in view of the striking developments reported. Although he describes the formalite reaction, he does not mention the Rakusin phenomenon. The subject of refined petroleum is hardly adequately discussed.

Chapter III on the sources of saponifiable oils treats, at unexpected length, the subject of extraction with solvents; or rather the solvents themselves, the chemical properties of the latter being described largely to the exclusion of a discussion of their operative qualities. For example, data on the preparation of tetrachloride of carbon, its specific gravity, boiling point, etc., is given, but no mention is made of the technically important fact that tetrachloride of carbon decomposes in the presence of water yielding acid which attacks the apparatus in which extraction is being conducted. Nor is it stated that ethylene trichloride which is now on the market and used not inconsiderably is generally more satisfactory than the tetrachloride on the score of stability.

The chapter which follows on technical methods of removing impurities from crude oils and fats in some respects is deficient from the standpoint of American practice. Only one or two lines are given over to fuller's earth, while considerable space is devoted to bichromate bleach and similar bleaches of lesser importance. Deodorizing fatty oils by treatment with superheated steam in partial vacuum is quite too general a method to fail of mention.

In Chapter V the topic of unsaturated acids is incomplete for a book published in the year 1913 because only the merest reference is made to the hardening of fats and fatty acids by hydrogenation. This generally regarded epoch-making development is alluded to on page 87 as follows: "A number of patents have been taken out purporting to effect the reduction by passing hydrogen gas over mixtures of the acids and finely-divided nickel which acts as a hydrogen carrier or catalyst." In view of the wide-spread adoption of hydrogenation methods we regard this brief mention as inadequate.

The chapter on Analytical Methods is on the whole commendatory, although some tests, such as that given for the detection of rosin oil, could be elaborated to advantage. The prevalent use of electric heating appliances makes it nowadays unfashionable to illustrate Soxhlet extraction apparatus with a Bunsen burner. On pages 134–135 photo-micrographs of cholesterol and phytosterol could well supplement the free hand sketches shown. The determination of melting point and titer is not given sufficient consideration. From Southcombe's discussion of viscosity one would think the only method for viscosity determination is by the Boverton Redwood Viscosimeter, which, although a widely used instrument in England, is not in general use in this country. No other viscosimeter is described and the treatment of the subject is regarded as incomplete. The subject of colorimetry receives no consideration.

Polymerized and blown oils and also Turkey red oils are briefly described under the industrial applications of fats and oils. The distillation of fatty acids (Chapter X) and candle manufacture, soap-making and glycerine (Chapter XI) complete the descriptive part of the book. A few pages of concluding matter on "Scientific and Technical Research on Problems in the Oil and Related Industries" are of considerable interest.

In spite of the foregoing comments the book is highly to be recommended as giving, in a comprehensive form, the important facts connected with this subject, remembering as the author would have us, "that in so small a volume it has been impossible to deal in any way completely with the multidude of facts and theories relative to such an extensive subject, and the object of the work is rather to fill the gap between the elementary text-books of pure chemistry and the numerous technical treatises and monographs of a highly specialized character."

CARLETON ELLIS

Explosives: A Synoptic and Critical Treatment of the Literature of the Subject as Gathered from Various Sources. By H. BRÜNSWIG. Translated and Annotated by Charles E. Munroe and Alton L. Kibler. 350 pp. Illustrations and Tables. John Wiley and Sons, New York, 1912. Price, $3.00.

The appearance of Dr. Brünswig's book in Germany in 1909 attracted widespread attention and much favorable comment. As stated in the preface the object of the book is to gather together the facts recorded in the literature of explosives, arrange them in accordance with physical chemical views, and make a survey of the present status of the chemistry of explosives and its most important aims. Although many volumes have been written on the subject of explosives from a technical standpoint, it remained for Dr. Brünswig to collect the various data pertaining to the scientific study of the subject and arrange them in an exact science of the chemistry of explosives.

Primarily intended as a text-book, an extended exposition of intricate mathematical problems related to the subject has been omitted for the benefit of those technical workers who do not possess an advanced mathematical knowledge but who are interested in a scientific treatment of explosives. On the other hand, all strictly technical terms have been avoided that the book may be intelligible to those who have only a theoretical and scientific knowledge of the subject. In adapting his book to these two classes of readers, Dr. Brünswig has produced a work which is readable by all classes interested in the subject—and yet at the same time is thoroughly scientific and more deeply technical than at first reading would appear.

Dr. Brünswig is peculiarly fitted to produce such a work as has been described above. His connection with the "Zentralstelle für wissenschaftlichtechnische Untersuchungen" at Neubabelsberg has brought him into close contact both with the practical and technical use of explosives on the one hand, and the theoretical and scientific investigations which have been conducted, on the other. In collecting his data he has not, by any means, confined himself to the German sources of literature but has laid the chemical literature of all countries under contribution. The German source of the book should therefore not deter any one from its use.

The book is divided into two parts. Part I, which is by far the larger and more important, deals with a scientific discussion of the laws and behavior of explosive systems. The following subjects are discussed in detail in as many chapters: Conditions governing explosive reactions, including a discussion of exothermal reactions, sensitiveness and initial impulse; velocity of explosive reactions, including discussions of the influence of temperature, pressure and catalytic agents, both on initial velocity and velocity of propagation; pressure developed by explosions, with rate of increase and maximum pressure; temperature of explosions; gases from explosive reactions, with influence of pressure and temperature; explosions by influence, with both velocity and intensity of explosive impulse; and the flame of an explosion.

Part II describes the characteristics of particular explosives, which are divided into propellants and blasting explosives. This part of the work is of necessity treated briefly in order to cover the whole ground. The details of manufacture are, of course, not described. The treatment is confined to a brief historical sketch of each explosive, its general properties, nature and purpose and an indication of the method of its manufacture.

We have seldom seen a book so thoroughly indexed. A table of contents gives at a glance the general arrangement of the subjects treated. An exhaustive index, both of authors and subjects, enables the reader to turn at once to any fact which the book contains. An idea of the large amount of literature laid under contribution in the preparation of the book is gleaned from the index of authors which covers fourteen pages. Throughout the book references to the original literature are cited so that the book may be used as a basis for an extended investigation into any line connected with explosives.

The translators have done their work remarkably well. It is not a literal translation of the German form of speech and sentence, but a sympathetic transference of thought from the German into the English channels. At the same time the idea of the original is strictly adhered to. A large number of additional references and notes from American sources have been added by the translators and this largely increases its value to American readers.

A. M. COMEY

Allen's Commercial Organic Analysis. Volume VII. By the editors and the following contributors: G. Barger, Vegetable Alkaloids; E. F. Armstrong, Glucosides; G. C. Jones, Non-glucosidal Bitter Principles; A. E. Taylor, Animal Bases; G. Barger, Ptomaines or Putrefaction Bases; J. A. Mandel, Animal Acids; W. A. Davis, Lactic Acid; and Herbert Philipp, Cyanogen and its Derivatives. Fourth edition. Entirely rewritten. Philadelphia, P. Blakiston's Son & Co., 1913. 558 pp. Price, $5.00.

This edition differs from the former in having been written by several men expert in the particular field to which the individual chapters are devoted. This ought to be of value, since it is difficult for any one to be so well versed in the whole field of organic analysis as a book of this kind requires. A large portion is descriptive matter rather than consisting of methods of analyses, which will always be of value to the analyst, although it does not conform exactly to the title of the book. The same plan of classification and subjects discussed has been followed, thus making it more convenient for those already familiar with the older edition. The material has been gotten up very well, and only a few errors were noticed such as on page 206, the definition of amic acids is rather vague, and on page 212 the term phenyl isocyanate is used for phenyl uramino-derivative. On the whole, the book is excellent and ought to receive a hearty welcome by all chemists interested in this field of work.

J. M. NELSON

Natural Rock Asphalts and Bitumens. By ARTHUR DANBY. D. Van Nostrand Co., 1913.

As stated in the preface, the book is written for those who are desirous of obtaining a deeper and clearer insight into the production, properties and uses of asphalts and bitumens, and who "find that such knowledge is inaccessible, owing to the lack of any recent English work dealing with them." This statement is undoubtedly correct if it alludes to publications appearing in Great Britain, but the author apparently overlooks the fact that during the past few years, a number of excellent books dealing with this same subject have been published in the United

States which are quite accessible to the English public. In fact, the author openly states that the two chapters on "American Deposits of Bitumen" have been compiled largely from Mr. Clifford Richardson's work "The Modern Asphalt Pavement."

The book under review is largely a reiteration of what has been published in other works, and contains either little new matter or the results of original research. It is written in a semi-scientific style, and fails to impart even to the lay reader a sufficiently lucid explanation of the physical and chemical properties of the asphalts and bitumens under discussion, to enable him to draw any conclusions as to what purposes they are adapted, and to what not. Reference is made to the hypotheses and conclusions of early writers, which however in view of recent disclosures are no longer tenable. These are presented to the reader as facts bearing on the subject under discussion, and without any explanatory statements. Thus on pages 139 and 140 the terms "petrolene" and "asphaltene" are stated to have originated with Boussingault in 1836, who separated the bitumen into these two bodies by distillation. The author goes on to say that the methods now in vogue for determining petrolene are by distilling the bitumen with water, by solubility in boiling alcohol, or by simply heating to a temperature of 250 to 260° C. and noting the loss in weight. Any one familiar with this subject will know that these alternative methods will fail to give equivalent results, and are at best grossly misleading.

The author's definitions of the terms "Bitumen," "Pitch," and "Asphalt," proposed on page 7 are untenable and at variance with the consensus of opinion. Thus bitumen is defined as "substances which are found in nature * * * which are *completely soluble in carbon bisulfide,* but only partially so in ether, and almost *completely insoluble in alcohol* * * *," and among other varieties are stated to include elaterite and wurtzilite. In this connection it is to be noted, as stated above, that the author recommends that petrolene be determined by the solubility of the material in alcohol. Furthermore, it is a well-known fact that elaterite and wurtzilite are practically insoluble in carbon bisulfide, and this is borne out on page 117, where the author himself contradicts his previous statement.

The chapter entitled "Tests and Analyses" includes a number of methods which on their face cannot possibly give reliable results. Thus on page 138 it is stated with reference to the determination of the mineral matter in asphalts: "If there are any mineral bodies present mixed with these organic substances, they remain unchanged even when the basin is brought to a constant white heat and that temperature sustained for a long time." This would certainly tend to decompose the limestone (calcium carbonate) which occurs in most of the continental rock asphalts. The method for determining the melting point (page 141) is inaccurate, and manifestly inferior to others in current use. Several methods are recommended for differentiating between asphalts of natural and artificial origin in spite of the fact that authorities have repeatedly questioned their reliability.

The chapters on "The Carrying Out of Rock Asphalt Work" and "The Carrying Out of Rock Asphalt Mastic Work" are quite comprehensive, although the methods described are at variance with the practice in this country. In marked contrast to the rest of the work, the section devoted to rock asphalt mastic work goes into the subject with the minutest detail, both in illustrations and in reading matter. This, however, will scarcely be of practical interest to the American reader.

Upon reading through the book, one cannot help noting the rambling way in which it is written, and the many digressions from the main theme.

HERBERT ABRAHAM

CORRECTION

Liquid Air—Oxygen—Nitrogen. BY GEORGES CLAUDE.

The price of $1.50 quoted in our review of this book (THIS JOURNAL, 5, 876) was a mistake. The price given by Blakiston's Son & Co., Philadelphia, is $5.50.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

Ammonia, The Oxidation of, to Nitric and Nitrous Acids. By ED. DONATH AND A. INDRA. 8vo. 110 pp. Price, $1.25. F. Enke, Stuttgart. (German.)

Analysis, Industrial Organic. By PAUL S. ARUP. Sm. 8vo. Price, $2.00. J. & A. Churchill, London.

Analysis, Qualitative. By F. P. TREADWELL. 3rd English ed. 8vo. 534 pp. Price, $3.00. John Wiley & Sons, New York. (Translation.)

Analysis, Quantitative, by Electrolysis. By ALEXANDER CLASSEN. 5th ed. 8vo. 308 pp. Price, $2.50. John Wiley & Sons, New York. (Translation.)

Analysis, Quantitative Chemical, Text Book of. By ALEX. C. CUMMING AND SYDNEY A. KAY. Demy 8vo. 396 pp. Price, $2.00. Gurney & Jackson, London.

Analysis, Quantitative Inorganic, A Treatise on. By J. W. MELLOR. 8vo. 778 pp. Price, $7.50. Chas. Griffin & Co., New York.

Catalysis in Organic Chemistry. By PAUL SABATIER. 8vo. Price, $2.50. Paris, 1913. (French.)

Celluloid. By PIEST, STICH AND VIEWEG. 8vo. Price, $2.25. Wilhelm Knapp, Halle.

Chemistry, Inorganic and Organic. By CHARLES L. BLOXAM. 10th ed. 8vo. Price, $5.25. J. & A. Churchill, London.

Chemistry, Textbook of. By WILLIAM A. NOYES. 8vo. 602 pp. Henry Holt & Co., New York.

Cyanids, The Chemical Processes of Extracting Silver Ores with. By EMIL KUEHN. 8vo. 108 pp. Price, $1.50. Wilhelm Knapp, Halle. (German.)

Distillation, The Modern Art of. By E. WALTER. 3rd ed. 8vo. 142 pp. Price, $2.25. G. Harnecker, Frankfurt a/O. (German.)

Food Inspection and Analysis. By ALBERT E. LEACH AND ANDREW L. WINTON. 3rd ed. L. 8vo. 1001 pp. Price, $7.50. John Wiley & Sons, New York.

Fuller's Earth. By CHARLES L. PARSONS. 8vo. 38 pp. U. S. Bureau of Mines, Bulletin 71.

Furnaces, Electric, in the Iron and Steel Industry. By W. RODENHAUSER AND I. SCHOENAWA. 8vo. 419 pp. Price, $3.50. John Wiley & Sons, New York. (Translation.)

Inflammability of Coal Dust, A Laboratory Study of the. By J. C. W. FRAZER, E. J. HOFFMAN AND L. A. SCHALL, JR. 8vo. 58 pp. U. S. Bureau of Mines, Bulletin 50.

Inorganic Chemistry, Handbook of the Methods of. I. By ARTHUR STAEHLER. Vol. 5. L. 8vo. Price, $7.00. Veit & Co., Leipzig.

Metals: The Quantitative Methods for the Examination of Molybdenum, Vanadium, Tungsten, their Ores, Steels, Alloys and Compounds. By H. MENNICKE. 8vo. Price, $2.25. M. Krayn, Berlin. (German.)

Milk, Its Production, Examination, Handling and Use. By H. TIEMANN. 8vo. 144 pp. Price, $1.50. H. Reichenbach, Leipzig. (German.)

Organic Substances, Table of the Most Important, Arranged According to Melting Points. By R. KEMPF. 8vo. Price, $1.50. F. Vieweg & Sohn, Brunswick. (German.)

Power for Factories, Determination of the Cheapest Source of. By KARL URBAHN. 2nd ed. 8vo. Price, $1.25. Julius Springer, Berlin. (German.)

Pumping and Hydraulic Machinery, Modern. By EDWARD BUTLER. 8vo. 473 pp. Price, $4.50. Chas. Griffin & Co. London.

Rare Earths, The Use of the. By C. R. BOEHM. 8vo. $1.25. Veit & Co. Leipzig. (German.)

Rubber: Caoutchouc and Gutta Percha Resins. By G. HILLEN. 8vo. 95 pp. $1.25. M. Drechsel. Berne.

Rubber, The Preparation of Plantation. By SIDNEY MORGAN. 8vo. Price, $2.75. Rubber Growers' Association, London.

Spectral Chemistry, Introduction to. By G. URBAIN. 8vo. 215 pp. Price, $2.50. Th. Steinkopff, Dresden. (German.) (Translation.)

Sugars and Their Simple Derivatives, The. JOHN E. MACKENZIE. Demy 8vo. 258 pp. Price, $2.00. Gurney & Jackson, London.

Sulfurous Acid and its Compounds with Aldehydes and Ketones. By W. Keip, *et al.* 8vo. 369 pp. Price, $3.00. Kaiserliches Gesundheitsamt, Berlin. (German.)

Textil Fibers, Textbook of the Chemical Technology of the. Vol. I. By G. von Georgievics. 4th edition. 8vo. Price, $3.75. E. Granmougin, Leipzig. (German.)

Water Bacteriology, Elements of, with Special Reference to Sanitary Water Analysis. By S. C. Prescott and C.-E. A. Winslow. 3rd ed. Sm. 8vo. 318 pp. Price, $1.75. John Wiley & Sons, New York.

Water Purification and Sewage Disposal. By J. Tillmans. 8vo. 143 pp. Price, $2.00. D. Van Nostrand Co., New York.

Waters, Underground, for Commercial Purposes. By Frank L. Rector. 12mo. 97 pp. Price, $1.00. John Wiley & Sons, New York.

RECENT JOURNAL ARTICLES

Acetone, The Determination of. By W. M. Marriott. *Journal of Biological Chemistry*, Vol. 16, 1913, No. 2, pp. 281–291.

Alcohol and Alcoholometry, Bibliography of the Literature of. By E. C. McElvey. *Bulletin of the Bureau of Standards*, Vol. 9, 1913, No. 3, pp. 436–474.

Alcohol, Ethyl, and Its Mixtures with Water, Density and Thermal Expansion of. By N. S. Osborne, E. C. McKelvy and H. W. Bearce. *Bulletin of the Bureau of Standards*, Vol. 9, 1913, No. 3, pp. 327–435.

Ammonia, The Inorganic Synthesis of. By Ottokar Serpek. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 83, pp. 606–609.

Calcium, Gravimetric Determination of, as Oxalate. By S. Gay. *Chemiker Zeitung*, Vol. 37, 1913, No. 131, pp. 1337–1338.

Chlorophyll. By R. Willstaetter. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 89, pp. 641–645.

Coals of Canada, The. Anonymous. *Bulletin of the Imperial Institute*, Vol. 11, 1913, No. 3, pp. 496–513.

Condensation Product, a Phenol-Formaldehyde; Juvelith. By Fritz Pollak. *Chemiker Zeitung*, Vol. 37, 1913, No. 121, pp. 1233–1234.

Dyeing of Wool, Studies in the. By J. Merritt Matthews. *Canadian Textile Journal*, Vol. 30, 1913, No. 11, pp. 347–349.

Furnaces, Electric, Their Design, Characteristics and Commercial Application. By W. McA. Johnson and G. N. Sieger. *Metallurgical and Chemical Engineering*, Vol. 11, 1911, No. 11, pp. 643–648.

Gas, Blast-Furnace, The Cleaning of. By W. A. Forbes. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 82, pp. 2477–2514.

Gas, Oil. By L. B. Jones. *American Gas Light Journal*, Vol. 99, 1913, No. 18, pp. 273–279 and 282.

Mercury, Occurrence, Distribution and Uses of. Anonymous. *Bulletin of the Imperial Institute*, Vol. 11, 1913, No. 3, pp. 479–495.

Metals and Alloys, Coloring Non-ferrous. By E. F. Lake. *Scientific American Supplement*, Vol. 76, 1913, No. 1973, pp. 266–269.

Milk, Qualitative Determination of Fat in. By Walter L. Croll. *Biochemical Bulletin*, Vol. 2, 1913, No. 8, pp. 509–518.

Nitrocelluloses, The Examination of, under the Polarization Microscope. By Hans Ambronn. *Kolloidchemische Beihefte*, Vol. 13, 1913, No. 4, pp. 200–207.

Ores: The Scientific Foundations of the Roasting Processes. By Rudolf Schenck. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 87, pp. 646–652.

Pyrophoric Metals. By W. Dederichs. *Welt der Technik*, Vol. 75, 1913, No. 19, pp. 370–371.

Silk, The Manufacture of Artificial, from Cotton. By H. R. Carter. *Cotton*, Vol. 78, 1913, No. 1, pp. 28–31.

Steel Making, Fuel Possibilities in. By William Whigham. *Coal and Coke Operator and Fuel Magazine*, Vol. 32, 1913, No. 1, pp. 595–598.

Steel, The Influence of Various Elements on the Absorption of Carbon by. By Robert R. Abbott. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 82, pp. 2389–2400.

Steel, The Over-Oxidation of. By W. R. Shimer and F. O. Kichline. *Industrial World*, Vol. 47, 1913, No. 42, pp. 1255–1257.

Stone: The Modern Manufacture of Artificial Marble. By Maurice de Keghel. *Revue de Chimie Industrielle*, Vol. 24, 1913, No. 286, pp. 245–251.

Sugar: Recent Developments in Evaporation. By Alfred L. Mebre. *Louisiana Planter*, Vol. 51, 1913, No. 18, pp. 306–310.

Titanium, Determination of, by Titration with Methylene Blue. By Bernhard Neumann and Robert K. Murphy. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 83, pp. 613–616.

Towers, Absorption and Reaction, for Chemical Works. By Rudolf Heinz. *Chemical Engineering and the Works Chemist*, Vol. 3, 1913, No. 29, pp. 273–277.

Zinc, Condensation of, Gas to Liquid, in the Presence of Inert Gas. By Clerc. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 11, pp. 637–640.

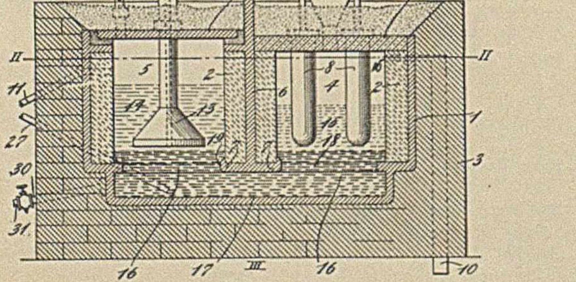
RECENT INVENTIONS

By C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Treatment of Metal-bearing Solutions. E. A. Ashcroft, Sept. 2, 1913. U. S. Pat. 1,071,856. Zinc is obtained from solution by adding calcium cyanamid and heating the mixture.

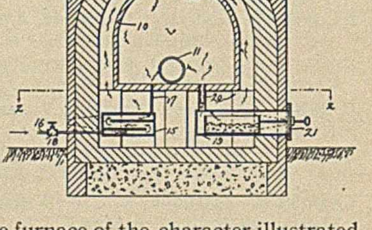
Iron and Steel Refined by Ferrochromium Alloy. J. Buchel, Sept. 2, 1913. U. S. Pat. 1,071,873. An expeditious and uniform distribution of the chromium introduced as ferro-chromium into the bath of the metal under treatment is obtained by adding carbon-free ferrochromium containing a reducing agent.

Cyanogen Compounds, etc. C. E. Acker, Sept. 2, 1913. U. S. Pat. 1,072,373. An impalpable amorphous carbid of some reactive metal such as barium, lithium, calcium, strontium or manganese, held in suspension in and diffused through a nitrogeneous salt, is reacted upon by a nitrogeneous reagent such as nitrogen, nitrids or ammonia, at a temperature above 500°. The product of the reaction is dissociated in the presence of an alkali metal, thereby causing the carbon and nitrogen to unite with such alkali metal to form the product sought.



Explosive. J. F. O'Brien, Sept. 2, 1913. U. S. Pat. 1,071,949. The composition contains potassium chlorate, naphthalene, asphalt dissolved in crude oil distillate, powdered carbon, potassium ferrocyanide and silica.

Rust Proofing Iron, Steel, etc. A. Bontempi, Sept. 9, 1913. U. S. Pat. 1,072,904. The metal is subjected to the fumes of a fused non-corrodible material such as zinc or lead while maintained at a temperature above the fusing point but below the fuming point of the coating material. The process may be practiced in a muffle furnace of the character illustrated.

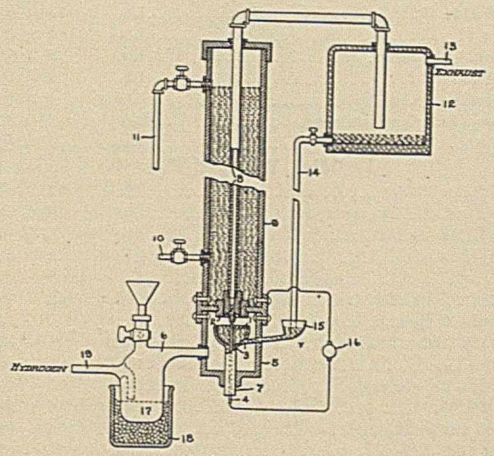


Caoutchouc Substance. C. Harries, Sept. 16, 1913. U. S. Pat. 1,073,116. The composition is produced by subjecting isoprene to the action of sodium.

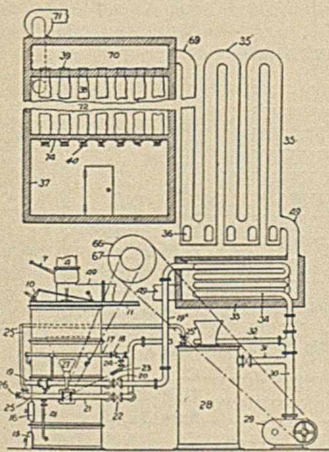
Explosive. J. F. O'Brien, Sept. 16, 1913. U. S. Pat. 1,073,279. The explosive contains potassium chlorate, sodium nitrate, liquid binitrotoluene and sawdust.

Portland Cement. J. W. Richards, Sept. 23, 1913. U. S. Pat. 1,073,820. This process is designed to produce Portland cement and iron in a single operation. A charge of iron is made up with the raw materials for producing a lime alumina silicate slag with an excess of limestone sufficient to produce a liquid product having the percentage composition of Portland cement clinker. The charge is heated in a reduction furnace having a basic lining to a sufficient temperature to reduce the ore and to cause the clinker to flow from the furnace in a liquid state.

Electrochemical Process. J. L. R. Hayden, Sept. 9, 1913. U. S. Pat. 1,072,945. This process is stated to be founded upon the patentee's observation that the chemical activity of an electrical arc is not entirely due to the high temperature existing therein but is due in part at least to an electrical effect which is distinct from the purely thermal action of the arc and that a high temperature in the arc therefore represents a waste of energy. In the process a gaseous mixture to be chemically acted upon is subjected to a low temperature arc formed between a cathode (1) of an easily vaporizable material such as mercury and a perforated anode (2) of some material inert under the conditions, such as copper.

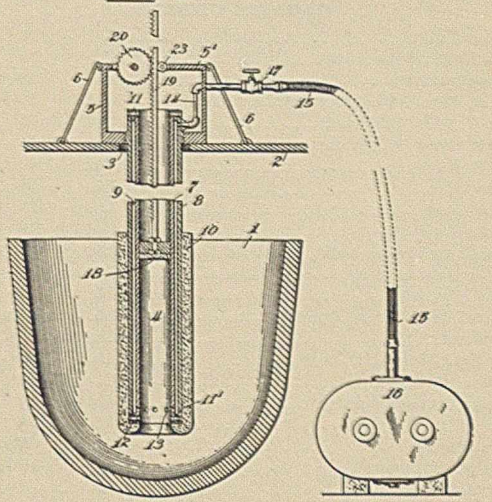


Treating Sulfid Ores. E. E. Banes, Sept. 16, 1913. U. S. Pat. 1,073,462. Finely pulverized lead sulfid ore is fed continuously into a furnace through the cores of impinging blowpipe flames whereby it is completely volatilized and projected in a volatilized condition into an enveloping oxidizing atmosphere. The resulting fume is drawn off and the white lead sublimate separated.



Making Iron and Steel. J. R. Billings, Sept. 23, 1913. U. S. Pat. 1,073,587. Powdered carbon is forced by plunger 18 downward into molten iron contained in the ladle 1. Regulated portions of this carbon escape and rise freely through the mass. Simultaneously with this operation regulated quantities of oxygen are forced through passages 9 and openings 13 into the iron, the quantity of oxygen employed being not greatly in excess of the amount required to effect the complete combustion of the carbon, with the production of the maximum quantity of carbon dioxid. The molten metal while heavily charged with carbon dioxid is converted into castings.

Fig. 1.



Synthesizing Gases. W. Siebert, Sept. 23, 1913. U. S. Pat. 1,073,823. Electric flame discharges are produced between the rod shaped electrode *l* and the annular electrode *b* by means of a large current of low voltage per unit distance of separation of the electrodes. The arc is caused to rotate by means of streams of the gases to be acted upon projected into the furnace through the angularly disposed nozzles *g*.

Fig. 1.

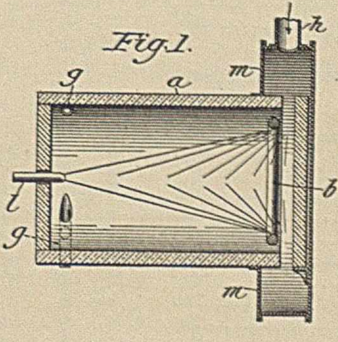
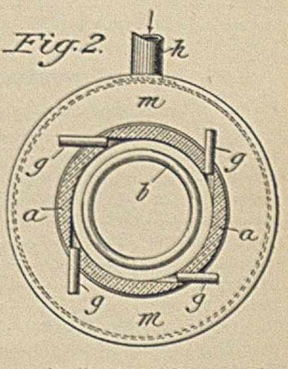
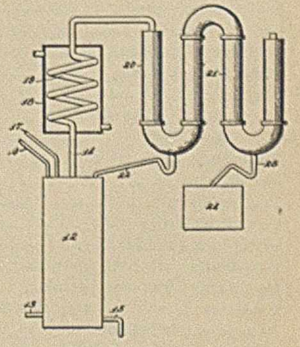


Fig. 2.



High Concentration of Watery Nitric Acid. H. Pauling, Sept. 30, 1913. U. S. Pat. 1,074,287. Dilute nitric acid to be concentrated enters the reaction column 12 through pipe 16 while sulfuric acid of 80% grade enters through pipe 17. The falling streams are met by a countercurrent of superheated steam which enters the column through pipe 13. In the reaction column the nitric acid is almost completely separated from the water which it contains. The steam is absorbed by the sulfuric acid and the latent heat liberated evaporates the nitric acid which escapes through pipe 14 into the cooling coil 19 from which it passes into condensers 20 and 21. The acid from the condenser 20 may be returned to the reaction column through pipe 22 for further treatment. The highly concentrated nitric acid which collects in condenser 21 is drawn off through pipe 23. The spent sulfuric acid which contains substantially all of the water originally present in the dilute nitric acid is drawn off through pipe 15 and is concentrated for reuse.



MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF NOVEMBER, 1913

ORGANIC CHEMICALS

Acetanilid	Lb.	21	@	23
Acetic Acid (28 per cent)	C.	1.75	@	1.90
Acetone (drums)	Lb.	13½	@	14½
Alcohol, denatured (180 proof)	Gal.	33	@	36
Alcohol, grain (188 proof)	Gal.	2.48	@	2.50
Alcohol, wood (95 per cent)	Gal.	46	@	48
Amyl Acetate	Gal.	2.00	@	2.10
Aniline Oil	Lb.	10	@	10⅛
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	21	@	23
Camphor (refined in bulk)	Lb.	42½	@	44
Carbolic Acid (drums)	Lb.	8	@	10
Carbon Bisulfide	Lb.	6½	@	8
Carbon Tetrachloride (drums)	Lb.	7⅜	@	7⅞
Chloroform	Lb.	25	@	35
Citric Acid (domestic), crystals	Lb.	55	@	56
Dextrine (corn)	C.	3.02	@	3.23
Dextrine (imported potato)	Lb.	6	@	7
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19½	@	20
Oxalic Acid	Lb.	7¼	@	7½
Pyrogallic Acid (bulk)	Lb.	1.20	@	1.40
Salicylic Acid	Lb.	25	@	30
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	2.24	@	2.90
Starch (potato)	Lb.	4½	@	5
Starch (rice)	Lb.	8	@	9
Starch (sago)	Lb.	2⅜	@	2¾
Starch (wheat)	Lb.	5¼	@	6½
Tannic Acid (commercial)	Lb.	35	@	36
Tartaric Acid, crystals	Lb.	31¾	@	32

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Acetate of Lime (gray)	C.	2.00	@	2.05
Alum (lump)	C.	1.75	@	2.00
Aluminum Sulfate (high-grade)	C.	1.25	@	1.75
Ammonium Carbonate, domestic	Lb.	8	@	8½
Ammonium Chloride, gray	Lb.	5⅞	@	6⅛
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3	@	4
Barium Chloride	C.	1.75	@	2.00
Barium Nitrate	Lb.	5¼	@	5½
Barytes (prime white, foreign)	Ton	19.00	@	23.50
Bleaching Powder (35 per cent)	C.	1.25	@	1.30
Blue Vitriol	Lb.	5	@	5¼
Borax, crystals (bags)	Lb.	3¾	@	4¼
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	60	@	90
Chalk (light precipitated)	Lb.	4	@	4½
China Clay (imported)	Ton	nominal		
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign	Ton	16.00	@	17.00
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.55	@	3.60
Lead Nitrate	Lb.	8⅛	@	8¼
Litharge (American)	Lb.	6¼	@	6½
Lithium Carbonate	Lb.	65	@	70
Magnesium Carbonate	Lb.	21	@	35
Magnesite "Calcined"	Ton	28.50	@	29.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	21½	@	25½
Phosphorus	Lb.	45	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°	Lb.	6¾	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%	C.	3.25	@	3.30
Potassium Chlorate, crystals	Lb.	7¼	@	7½
Potassium Cyanide (bulk), 98–99%	Lb.	19	@	24
Potassium Hydroxide	C.	4.00	@	4.25
Potassium Iodide (bulk)	Lb.	2.95	@	3.00
Potassium Nitrate (crude)	Lb.	4½	@	5
Potassium Permanganate (bulk)	Lb.	9¾	@	10
Quicksilver, Flask (75 lbs.)		38.00	@	40.00
Red Lead (American)	Lb.	6½	@	6¾
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	37⅝	@	38
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	67½	@	72½
Sodium Acetate	Lb.	3¾	@	4⅛
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	4⅝	@	5⅛
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	7¼	@	7½
Sodium Hydroxide, 60 per cent	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	2.25	@	2.30
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulfur, Flowers (sublimed)	C.	2.20	@	2.60
Sulfur, Roll	C.	1.85	@	2.15
Sulfuric 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.	12½	@	13½
Tin Oxide	Lb.	45	@	45½
White Lead (American, dry)	Lb.	5¼	@	5½
Zinc Carbonate	Lb.	9	@	10
Zinc Chloride (granulated)	Lb.	4½	@	5
Zinc Oxide (American process)	Lb.	5⅜	@	6⅜
Zinc Sulfate	Lb.	2½	@	3

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	42	@	45
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8⅞	@	10
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6.60	@	6.65
Cottonseed Oil (crude), f. o. b. mill	Gal.	45	@	45½
Cottonseed Oil (p. s. y.)	Lb.	7⅛	@	7¼
Cylinder Oil (light, filtered)	Gal.	21½	@	32
Japan Wax	Lb.	9⅝	@	9⅞
Lard Oil (prime winter)	Gal.	92	@	94
Linseed Oil (raw)	Gal.	46	@	47
Menhaden Oil (crude)	Gal.	35	@	—
Neatsfoot Oil (20°)	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.)	Lb.	3½	@	3¾
Paraffine Oil (high viscosity)	Gal.	26	@	28
Rosin ("F" grade) (280 lbs.)	Bbl.	4.20	@	4.35
Rosin Oil (first run)	Gal.	27	@	28
Shellac, T. N.	Lb.	21	@	22
Spermaceti (cake)	Lb.	30	@	35
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Spindle Oil, No. 200	Gal.	18	@	19
Stearic Acid (double-pressed)	Lb.	9	@	12
Tallow (acidless)	Gal.	62	@	63
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	47	@	47½

METALS

Aluminum (No. 1 ingots)	Lb.	19	@	19½
Antimony (Hallet's)	Lb.	7¼	@	7½
Bismuth (New York)	Lb.	2.05	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	Lb.	15¼	@	15½
Copper (lake)	Lb.	15⅝	@	15⅞
Lead, N. Y.	Lb.	4.30	@	—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43.50	@	44.50
Silver	Oz.	59	@	60
Tin	C.	40.00	@	41.00
Zinc	C.	5.25	@	5.30

FERTILIZER MATERIALS

Ammonium Sulfate	C.	3.02½	@	3.05
Blood, dried	Unit	3.30	@	—
Bone, 4½ and 50, ground, raw	Ton	27.25	@	28.00
Calcium Nitrate (Norwegian)	C.	2.05	@	2.10
Castor meal	Unit	3.30		
Fish Scrap, domestic, dried	Unit	nominal		
Mowrah meal	Ton	nominal		
Phosphate, acid, 16 per cent bulk	Ton	—	@	6.75
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.75	@	3.00
Tennessee, 70-80 per cent	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	38.55	@	—
Pyrites, furnace size, imported	Unit	0.13¼		
Tankage, high-grade	Unit	3.25 & 10		