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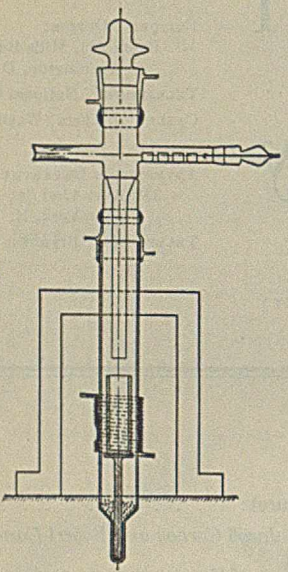

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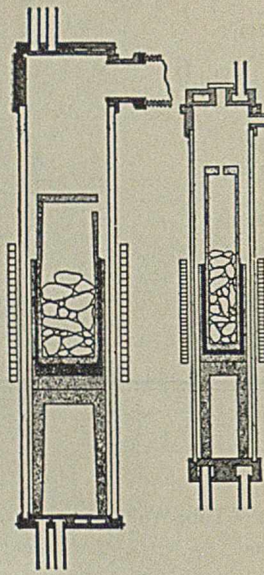

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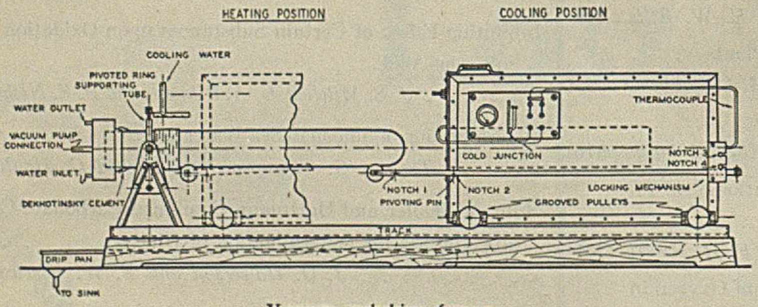

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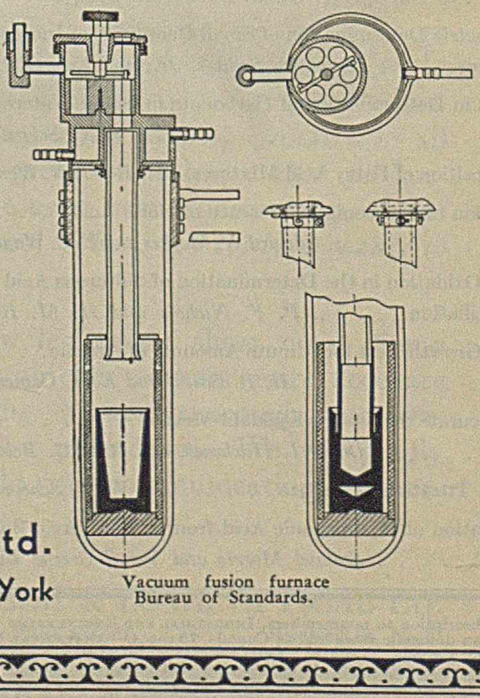

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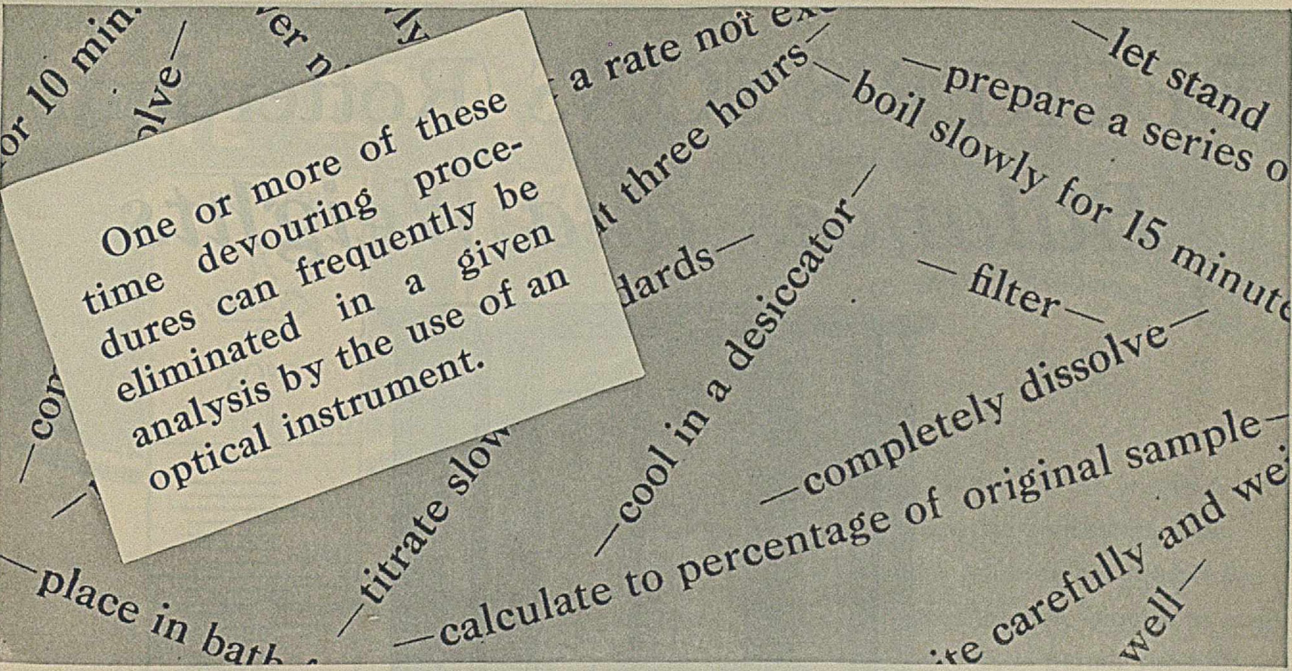

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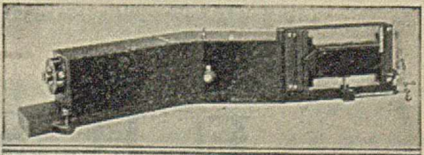

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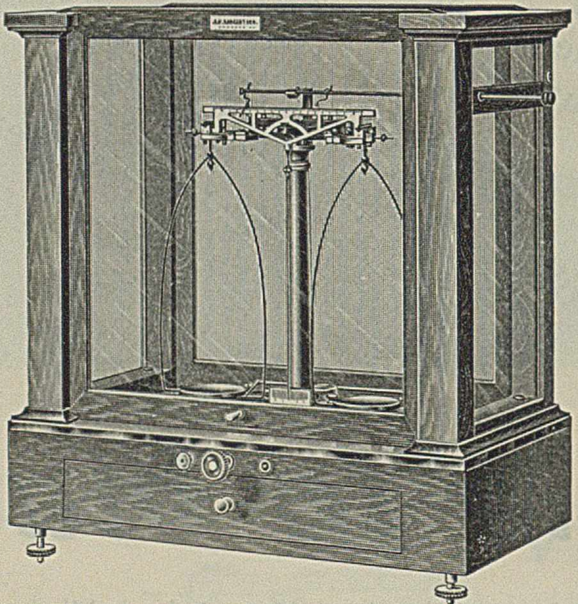

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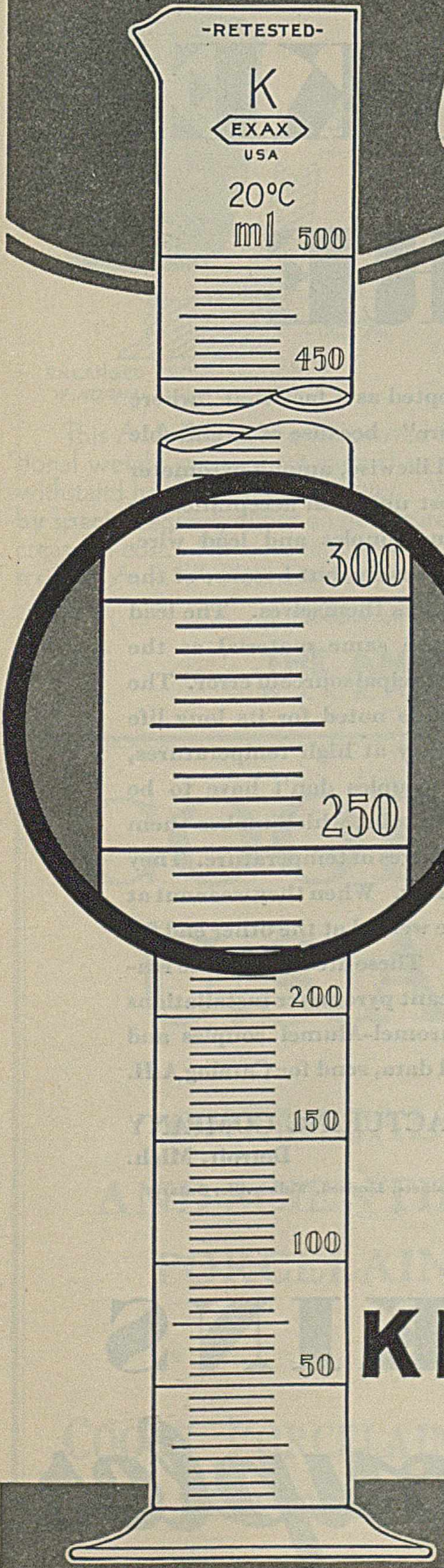

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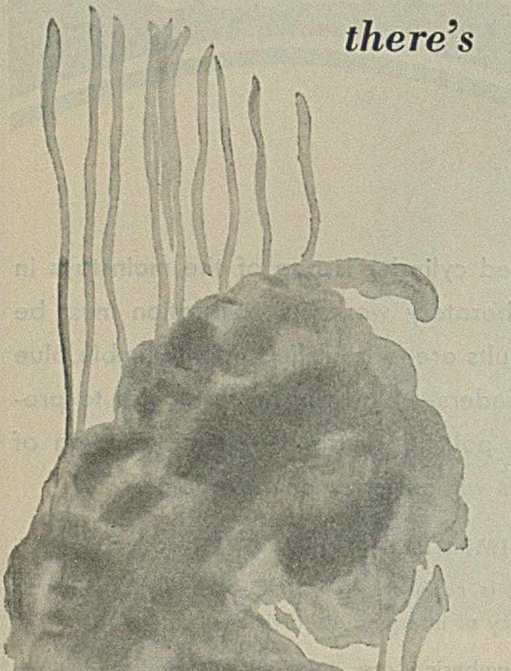

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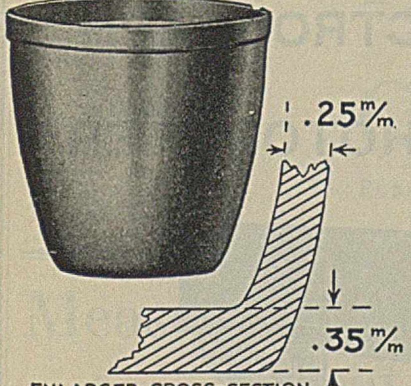

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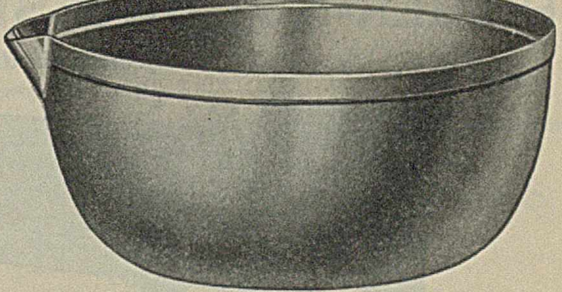

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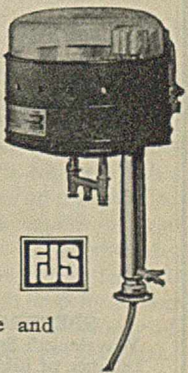

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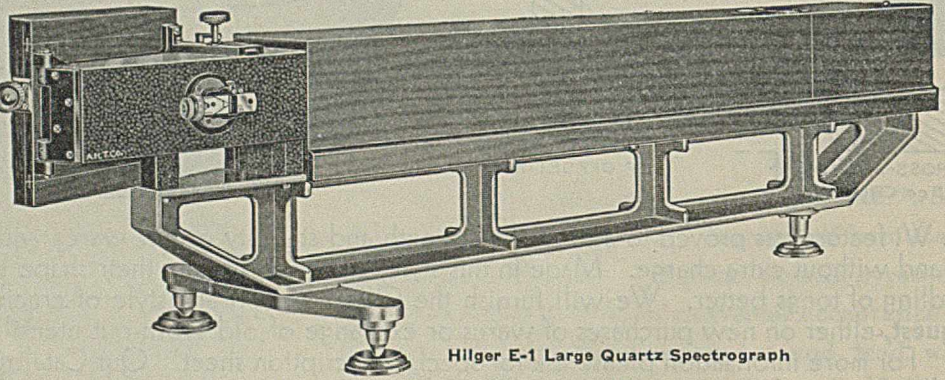

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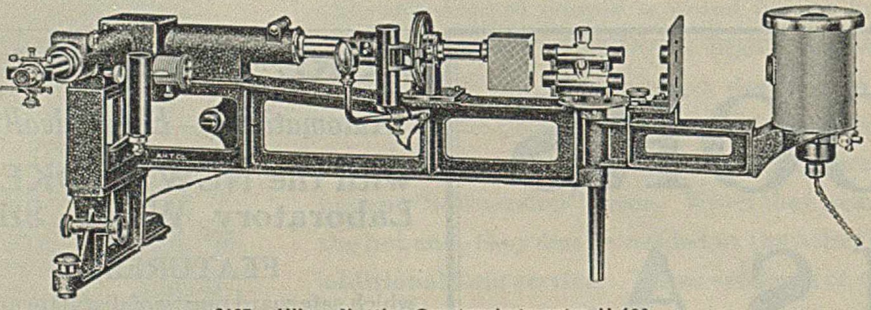

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Measurement of Tube Wall Temperatures in Heat Transfer Experiments

G. M. Hebbard[1] and W. L. Badger, University of Michigan, Ann Arbor, Mich.

DETERMINATION of the temperature of tube walls is an integral part of most experimental work involving a study of heat transfer coefficients to and from these surfaces through the enveloping films. The final degree of accuracy obtained in such work is usually controlled by the accuracy of determination of the surface temperatures.

Recent important investigations concerning the condensation of vapors and heating of liquids have required more than an approximate knowledge of the wall temperatures of the experimental tubes. Some few investigators, justified by accepted data, have preferred to assume approximate heat transfer coefficients for one or another of the films rather than to carry out the work necessary for the actual measurement of the desired temperatures. Others have adopted or developed methods that have not eliminated this part of heat transfer studies as a source of considerable error. The amount of error involved in any given case can only vaguely be estimated, but it is certain that a better correlation of all such work would be possible with improved methods of measurement.

Reviews of the methods utilized have recently been made by Othmer and Coats (*8*) and Colburn and Hougen (*4*). Additional references supplementing these are included in this paper. Installations as applied to tubes alone are considered.

By far the major portion of the work done on this problem has been carried out with thermocouples, which, because of their inherent economy and flexibility of installation, may be considered the most likely instrument to be chosen. Installations of resistance thermometers (*3*, *7*), mercury thermometers (*2*), portable contact recorders (*1*, *5*), and extensiometers (*9*, *10*) have been made. These latter methods are not generally applicable and are not to be preferred if a successful thermocouple method is an alternative.

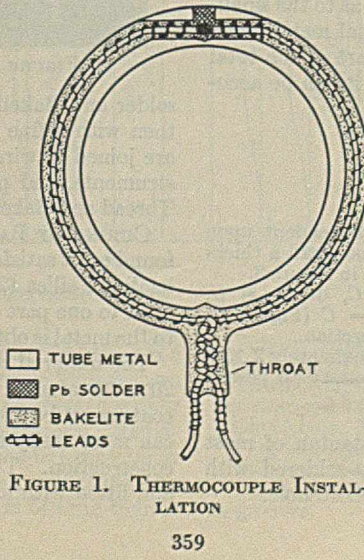

Figure 1. Thermocouple Installation

Use of Thermocouples

Any installation involving thermocouples should meet the following requirements:

1. The temperature recorded by any given junction must be that of the corresponding wall temperature or one from which the wall temperature may be calculated by the use of known relations.
2. The effect of heat conduction to the junction by the leads should be minimized or eliminated.
3. The characteristics of the normal film on the wall must not be disturbed by the installation.
4. Any installation should be in mutual agreement between different couples and should be capable of accurate reproduction.
5. The assembly should be sufficiently rugged to withstand all conditions encountered during installation of the tube in the test apparatus.
6. A minimum of time should be required for installation and calibration unless the permanency of the set-up warrants additional work.
7. Frequent recalibration and attention to the couples should not be necessary.

As most investigations are carried out with tubes of relatively small diameter and of considerable length, mechanical considerations will restrict the operator to the use of the outside wall of the tube. When it is necessary to contend with a vapor condensing on this wall, the problem of an undisturbed film becomes paramount, particularly with vapors of large latent heats which form very thin films of condensate. Since relatively large temperature differences occur through these thin films, any mechanical imperfection or deformation of the natural surface in the vicinity of the couple junction that causes a penetration or distortion of the film will result in abnormal heat conduction to the junction (peened, plated, and slotted installations). If the lead wires from the junction are carried out directly into the higher temperature of the vapor space, the effect of heat conduction along the leads becomes considerable (peened and plated installations). There is no way at present by which this effect can be calculated.

No single thermocouple method developed to date, on the basis of data presented, can be said to be free from either or both of these objections, with the possible exception of the Kraussold installation (*6*).

The latter utilizes a longitudinal groove [0.0625 inch (0.16 cm.) deep, 0.125 inch (0.3 cm.) wide, and 6 inches (15 cm.) long]

---

[1] Present address, Dow Chemical Co., Midland, Mich.

milled in the tube wall. A spline of the tube material, made with a concave bottom to allow for the couple and leads, is cut to fit the groove snugly. When the spline has been driven into place an equivalent of the original surface remains. The leads are brought through the film at opposite ends of the spline and well away from the junction. It has been found extremely difficult to make even a passably good job by this method. Even if a smooth external surface is obtained, the spline has a tendency to work loose on repeated heating and cooling. Further, the leads in the Kraussold method disturb the drainage of the condensate if the tube is vertical. It is only necessary to try the Kraussold method and the one here suggested to decide which is superior.

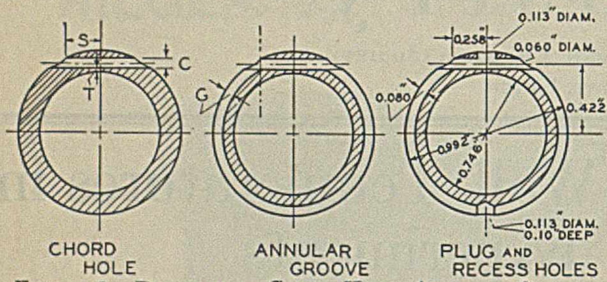

Figure 2. Diagram of Chord Hole, Annular Groove, and Plug and Recess Holes

Dimensions are for installation in 1-inch 11-gage tube.

The solution to both the requirements of unchanged surface conditions and freedom from abnormal heat conduction to the junction may be reached in a logical fashion. The couple junction should be placed under a surface over which the film drainage is not disturbed, and the leads must be withdrawn for an appreciable distance from the junction through a section of the wall that is isothermal with the point at which the couple is embedded.

Proposed Method

Reference to Figure 1 will illustrate the features of the method. The thermocouple is inserted in a hole drilled through a chord of the wall, and the leads are carried around the tube in an annular groove to be withdrawn at the back, 180° from the junction. The junction itself is brought into metallic contact with the wall by solder admitted through the plug hole above. Bakelite cement of special composition provides electrical insulation and fills the groove and chord hole up to the junction. The excess solder and Bakelite may be removed with fine emery cloth to produce a continuous and polished surface at all points except where the leads leave the tube, 180° from the point of measurement.

It is necessary to employ tubes of somewhat heavier walls than those ordinarily used in order to provide sufficient metal for the chord drill, which is necessarily limited as to the smallest size that can be employed. The additional metal offers no disadvantage as it is only a very small part of the total resistance to heat flow, and transfer through it can be accurately calculated.

Details of Method

Steps in machining are as follows (Figure 2):

Chord Hole. Diameter of drill chosen is dependent upon obtaining greatest distance S without causing too small a thickness at T. Drilling is done with template shown in Figure 3.

Annular Groove for Leads. Width = C, depth = G. Cut on lathe with round-nosed tool of width = C (Figure 3). Lathe is moved by hand, lifting tool over uncut section.

Plug and Recess Holes. Diameter = approximately 2 × C to a convenient drill size. Recess hole is necessary to permit proper footing for lead throat of Bakelite.

Thermocouples are made from copper-constantan of most convenient wire diameter. Junction is butt-soldered with silver to give neat bead that threads through chord hole.

Installation of Couples. The plug hole is first tinned. The chord hole must be packed with asbestos thread during this operation. The couple is then threaded in. To center the junction and prevent sweating of solder into the chord hole while soldering the junction, short pieces of metal tubing, that fit closely over the leads and in the chord hole, are threaded over the leads and up to the junction. The tips of these tubes should be covered with melted borax to prevent solder from adhering to them. If hypodermic needles of proper size can be found, they are the most convenient type of tubing for the above work (D, Figure 3). The couple is soldered in, using a blast lamp to maintain the tube at the proper temperature. The solder must be allowed to flow naturally into the hole and must cool slowly. Ordinary lead-tin solder is recommended as satisfactory and most easily handled. When the couple is soldered in place, each lead is hand-wrapped in two steps (E, Figure 3): First, a cotton thread, of sufficient diameter to allow only slight clearance from the walls when well smeared with Bakelite, is wrapped around the portion of the leads in the chord hole, and well packed into the holes with the tubing previously mentioned. Lighter cotton is then wrapped around the leads from the holes and carried along a distance sufficient to provide for insulation in the groove and about one inch additional. A light coat of Bakelite is then laid in the groove and on the thread, and cured. Next, the leads are brought together at the recess hole, twisted around each other for about 0.5 inch (1.26 cm.), and then carefully bent or pushed into the very bottom of the groove at all points. With successive coats of Bakelite, the groove is completely filled and a throat of supporting Bakelite is built around the twisted leads. Excess solder and Bakelite are removed, first with sand paper, and then with a fine grade of metallographic paper. The leads are joined to wires of similar composition, leading to the instruments, and proper insulation is applied to these joints. Thread and Bakelite will serve the latter purpose.

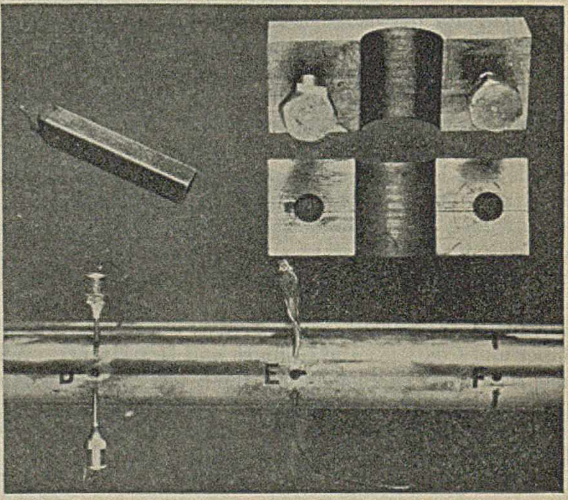

Figure 3. Photograph of Installation

Curing of Bakelite. Bakelite resin BR-0013 has been found most satisfactory. This material should be mixed with kaolin or silica (200 mesh) in the proportions of two parts of resin to one part of filler. Better adhesion of the cured resin to the metal is obtained by use of the filler.

The material recommended will harden completely within 20 to 30 minutes at a temperature of 120° to 130° C. Thin coats must be applied. Curing the resin on the installations can most easily be effected by the use of an oven of special construction. This latter can be a transite box, split laterally and fitted with hinges. The ends are cut out to fit the tube

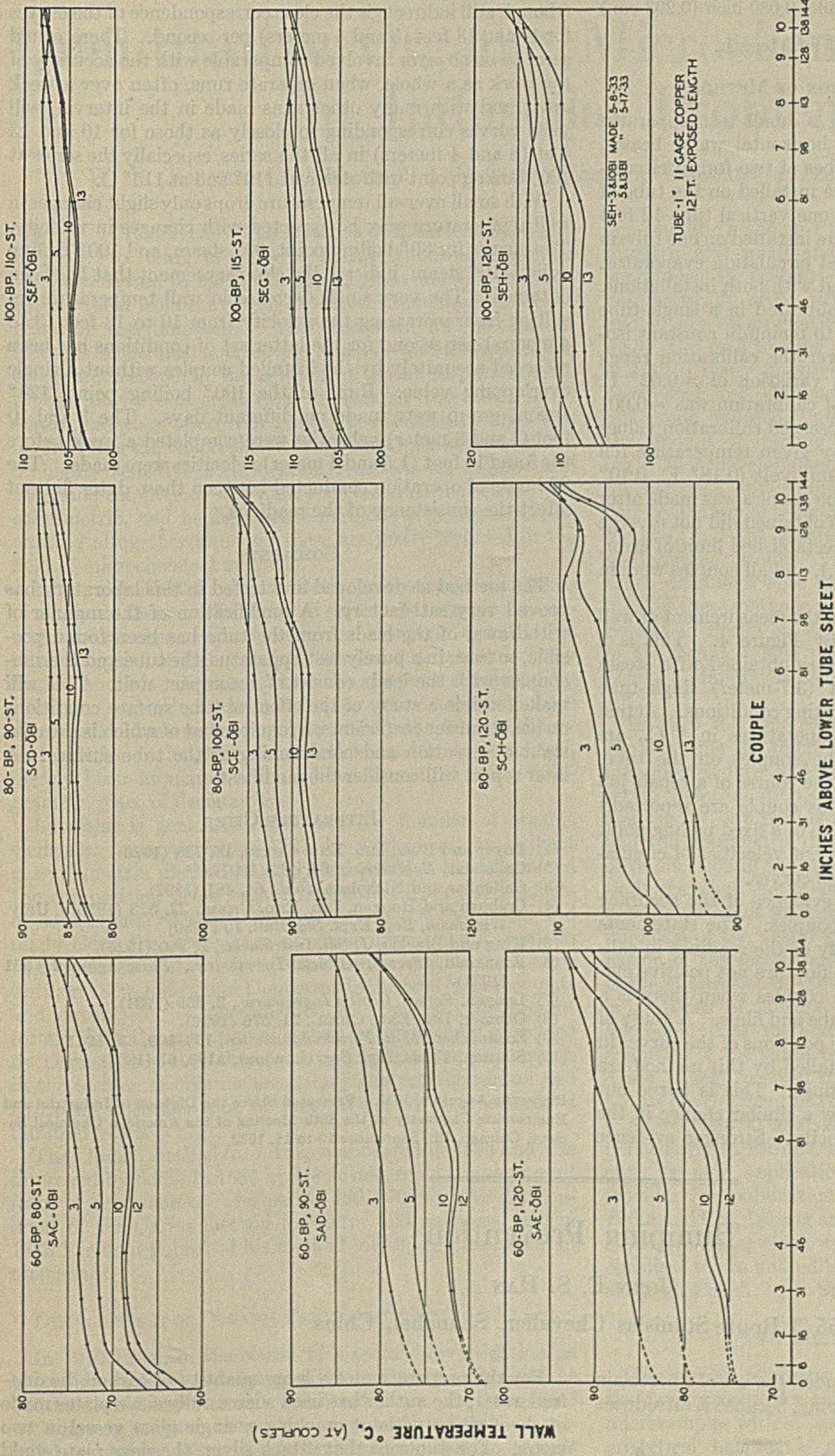

FIGURE 4. RESULTS ACHIEVED IN MEASUREMENT OF WALL TEMPERATURES

snugly. Sufficient coiled resistance wire is distributed on the inner walls of the box to maintain the desired temperature within the oven. Temperature control can be effected within the desired limits by additional series resistances. Radiation losses from the length of tube outside the box may be so high that it will be impossible to maintain a proper intensity of heat in the tube itself, and a longer period of time than is necessary will be required for curing. This difficulty may be overcome by the use of an internal heater for the tube, constructed of a short length of small-diameter iron pipe. The pipe is covered with an asbestos sleeve, wrapped with resistance wire, and then further covered with a spaced spiral wrapping of asbestos tape. This heating element is placed in the tube at a point under the junction. A moderate heat input will maintain the tube temperature at the same degree as that of the oven.

INSULATION OF LEADS THROUGH VAPOR SPACE. A satisfactory insulation of the leads through the vapor space is essential. Tests of various materials subjected to steam and hot water at temperatures of 250° to 280° F. (121° to 138° C.) for periods of 100 to 200 hours definitely proved that the usual forms of insulation are unsatisfactory. The insulations examined and found to be unsatisfactory include ordinary red rubber tubing, soft and lightly vulcanized black rubber, pure gum rubber, varnished cambric tubing (radio spaghetti), and enameled coverings. The form of insulation employed on R. C. fixture wire stood up best and suffered no apparent loss of insulating properties or any deformation. This type of covering was applied to the leads used in the investigations made in this laboratory and gave excellent service. No deterioration was found after more than 300 hours of exposure to saturated steam. These leads are flexible and may be brought out from the vapor space between flanged surfaces.

DATA FOR PRESENT INSTALLATION

Machining dimensions, see Figure 2.

Tubes: 1-inch 11-gage copper, 0.992 inch (2.5 cm.) outside diameter, 0.750 inch (1.9 cm.) inside diameter.

Thermocouple: Copper-constantan, No. 24 B. & S. wire, junction centered 0.074 inch (0.188 cm.) below outer wall.

Chord hole: No. 53 drill (0.0595 inch, 0.151 cm.).

Plug and recess holes: No. 33 drill (0.1130 inch, 0.287 cm.).

Bakelite: No. BR-0013, 2 parts, with 1 part 200-mesh kaolin.

Thread insulation: No. 20 cotton in chord holes, No. 60 cotton in grooves.

Grooves: 0.060 inch (0.152 cm.) wide, 0.080 inch (0.203 cm.) deep.
Hypo needles: No. 17 gage, 2 inch (5 cm.) length.

Experimental Application of Method

Preliminary trials were made in a small test apparatus which functioned as a single-tube horizontal water heater. Installations were then made on tubes of two forced circulation evaporators. Ten couples were installed on the tube of an experimental evaporator having one vertical tube 12 feet (3.7 meters) long, and six couples were installed on one tube in an eight-tube semicommercial forced circulation evaporator. Consistent results have been obtained with both installations.

Both of the above tubes were calibrated in a single-tube apparatus in which it was possible to maintain constant isothermal conditions at all points over the calibration range (30° to 120° C.) with a maximum variation of ±0.02° F. (0.01° C.). The known accuracy of calibration was ±0.001 millivolt (0.04° F. or 0.02° C.). Observed calibration values for the couples of each tube at any given temperature fell within a maximum range of 0.005 millivolt (0.18° F., 0.10° C.). Recalibration of the single-tube couples was made after 150 hours of operation. The values obtained did not diverge from the original results within the established limit of error, (0.005 millivolt = 0.18° F., 0.10° C.), and all couples were in the same relative agreement.

Results that have been achieved in the measurement of wall temperatures are well illustrated by Figure 4. This is a plot of the observed wall temperatures obtained with steam and distilled water in the 12-foot (3.7-meter) single-tube evaporator over a wide range of operating conditions. Actual couple readings, transferred to temperatures in ° C., are plotted against the locations of the couples on the tube. (No. 5 couple was damaged during the course of a repair job on the machine. No results for this couple are reported.) Each group of curves is representative of a fixed boiling point and steam temperature. Four different velocities of circulation were employed to give the several curves.

It is difficult to adduce positive evidence of the accuracy and reproducibility of wall thermocouples. The statements made above as to the reproducibility of the readings in calibration under conditions of no heat flow are not positive evidence of the behavior of the same couples when there is a temperature gradient through the tube and films. A study of Figure 4 will show, from the relative positions of the curves in all the groups, that the couples installed by this method are apparently giving dependable readings. This is borne out by the fact that all the groups show a similar change in the curves caused by a change in velocity. Stronger evidence (though still indirect) is the close correspondence of the curves for 10 and 13 feet (3 and 4 meters) per second. There would seem to be no error involved comparable with the accuracy of the work as a whole, when separate runs, often over a week apart and with many other runs made in the interval, will yield curves corresponding so closely as those for 10 and 13 feet (3 and 4 meters) in all the series, especially the series at 100° boiling point with steam at 110° and at 115° C.

With small over-all temperature drops only slight changes in wall temperature may be expected with changes in velocity. The curves for 80° boiling point, 90° steam, and 100° boiling point, 110° steam, indicate the close agreement that has been obtained. The very small decrease in wall temperature resulting from increasing the velocity from 10 to 13 feet (3 to 4 meters) per second for the latter set of conditions has been recorded accurately by the installed couples without a single overlapping value. Runs of the 100° boiling point, 120° steam, group were made on different days. The 3 and 10 foot (1 and 3 meter) velocities were completed a week before the 5 and 13 foot (1.5 and 4 meter) velocities were made. The 80 hours of operation conducted between those dates did not affect the consistency of the readings.

Comments

The method as developed and tested in this laboratory has proved very satisfactory. A modification of the manner of withdrawal of the leads from the tube has been found possible, so that, in a purely test apparatus, the tube and thermocouples with the leads consist of a compact unit. This will make feasible a study of the effect of tube surface conditions on heat transfer coefficients, a requirement of which is the constant observation and conditioning of the tube surface. A later report will consider the modification.

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Bumping Prevention

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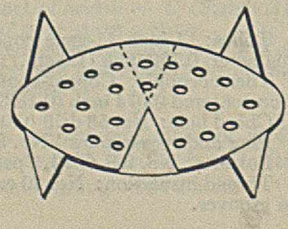
The author (*1*, *2*) has recommended the use of a porcelain sieve plate for preventing bumping, because it introduces no impurity and causes no oxidation. It is excellent for liquid boiled in a small round-bottomed vessel. For a thick layer of liquid, the plate is liable to rest on the bottom, cause overheating of the covered area, and result in the cracking of the vessel.



For the preparation of a large quantity of carbon dioxide-free water, the author has used successfully sieve plates made of sheet silver without cracking a single glass vessel in two years. For solutions that attack silver, the sieve plate could be constructed of platinum.

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Quantitative Organic Microchemical Analysis in Industrial Problems

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MICROCHEMICAL methods deal, arbitrarily, with 1 to 10 mg. of material; such methods have been referred to by Emich as milligram methods to differentiate them from centigram or semi-micromethods and decigram or macromethods. This discussion will not include methods of chemical microscopy, which involve the application of the microscope to the solution of chemical problems, although they are of great value as research tools; Chamot (*6*) states that they offer even greater possibilities in time- and labor-saving than microchemical methods. Finally, discussion of highly sensitive identification reactions on organic and inorganic compounds and ions, spot tests, and spectroscopic, colorimetric, and nephelometric methods of analysis will be omitted altogether although these are justly included in the field of microchemical methods.

In the classification of quantitative microchemical methods of analysis there is the usual division into organic and inorganic branches. The technic for inorganic quantitative microanalysis has been carefully worked out, particularly by Emich and his co-workers, but the methods developed by Pregl for organic compounds appear to be receiving more attention. These methods are essentially the same in theory and practice as the older macromethods and have, in general, merely been improved and modified to permit using milligrams in place of decigrams.

Lavoisier is generally considered the founder of organic elementary analysis for, in 1781, he worked out an indirect gas-volumetric method of analysis by which he determined the composition of an organic substance from the products of its complete combustion to carbon dioxide and water and made clear the importance of elementary organic analysis to the science of chemistry. Minor improvements were made until, in 1830, Liebig and Dumas made the final improvements and developed the macromethod to practically its present form. With the exception of certain improvements suggested by Dennstedt in 1903 there were no important improvements in the technic of organic elementary analysis for carbon and hydrogen until the time of Pregl, a period of practically a hundred years.

The Dumas method for nitrogen appeared in 1883 and was improved by Schiff in 1886 by his development of the present form of azotometer. The period 1861–70 saw the development of the Carius method for sulfur and halogens, and in 1883 Kjeldahl published his method for the determination of nitrogen.

Development of Organic Elementary Microanalysis

In 1910 Pregl, in the course of a tedious investigation on bile acids, isolated a decomposition product which could be obtained only in extremely small amounts. He was faced with having to start anew with very large amounts of material or else to refine the methods of quantitative organic analysis so that he could get correct analytical results on previously unheard of small amounts of material which would lead with certainty to the empirical formula of his substance. Pregl was encouraged in deciding in favor of the second alternative by the success which Emich had attained in quantitative inorganic microanalysis.

By the end of 1911 the determination of carbon and hydrogen could be made on 7 to 13 mg. of organic material, even if nitrogen and small amounts of sulfur and halogens were simultaneously present; nitrogen could be determined either gasometrically or by titration, on 4 to 8 mg. of substance; and finally determination of sulfur and halogens could be made, also on 4 to 8 mg., by the method of Carius. In 1912 and 1913 many improvements were made, sources of error discovered and eliminated, necessary stringent conditions of technic imposed, time of analyses shortened, and finally the amount of starting material diminished to as low as 2 mg. New developments included the combustion method for halogens and sulfur, the electrolytic determination of copper, molecular weight determination by the ebullioscopic method, and the determination of methoxyl, ethoxyl, and methylimino groups. During this period, about 10,000 exact weighings were made. Pregl's first public announcement of these methods was made before the German Chemical Society in Berlin on February 27, 1911, with demonstration of his technic. The results were first published in Abderhalden's Handbuch der Biochemischen Arbeitsmethoden in 1912.

In 1916 the first edition of Pregl's book was published. By this time the micromuffle for the microdetermination of metallic residues had been worked out, also the carboxyl group determination, and the technic developed for the analysis of low-boiling liquids for carbon and hydrogen, and the gravimetric determination of arsenic. At the time of publication of the second edition in 1922 new determinations included the volumetric determination of arsenic, the determination of mercury in organic compounds, the determination of the acetyl group, and the ebullioscopic determination of the molecular weights of liquids. Up to the time of the publication of the third edition in 1930 many industrial laboratories of Europe had adopted quantitative organic microanalytical methods, which had been spread to all countries of the world by over three hundred of Pregl's students. Pregl received the Nobel Prize in Chemistry in 1923 for his development of these methods.

Microchemical analysis had such widespread acceptance, particularly in Europe, that many new methods were worked out, or new applications discovered, and some suitable medium for publication had to be found. In 1922 Emil Haim and Co., Leipzig and Vienna, undertook the publication of *Mikrochemie*, which was devoted solely to papers on microchemical topics and edited by such well-known microchemists as Pregl, Emich, Lieb, Strebinger, and Feigl.

The Microchemical Balance

The success of all the above methods was dependent upon the development of a balance which was capable of weighing microsamples with at least the same precision as the ordinary analytical balance is capable of weighing macrosamples. The main contributor to this development was W. H. F. Kuhlmann of Hamburg, Germany. His first balances had a capacity of 20 grams and weighed accurately to 0.01 to 0.02 mg. At the suggestion of Pregl, and with advice offered by him, Kuhlmann attempted to increase the sensitivity one more decimal place by improving the grinding of the knife edges and using the utmost care in having the agate bearings not only all in one plane but also absolutely plane parallel. In 1911 Kuhlmann assembled the first balance having a sensitivity of 0.001 mg., the last two decimal places being read on the fixed scale in front of the pointer. Thus it became possible for an experienced microanalyst to weigh a 2-mg. sample with approximately the same precision (1 part in 2000) as one could formerly weigh a 0.2-gram sample on an ordinary analytical balance; by using 3 to 5 mg. of substance the error is less than that made when weighing a 0.2-gram sample on an analytical balance. Despite its high sensitivity, this balance has proved very durable and there are cases where it has been in daily use in industrial laboratories for six years, with 36,000 estimated weighings being made before any adjustments, other than periodic cleaning, were necessary. A rather large number of firms now make microchemical balances but, besides the Kuhlmann balance, the only other balance recommended by Pregl is that of Starke and Kammerer of Vienna. This balance has two interchangeable sensitivities (0.01 and 0.001 mg.), so that it is unnecessary to arrest the balance and move the rider so often, which makes for less wear on the knife edges, agate bearings, and other moving parts. Other manufacturers of microchemical balances include: Sartorius, Göttingen; Bunge, Hamburg; Stückrath, Friedenau b. Berlin; Nemetz, Vienna; Rueprecht, Vienna; Ainsworth, Denver, Colo.; and Becker, New York, N. Y.

Microchemical Apparatus

The necessary apparatus was developed by Pregl during the progress of each investigation; in general, the glass apparatus was made originally by Pregl himself and later by the firm of Paul Haack in Vienna, under Pregl's supervision; the iron ware and metal apparatus was made by the university mechanic. The refined chemicals were at first purified by Pregl, but later E. Merck and Company furnished them according to his specifications.

At present this apparatus can be purchased from Paul Haack in Vienna. Haack has appointed an authorized American agent, Microchemical Service, Douglaston, N. Y., from whom these apparatus and reagents can be procured, as well as the Kuhlmann and Starke-Kammerer microchemical balances.

Microchemical Equipment of Coal Research Laboratory

The installation of a microchemical division in the Coal Research Laboratory of the Carnegie Institute of Technology seemed particularly important, since a large part of its investigations were to be on a laboratory scale where relatively small amounts of material would be available. Because of the complexity of the coal molecule, one is certain to obtain a complex mixture of products from any reaction conducted upon it, and if a relatively small amount of starting material is used the separation, purification, and identification of the products is obviously a problem best solved by the application of microchemical technic. Most completed, successful investigations on coal which deal with the isolation of products have started with extremely large amounts of material; others have not been successfully completed because "an insufficient amount of material was at hand to permit further identification." The quotation just cited is a constantly recurring one, especially in the older literature and before the development of microchemical technic.

The Coal Research Laboratory purchased a complete set of apparatus for all procedures involving the following microdeterminations:

Carbon-hydrogen
Nitrogen (Dumas)
Nitrogen (Kjeldahl)
Halogens and sulfur (by combustion)
Halogens and sulfur (by Carius method)
Molecular weight (by elevation of the boiling point)
Molecular weight (Rast method)
Methoxyl and ethoxyl groups
Methylimino group
Phosphorus in organic compounds
Arsenic in organic compounds
Acetyl group
Carboxyl group
Residue or ash

Subsidiary apparatus includes apparatus for purification of small amounts of material, Kuhlmann microchemical balance, and Starke-Kammerer microchemical balance. The laboratory is thus equipped to do routine or special elementary analyses on practically any organic product which may be obtained in the course of the work. This apparatus was all purchased directly from the foreign manufacturers or distributors, the total cost, including duty, consular fees, transportation, packing, etc., being: Apparatus (Paul Haack), $400; Kuhlmann balance, $185; Starke-Kammerer balance, $275; a total of $860.

Sampling for Microchemical Analysis

This subject has been thoroughly discussed by Benedetti-Pichler (*2*). A criticism often directed against microchemical methods of analysis is that it is impossible to get a true representative of the whole sample in the very small amount of material (2 to 3 mg.) necessary for a microanalysis. In macro- or microanalysis it would be impossible to get a representative sample if the particle size of the mixture was so large that only a few grains were taken for weighing. In each case one is forced to pulverize the sample if one cannot, or does not wish to, increase considerably the size of the sample for analysis. If it is possible to take from a carload, containing 15 short tons of large-sized material, 100 kg. (0.75 per cent) and then, after thoroughly grinding and mixing this amount to take a representative sample of 10 grams (0.01 per cent of 100 kg.) or less, it is just as possible to get a representative sample weighing 1 mg. (0.1 to 0.01 per cent) from 1 gram or 10 grams of the original substance which had first been finely pulverized.

The following factors are of importance in the preparation of representative samples for microanalysis:

The sample should be capable of being very finely pulverized, for, in the weight of an individual particle, the third power of the diameter of the particle appears in the calculation. Generally, metals and alloys cannot be pulverized sufficiently fine to yield a representative sample weighing but 5 mg. In this case the sample may be made homogeneous by fusing it so that each filing from the fusion product is a representative sample in itself. One must insure that in the cooling of the melt selective crystallization or segregation does not occur.

The density of the material only linearly influences the weight of an individual particle. One must guard against a settling out of various constituents of different densities during the mixing and grinding, particularly if the densities differ greatly.

Very different hardness of the constituents of the mixture may cause the hard particles to become imbedded in the softer material during grinding and to escape being pulverized.

The procedure of fine grinding was tested experimentally on synthetic mixtures involving two and three constituents: (1) potassium sulfate and sodium chloride; (2) sulfonal and potassium sulfate; (3) sulfonal, azobenzene, and potassium sulfate. These mixtures were analyzed, respectively, for chlorine; carbon, hydrogen, and ash; and carbon, hydrogen, nitrogen, and ash. Completely satisfactory results were obtained, and it was concluded that this method is applicable to all mixtures of a salt-like character which can be finely pulverized. Samples weighing less than 3 mg. could be used for the analysis, while for residue determinations a fraction of a milligram sufficed.

Next, bituminous coal was analyzed. Microdeterminations of moisture are not possible where, as a result of the official sampling of several carloads of coal, the chemist gets a number of samples of various particle size. This determination should show the moisture content of the mine run coal and very little mixing and pulverizing should be done.

For the determination of all the constituents, the chemist receives a bottle containing the more or less finely pulverized coal representing the final result of the sampling process. The moisture content no longer represents the mine condition, and there is no harm in pulverizing the sample as finely as possible and carrying out analyses on the pulverized sample. Such microdeterminations have previously been made on coal in Pregl's laboratory, in Lipp's commercial laboratory in Graz, and by Strebinger and Radlberger (*23*).

Fifty grams of German bituminous coal, in fairly large pieces, were crudely ground in a mortar (sample A). Five grams of sample A were pulverized for 5 minutes (sample B). A carbon-hydrogen determination on sample B showed that the mixing was not yet sufficient to yield concordant results; according to Müller and Willenberg (*19*), one can recognize a nonhomogeneous sample by the fact that the analytical results may vary by as much as 1 per cent. Consequently 1 gram of sample B was pulverized for 5 minutes in an agate mortar (sample C). The analytical data follow:

TABLE I. GERMAN BITUMINOUS COAL

MACRODETERMINATION OF MOISTURE AND ASH, SAMPLE A

Weight of sample = 4.7960 grams
Loss in weight = 0.0400 gram after drying 2 hours at 110° C. = 0.83% H_2O
Weight of ash = 0.0864 gram = 1.81% ash

MACRODETERMINATION OF ASH, SAMPLE B

Weight of sample = 1.0000 gram
Weight of ash = 0.0180 gram = 1.80% ash

MICRODETERMINATION OF CARBON-HYDROGEN AND ASH, SAMPLE B

WEIGHT OF SAMPLE		CARBON	HYDROGEN	ASH
Mg.		%	%	%
4.562		84.62	5.35	2.35
4.971		84.55	5.17	1.85
3.720		85.61	4.96	1.61
	Mean	84.93	5.16	1.94

MICRODETERMINATION OF CARBON-HYDROGEN AND ASH, SAMPLE C

WEIGHT OF SAMPLE		CARBON	HYDROGEN	ASH
Mg.		%	%	%
4.392		84.51	4.71	2.32
3.455		84.35	5.21	2.08
4.679		84.48	4.42	2.14
3.458		84.49	5.18	2.11
4.736		84.50	5.39	2.18
4.212		84.65	5.21	1.90
	Mean	84.50	5.02	2.12

VOLATILE SULFUR AND ASH DETERMINATION, SAMPLE C
(Combustion method)

WEIGHT OF SAMPLE		SULFUR	ASH
Mg.		%	%
6.724		2.65	1.99
5.483		2.63	2.04
5.097		2.56	1.97
	Mean	2.61	2.00

MOISTURE DETERMINATION, SAMPLE C
(Pregl drying block)

TEMP.	WEIGHT OF SAMPLE	DECREASE IN WEIGHT AFTER MINUTES: 20	40	45	60	H_2O
° *C.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	%
107	5.372	0.039	0.045	...	0.045	0.84
107	4.925	0.039	0.043	...	0.043	0.87
102	3.582	...	...	0.028	...	0.78
					Mean	0.83

MOISTURE DETERMINATION, SAMPLE C
(Pregl microdesiccator)

Weight of sample = 5.014 mg.
Temperature = 107° C.
Decrease in weight = 0.018 mg. after 5 minutes
Decrease in weight = 0.030 mg. after 20 minutes
Decrease in weight = 0.030 mg. after 45 minutes = 0.60% H_2O

MOISTURE DETERMINATION, SAMPLE C, WITH UNINTERRUPTED DRYING
(Pregl microdesiccator, temp. 107° C.)

WEIGHT OF SAMPLE	DECREASE IN WEIGHT	H_2O
Mg.	*Mg.*	%
7.094	0.041 after 20 min.	0.58
4.010	0.022 after 25 min.	0.55
3.320	0.013 after 45 min.	0.39

The values obtained for carbon on sample C show the complete homogeneity of the sample that had been obtained for the microanalyses.

The values obtained in the microdeterminations of ash are somewhat discordant because of spattering. Since spattering is caused by decrepitation of the coal due to its moisture content, this effect is diminished by fine grinding and losses in the ash determination are smaller in microdeterminations than in macro- because the combustion proceeds much more slowly. The mean value obtained from the microanalyses is therefore probably more accurate than that yielded by the macromethod.

The hydrogen values vary considerably because of the hygroscopicity of the coal. In the above experiments the coal was always weighed in an open boat. If somewhat more time was used and Pregl's stoppered weighing tube employed, a greater constancy of hydrogen values would undoubtedly be obtained. In practice one would combine the moisture determination with the carbon-hydrogen determination and thus burn the dried coal. Reabsorption of moisture would be excluded by using microanalytical technic, for the dried sample would be put directly into the glass-stoppered weighing tube while still hot, and exposed to the outside atmosphere for only a few seconds while being transferred to the combustion tube.

Using Pregl's microdesiccator for the determination of moisture and drying at 107° C. for 20 minutes in a partial vacuum gives results which are about 0.2 per cent low. That this is due to oxidation of the sample by the small amount of air which passes over it is confirmed by the fact that uninterrupted drying in this apparatus for 45 minutes gives results about 0.4 per cent low. More rapid and accurate results would be obtained by passing an inert gas, such as carbon dioxide or nitrogen, over the sample in place of air.

For the sake of speed and convenience the determination of sulfur could be made acidimetrically, rather than gravimetrically, by titrating the solution obtained from the combustion. If one used Pregl's procedure the results would not be absolutely precise, owing to the presence of nitrogen (and possibly halogens) in the coal, but might be sufficiently precise for certain cases. By using Friedrich's method (*11*) precise results can be obtained titrimetrically despite the presence of these elements.

The determination of carbon, hydrogen, and ash can be made in 45 minutes with a little practice. No special precautions need be taken in the combustion of coal. The small sample is rapidly gasified and then almost nothing but carbon remains and one can proceed with the movable burner directly under the boat, because in the reaction $C + O_2 = CO_2$ there is no volume change in the gas phase and no danger of a backing-up of the gas with subsequent cessation or back-flow of the bubble-counter.

The determination of sulfur, volumetrically, coupled with an ash determination requires about 2 hours, of which 1.25 hours represents actual working time. Determination of moisture, using the drying block, requires 45 minutes but only 25 minutes if one uses the microdesiccator. Thus a complete ultimate analysis of coal, plus moisture and ash determinations, requires but 3 or 4 hours. The time per analysis is further shortened if a series of analyses is made.

SAMPLING INDUSTRIAL MATERIALS FOR MICROANALYSIS

Lucas and Grassner (*16*) state that the results of analysis on 10-mg. coal samples are the same as those obtained with twenty times this amount in a macroanalysis and that no special sampling is required for microanalytical determinations. The final 125-gram sample, which is taken in a definite way, is finely ground and sieved through a metal sieve having 1600 meshes per square centimeter (about 100 meshes per inch), so that a dust-fine, homogeneous powder is obtained. Table II illustrates the excellent agreement obtained.

TABLE II. COMPARATIVE DETERMINATIONS

COAL	MACROSAMPLE (APPROX. 200 MG.) Carbon	Hydrogen	MICROSAMPLE (APPROX. 10 MG.) Carbon	Hydrogen
	%	%	%	%
Run of mine	77.94	4.28	77.82	4.17
Nut	82.59	4.67	82.49	4.64
Anthracite	81.20	4.30	81.33	4.26
Mid-German brown	59.44	6.28	59.26	6.29
Humus	50.18	5.22	50.20	5.41
Lignite	41.90	5.81	41.86	5.85

Strebinger and Radlberger (*23*) carried out microanalyses on coal as a test of the possibility of getting a homogeneous representative sample from a nonhomogeneous material. Even in macroanalysis the sample taken for analysis is usually representative of many tons and is made homogeneous by pulverizing. Any inorganic impurities which are present and not uniformly distributed will cause large errors whether 3 mg. or 0.3 gram are weighed. One must thus proceed in the same way for preparing samples for either macro- or microanalyses and the sample must be thoroughly pulverized in an agate mortar. Comparative results on different types of coal are given below.

Table III. Comparative Determinations

Coal	Macrosample				Microsample			
	Carbon	Hydrogen	Ash	H_2O	Carbon	Hydrogen	Ash	H_2O
	%	%	%	%	%	%	%	%
Brown	41.01	3.50	6.38	25.80	41.33	3.58	6.21	25.92
Russian I	52.26	6.75	13.39	16.13	52.40	6.77	13.50	16.27
Russian II	67.50	4.81	3.97	11.81	67.76	4.67	4.02	11.97

The results agree satisfactorily and because of the great advantages of the micromethod the authors decide in favor of it.

Strebinger and Radlberger also made comparative micro- and macroanalyses on two other industrial materials, nickel in a nickel steel and sulfur in pyrites; satisfactory agreement was obtained by the two methods. In the macroanalysis of the steel, because of its low nickel content, 20 grams were used, whereas 10 mg. sufficed for the microanalysis.

For a theoretical discussion of sampling for microanalysis, see Mika (*18*) and Baule and Benedetti-Pichler (*1*).

Advantages of Microanalytical Methods to Industry

Economy of Materials. Goubau (*14*) points out that one of the principal advantages of microchemical methods is that they use very small amounts of material. This advantage, of little importance in ordinary industrial analysis, may be very important in industrial laboratories dealing with biological, mineralogical, or organic products. Very often in a research one obtains a very small amount of a substance which is not sufficient for analysis using macromethods. Micromethods may be the deciding factor in the success of the research and, for this reason alone, deserve a place in all scientific, research, and industrial laboratories. Von Braun (*5*) stresses the importance of the saving of valuable materials, particularly at the present time when organic chemistry is working farther into the field of biochemical processes where the investigator often has a minimum amount of exceedingly valuable substance isolated from plant or animal bodies. Thus, a series of valuable investigations, such as those of Wieland on toad poisons, or Levene on nucleic acids, or work dealing with enzymes, hormones, vitamins, etc., would probably have not been possible without the aid of microchemical methods of analysis.

An illustration of the economy of microchemical analysis is cited by Cornwell (*9*): A certain company required an analysis on a substance worth $5000 per gram, only 0.3 gram being available. A macrodetermination of carbon and hydrogen would completely destroy 0.2 gram having a value of $1000. A microdetermination would use but 2 mg. worth but $10. Flaschenträger (*10*) estimated that he and his co-workers, in the period from 1920 to 1926, made 3000 carbon-hydrogen, 1000 nitrogen, 200 halogen, sulfur, and methoxyl, and 500 residue microdeterminations. Cornwell, assuming a 0.2-gram sample for each macrodetermination, calculates that 940 grams of material would have been burned in the making of these 4700 analyses by macromethods, whereas, assuming an average of 2-mg. samples for each microanalysis, only 9.4 grams were destroyed. If smaller samples are used, other materials—gas or electricity, tap and distilled water, reagents, etc.—will be reduced proportionately and there is also a considerable saving of space.

Microchemical methods also permit working safely with extremely explosive substances. Thus, Riesenfeld and Schwab (*21*) were able to make a complete study of very pure ozone, using but a few milligrams. Working with large amounts would have been very dangerous.

The economy of reagents is very great, usually requiring from one-tenth to one-hundredth the amount necessary for a macrodetermination.

Using microtechnic and a Schwarz-Bergkampf filtering beaker, Benedetti-Pichler (*3*) made a single nickel determination in 1 hour, of which but 0.5 hour was actual working time. Less time per analysis would be necessary if a series was made. Only 5 mg. of dimethylglyoxime and 0.5 cc. of absolute alcohol were necessary, which is approximately one-hundredth that required for a macroanalysis. The precision of this method is attested by the fact that Schwarz-Bergkampf, using 1 to 1.5 mg. of nickel ammonium sulfate, got the following results in five analyses: 14.72, 14.85, 15.07, 14.78, and 14.63 per cent of nickel; mean, 14.81; theory, 14.86 per cent.

Because of the economy of reagents it is permissible to use precious substances such as platinum or palladium salts, smaller apparatus is used, and the expense due to breakage is less. This also permits the more general use of platinum apparatus, so that errors due to inclusion of soluble portions of glass, etc., in precipitates are avoided, making the determinations more precise.

To illustrate comparative costs of apparatus for micro- and macrowork, Pichler discusses Pregl's electrolytic copper determination. For the microdetermination the electrolysis is carried out in a small test tube. The platinum wire gauze cathode and platinum wire anode, if of heavy construction, weigh but 2 grams, while the macroelectrodes total 16 to 18 grams. Electrolyzing 4 to 5 cc. of a sulfuric acid solution requires 10 to 20 minutes for quantitative deposition. With one stand and two pairs of electrodes (4 grams of platinum), one analyst could make 30 microdeterminations of copper in 10 hours. To make the same number of macrodeterminations in the same time would require at least six pairs of electrodes (100 to 110 grams of platinum).

Economy of Time. This is one of the most important advantages of micromethods. The determination of carbon, hydrogen, and nitrogen by macromethods represents nearly a day's work, whereas the same determinations can be made microanalytically in 1.5 to 2 hours.

Flaschenträger (*10*) states that the normal day's work for an experienced microanalyst is eight carbon-hydrogen and four nitrogen determinations. Meixner and Kröcker (*17*) state that in their laboratory a carbon-hydrogen determination requires 50 to 55 minutes (which confirms Pregl's estimate), but that one analyst cannot make eight determinations in an 8.5-hour day if he has to pulverize and dry the samples to constant weight before each analysis.

The micro-Kjeldahl method requires about 5 to 15 minutes for complete digestion and only 4 minutes for distillation of the ammonia; a single determination can be made in less than a half-hour, the time factor becoming more favorable if a series of analyses is conducted at one time. Bermann (*4*) points out the advantage of this micromethod over other methods, under actual technical conditions. He used barley, yeast, and molasses, all of which differ considerably and show the practicability of the method. Here also, the contention that a few milligrams of substance cannot be a representative sample of a large amount of material was disproved. Comparative results obtained from the two methods (macro and micro) differed by but 0.03 to 0.04 per cent.

From the practical standpoint Bermann claims that one can make eight microdeterminations of nitrogen in the same time, with the same precision and with only one-tenth the reagents necessary to make one macrodetermination. From the scientific standpoint the microdetermination of nitrogen is very important to the fermentation industry because it opens up possibilities which are not attainable by macromethods—for example, a study of the morphological elements of the barley seed, the change in the nitrogen content during germination, etc., which can be studied with a single granule. Technically, the method is important because of its great speed which makes it possible to change the mash ratios immediately and while the fermentation proceeds.

> The micro-Dumas method for nitrogen, using a 1- to 4-mg. sample, can be made in 1 to 1.25 hours, including weighings, and is more accurate than the macromethod. In the latter method correct results were due to fortuitous compensation of errors, whereas the micromethod is rational. The refinements, discovered during the establishment of the method, include an exact definition of combustion velocity as measured by the number of gas bubbles per second, improvement in the preparation of air-free carbon dioxide, and finally placing the reduced copper section in the middle of the tube rather than at the end. Pregl showed that glowing copper, especially if impure, reduced carbon dioxide to carbon monoxide, causing the nitrogen values to be too high. By having the reduced copper layer followed by copper oxide at the proper temperature this error was removed.
>
> For the determination of halogens and sulfur the microcombustion method is advantageous if one wishes to get a single result quickly, requiring about 1.5 to 2 hours, of which about one-half is actual working time. If the volumetric determination is substituted for the gravimetric there is a still greater saving of time and the tedious filtration of the small amounts of precipitate is avoided as well as the elimination of two weighings of the filter tube, microcrucible, or filter stick and crucible. For a series of determinations of halogens or sulfur the micro-Carius method is probably best, since several tubes may be placed in the bomb furnace at once. An average of about 4 hours' heating is necessary for complete decomposition, compared to 8 to 24 hours for macrosamples; the micromethod has the advantage also that the small tubes can be rapidly brought to 275° to 300° C. in the furnace and rapidly cooled again to room temperature, whereas this occupies considerable time in the macro-Carius method. The danger of explosion of these small pressure tubes with resulting injury to the analyst is nil.
>
> The other determinations, such as microcarboxyl, methoxyl, ethoxyl, acetyl, etc., are similarly rapid when compared with the corresponding macromethods.

The advantage of rapidity coupled with precision is especially great in an industrial laboratory where a large series of analyses is made. The rapidity in getting results enables a process operator to know, during the progress of his process, just what is going on and, if necessary, to make rapid corrections as suggested by the analysis.

EXPERIENCES OF VARIOUS LABORATORIES

Meixner and Kröcker (*17*) state that the I. G. plant at Höchst a/M chose microanalytical methods because of their certainty, precision, and economy of materials. Grassner (*15*) points out that microchemical methods first gradually extended from university laboratories to medico-chemical laboratories of the pharmaceutical industries where they were applied in the scientific investigation of medicinals. Later microanalysis went into the chemical-technical research laboratories of industry where it was at first skeptically received. However, it proved of value to industry and is used in an increasing circle of chemical-technical investigations. These methods are used in industries where there is no shortage of material, because of the economy of space, energy, and time and because of their increased precision. They are also most useful in searching for "traces" in industrial products. In the I. G. chemical-technical research laboratory quantitative organic microanalysis was introduced in 1922 and is used almost exclusively.

Microchemistry as an industrial economy has been discussed by Gesell and Dittmar (*13*), who state that one of the chief factors in the cost of chemicals is the cost of control and a reduction of this item by means of the practical application of microchemical methods seems promising. Three serious difficulties are: The assumption that specialized workers are necessary and that the average analyst is not capable of adapting himself to methods using smaller quantities of material where the factor of error would be greater; the difficulty of sampling for microchemical methods; and the difficulty of obtaining equipment not too complicated nor too delicate for practical purposes. Experience has shown that these are easily overcome. The average, capable, intelligent analyst can easily adapt himself to microtechnic; representative samples can be obtained if proper precautions are taken; and, finally, the equipment is easily obtainable and no more complicated or fragile than ordinary apparatus. Gesell and Dittmar present data on parallel macro- and semi-microanalyses on the same materials involving ash, Kjeldahl, and residue determinations, and conclude that microchemical methods would effect marked economy in the cost of analytical control. They estimate that in large concerns, where the laboratory costs run between $20,000 and $100,000 per year, a saving of 50 to 60 per cent could be effected.

Goubau (*14*) points out certain disadvantages of microchemical methods, which necessitate meticulous, painstaking technic, not always applicable in an ordinary laboratory. However, Pichler states that microchemical methods require no special ability on the part of the analyst. It is true that the microchemical balance is a very sensitive instrument which must be handled delicately to yield good results and have a long life, but the technic of weighing with it and of cleaning it at definite intervals is very easily learned.

Gault and Nicloux (*12*) discuss the analysis of some bituminous minerals submitted to the petroleum laboratory of the University of Strasbourg. These samples contained only 11 to 30 per cent of carbon and 1.7 to 3.0 per cent of hydrogen. To get satisfactory macroresults the combustion had to be conducted for 4 to 5 hours; for satisfactory microresults, because of the low percentage of hydrogen present, samples weighing 15 to 20 mg. were used, the combustion requiring but 50 to 60 minutes. The following data show comparative results on the same samples:

TABLE IV. COMPARATIVE RESULTS ON SAME SAMPLES

SAMPLE	MACROANALYSIS		MICROANALYSIS	
	Carbon	Hydrogen	Carbon	Hydrogen
	%	%	%	%
1	24.60	3.68	25.15	3.65
2	11.02	1.45	11.27	1.53
3	21.80	2.29	22.27	2.38
4	23.63	2.65	23.70	2.73
5	14.65	1.82	14.57	1.85
6	29.94	3.18	29.90	3.21
7	16.50	1.66	16.98	1.83

The authors conclude that micromethods are not only more simple and rapid but are more exact and more general than macromethods. Pregl's methods can also be extended to the analysis of fuels in general.

In a recent article Clark (*7*) points out that Pregl's micromethods are as accurate as standard methods and, aside from the economy of material, they require less time, reagents, and space for the execution of the work and are preferred even when a plentiful supply of material to be analyzed is available. Adoption of micromethods is not confined to research laboratories but routine and control laboratories are also using these methods with an appreciable saving in financial upkeep.

However, the change from macro- to micromethods in routine and control work has not been as general as appears warranted. To overcome the arguments often directed against Pregl's methods—namely, that for routine and control work the technic of this system demands too high a degree of analytical skill, the work tends to become tedious, and a special laboratory must be used—Clark recommends a semimicromethod using samples ranging from 5 to 25 mg. and claims that requirements as to details, laboratory conditions, balances, etc., are not nearly so exacting as those imposed by the microsystem but possess the other advantages as to economy of time, space, and reagents.

In numerous cases cited in the literature increasing the size of the sample is recommended to make the results surer and the technic simpler. Probably the foremost advocate of the semi-micromethod is J. Dubsky. However, Pregl has stated (*20*) that the advantages claimed for the increase in the size of the sample are questionable. Schöller has also pointed out (*22*) that beginners often attempt to make the work easier by increasing the size of the sample. However, with careful weighing, errors in technic do not occur during weighing but rather are due to incomplete combustion, and the probability of error is considerably increased by enlarging the size of the sample. One of the most important advantages of the micromethod is immediately lost by increasing the size of the sample used in the analysis.

No special skill is required to master the technic of the micromethods as devised by Pregl. There is also probably little to choose between the tediousness of the micromethod compared to the semi-micro- or the macromethod; but since the micromethod is more rapid than either of the other two methods the long extended waiting periods for reactions or processes to complete themselves are very much shortened. For ordinary routine analyses no special room is necessary for use as a microanalytical laboratory. Some care must be used in the selection of a proper place for the microbalance as is also advisable in case of a high-grade analytical balance. The room in which analyses are carried out should be as free as possible from dust, corrosive fumes, and organic vapors, but these same conditions should apply, in general, to an ordinary analytical laboratory.

It is not to be implied that micromethods must, of necessity, ultimately completely replace macromethods; the two methods should be used together. Working with small quantities increases our knowledge of the errors in macroprocesses and often points the way to new methods. Clarke (*8*) states that the microanalytical group, in addition to its obvious function of performing analyses on samples too small for macrochemical attack, is also charged with the task of subjecting to critical scrutiny the methods employed in the general laboratory, with a view towards incorporating into these methods any points of technic derived from microanalysis that will reduce the time required for their performance or increase their precision.

The substitution of micro- for macromethods will occur only where it is found that the former are better suited to the particular needs and conditions of a given laboratory. Likewise, microchemistry need not be considered as a special field but rather as a supplement to macrochemistry. It is impossible to deny the value of micromethods to both the scientific and industrial laboratory, for microanalysis today is one of the indispensable tools of research and has already rendered much valuable service in many branches of science. Industry would be making a mistake if it too did not take advantage of the aid microchemical methods can offer in the solution of its problems.

EXPERIENCE OF COAL RESEARCH LABORATORY

Experience in the Coal Research Laboratory confirms the statements concerning the precision, speed, and economy of microchemical methods.

The sample of bituminous coal which all units of the laboratory are investigating has been analyzed by Silbert, using samples of various particle size. After pulverizing thoroughly in an agate mortar these samples were analyzed and the following data (Table V) show that there is no difficulty in getting a representative sample for microanalysis, for results satisfactorily check those reported by the Bureau of Mines for the same coal and are, of course, made with much greater speed and economy of reagents and materials.

The considerable difference in the values obtained for ash and moisture are not unexpected and are accounted for by the fact that the samples were prepared in another department by grinding in a rod mill in a current of natural gas. Such treatment would tend to raise the ash content of the sample and diminish the moisture content. On a moisture- and ash-free basis, however, the checks are satisfactory. Table VI shows the excellent checks which are obtainable on the same sample (4 to 8 mesh) in the determination of carbon-hydrogen, nitrogen, sulfur, and ash, which proves the sample to be homogeneous.

TABLE V. ANALYSIS OF COAL SAMPLE FROM EDENBORN MINE

SAMPLE	MOISTURE	ASH	CARBON	HYDROGEN	NITROGEN	OXYGEN	SULFUR
	%	%	%	%	%	%	%
BUREAU OF MINES ANALYSIS							
As received	1.9	7.5	77.4	5.2	1.6	7.3	1.0
Moisture-ash free	..	..	85.5	5.5	1.8	6.1	1.1
COAL RESEARCH LABORATORY MICROANALYSIS							
4–8 Mesh[a]							
As received	1.19	8.30	77.27	5.25	1.60	6.59	0.99
Moisture-ash free	..	..	85.38	5.57	1.77	6.19	1.09
16–20 Mesh[b]							
As received	1.01	7.48	78.26	5.25	1.63	6.40	0.98
Moisture-ash free	..	..	85.52	5.55	1.78	6.07	1.08
60–80 Mesh[b]							
As received	1.12	8.30	77.39	5.32	1.61	6.41	0.97
Moisture-ash free	..	..	85.44	5.67	1.78	6.04	1.07

[a] Results are mean of 5 determinations.
[b] Results are mean of 3 determinations.

TABLE VI. CHECK DETERMINATIONS

SAMPLE	MOISTURE	ASH	CARBON	HYDROGEN	NITROGEN	OXYGEN	SULFUR
	%	%	%	%	%	%	%
As received	1.19	8.31	77.19	5.28	1.55	5.48	1.00
Moisture-ash free	..	..	85.32	5.61	1.71	6.26	1.10
As received	1.19	8.31	77.28	5.24	1.58	..	..
Moisture-ash free	..	..	85.39	5.57	1.74	..	..
As received	1.19	8.32	77.27	5.21	1.61	5.40	0.99
Moisture-ash free	..	..	85.40	5.53	1.79	6.19	1.09
As received	1.19	8.29	77.32	5.30	1.64	..	..
Moisture-ash free	..	..	85.41	5.63	1.81	..	..
As received	1.19	8.29	77.30	5.21	1.61	5.42	0.98
Moisture-ash free	..	..	85.39	5.53	1.78	6.22	1.08

Analyses have also been made on a wide variety of products isolated by the various units of the laboratory, and on gas gums furnished by the research laboratory of the Koppers Company. The formation of these gums at small orifices (pilot burner tips) was a great annoyance, as it led to the extinction of the pilot light with the resulting danger of asphyxiation or explosion. The accumulation of even a few milligrams of these gums requires several weeks and the amount of time necessary to collect 0.2 gram, the amount needed for an ordinary macroanalysis, can be readily calculated. This represents a case where there is not only a saving in the time for the actual conduct of the analysis but a tremendous saving in time in the collection of a sample of suitable size for analysis.

CONCLUSION

In general, American chemists have been slow to realize the advantages to be gained by the use of microanalytical methods, not only in industrial laboratories but also in university and scientific laboratories. European laboratories adopted micromethods shortly after the first work of Pregl appeared; practically every university and technical institute has its microanalytical laboratory, and European industrial laboratories have also widely adopted these methods. Some progress has been made in this direction in this country, however, as judged by American scientific and industrial journals which are reporting an increasing number of microanalyses.

The advantages of microchemical methods are so numerous and so obvious that their general adoption in American laboratories is certain to occur. Those laboratories which postpone their adoption are losing an opportunity to save time, energy, and money. Now, when economy is almost a world religion, would seem to be an ideal time in which to introduce these methods generally into American laboratories.

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Apparatus for Microanalysis of Gas

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The need for a device for microanalysis of a large number of gas samples led to the design of the apparatus herein described. It is intended to be easily constructed, convenient, and simple to operate, and to eliminate much of the time-consuming tediousness so often present in both micro- and macromethods. The method is identical in principle with that of Blacet and Leighton (*1*) and the same accuracy is attained. It differs in the mechanical arrangement of the essential parts and in the mode of operation. Two sets are in use in the authors' laboratories and have been found satisfactory.

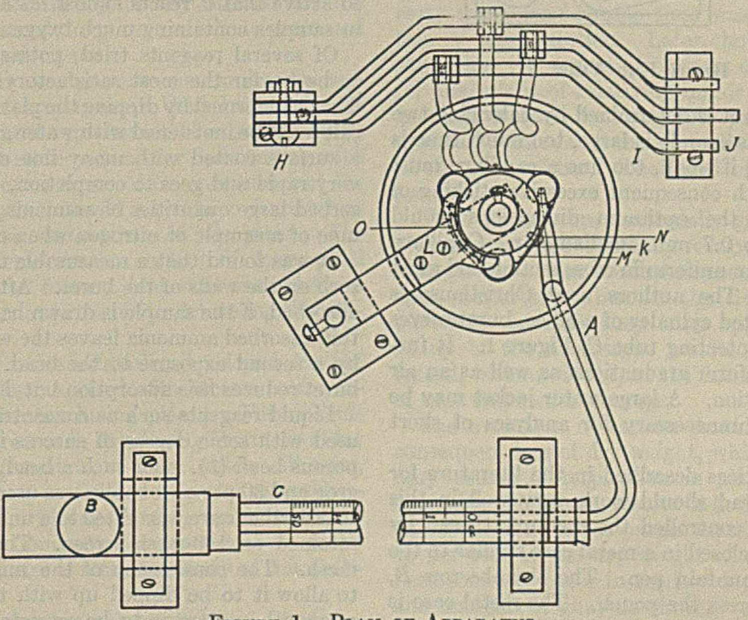

Figure 1. Plan of Apparatus

The advantages of the arrangement lie in the use of a horizontal capillary buret instead of the vertical type used by Reeve (*5*), Christianson (*3*, *4*), and Blacet and Leighton (*1*), and in the use of separate lever mechanisms for convenient introduction of the various solid reagents into the gas. The horizontal buret has several distinct advantages. It permits the tip of the buret to be quickly and easily raised into the gas containers with the fingers. It eliminates the tendency to leak because there is no pressure on the rubber pouch due to a column of mercury. Readings may be made in any section of the buret, as the pressure is not changed by the position of the gas. A trap is not needed to protect the buret from bits of sealing wax, gas bubbles, etc. These impurities float to the top, whereas the outlet into the buret is on the side. The customary trap or enlargement at the end of the buret to guard against loss of gas into the rubber pouch will not work in a horizontal position. A piece of large capillary tubing may be inserted instead, reserving the last fourth of the buret for this protection.

Apparatus

Figure 1 is the plan of the apparatus drawn to scale. The parts are mounted on a moderately heavy board, such as 1.25 × 12 inches × 2.5 feet, which stands on rubber-headed tacks for legs to prevent sliding on the table.

The solid reagents, or beads, must be kept submerged in mercury when not in use and must not touch the walls or bottom of the inverted gas container while being used (*5*). To move the beads accurately and quickly they and their accompanying glass supports are attached to levers. This gives each bead a path of motion along an arc which is practically a straight line. If the level of the center is that of the midpoint of the arc, the lateral motion will be a minimum. For 1 inch (2.5 cm.) of vertical motion the lateral motion d is given as a function of the radius r by the expression

$$d = r - \sqrt{r^2 - 0.25}$$

For a radius of 2 inches (5 cm.) the lateral deviation is about 0.0625 inch (0.16 cm.), and any greater radius would allow only a negligible lateral motion.

Figure 1 shows the top view of the levers each carrying a bead and glass support. The glass supports are curved so that their proximity to each other does not interfere with their motion about the center at H. A thin sheet of brass is soldered to the lever at I to give friction. Obviously the bead must be placed in the gas with some precision: it must be well up into the gas space but must not touch the top of the tube. If the levers had been made straight, any rotary motion about the line HJ, as by twisting at J while adjusting the position of the bead, would make this adjustment more difficult and inaccurate in the event that the bearing at H was not well fitted. To reduce this effect the levers are bent as shown in Figure 1 to bring the bead nearer in line with the movable end J and the pivot H.

The tip of the buret is raised up into the gas containers by rotating the whole buret about its axis. This motion is conveniently and accurately produced by movement with the fingers at *A*, better shown in Figure 2. The distance from the center of rotation to the tip is about 4 inches (10 cm.), so the lateral motion here is only about 0.03 inch (0.07 cm.)

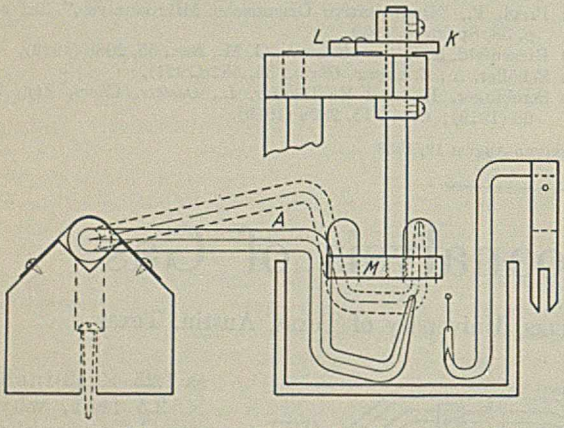

Figure 2. Right End View

The diameter of the buret is determined by balancing two opposing factors. If a gas sample is large, too much time is required for reaction and, if small, too fine a capillary must be used for the buret with consequent excessive sticking of the mercury. Probably the optimum dimensions would require a capillary 0.5 to 0.7 mm. in diameter. Capillary tubes are generally far from uniform in cross section and must be carefully calibrated. The authors used Christianson's method (*3*). The graduated cylinder of a 50-cc. buret serves very well for the glass protecting tube *C*, Figure 1. It furnishes easily readable uniform graduations as well as an air jacket for thermal protection. A large water jacket may be used but it is generally unnecessary for analyses of short duration.

Any of the various devices described in the literature for moving the mercury thread should work very well in this apparatus. The authors controlled the mercury thread by means of a rubber tube inclosed in a metal case similar to the pouch and barrel of a fountain pen. The thumbscrew *B*, Figure 1, is used to compress the pouch. The metal case is rigidly sealed to the protecting tube *C* with sealing wax.

Again looking at Figure 1, three marks or graduations may be seen on the knob or dial indicated by *K* and four marks corresponding to the position for the buret and to positions for the three beads may be seen on the plate *L* fitting up to this dial. These are for setting the gas container assembly in proper position for use of the buret or a reagent as the case may be. The gas container support *M* is shown as a triangular block of iron 0.25 inch (0.62 cm.) thick with circular grooves cut at the corners for accommodation of the glass gas containers. The latter are held in place by a very thin iron band whose ends are both held by the screw at *N*. This iron strap is kept tight by the easily removable arched piece of thin clock spring slipped between it and the block shown by the heavy dotted line at *O*.

A fourth gas container would sometimes be convenient for holding extra samples. A fifth space open to the air, through which to examine a bead or to empty the buret, would also be a convenience. In the authors' apparatus there is barely room on the side of the triangular block for this purpose.

Gas samples are stored and transferred by means of suitable capillary pipets, having the same ground tip and shape as the bent portion of the capillary buret with one change. The capillary pipet comes up 1 inch (2.5 cm.) higher than at *A*, Figure 2, and is then bent down and enlarged for a short distance to give the necessary volume. A strong medicine dropper bulb or a plugged piece of flexible rubber tubing is attached to the end of this enlarged portion. The operation of the pipet is similar to that of the buret.

Reagents

The reagents for oxygen and ammonia as found in the literature—yellow phosphorus and moistened phosphorus pentoxide, respectively—were found to be very slow and the following improvements are recommended: In preparing the phosphorus bead for oxygen, extreme care must be exercised to have it dry because a film of phosphoric acid may increase the time required for reaction as much as a hundred fold. By washing the bead in water, then in alcohol, and then drying it in a stream of dry natural gas, the bead may be made so active that it reacts almost instantly and will even ignite in samples containing much oxygen.

Of several reagents tried, potassium bisulfate was found to be by far the most satisfactory for absorbing ammonia. The bead formed by dipping the platinum loop into the molten salt must be moistened with water and dried in order to leave a surface coated with many fine crystals. The reaction is very rapid and goes to completion. A bead after having absorbed large quantities of ammonia will not increase the volume of a sample of nitrogen when exposed to it.

It was found that a measurable trace of ammonia will adsorb on the walls of the buret. After the ammonia has been adsorbed, if the sample is drawn back into the buret most of this adsorbed ammonia leaves the walls and may be removed by a second exposure to the bead. Careful cleaning of the buret reduces this adsorption but does not eliminate it.

Liquid reagents such as concentrated sulfuric acid may be used with some degree of success if contained in a suitable porous bead (*2*). For such a bead, a mixture of 70 per cent grog and 30 per cent kaolin was used. The grog, ground porous earthenware, was sifted to a uniform size, passing 120- and retained on 140-mesh screen. The kaolin should pass 200-mesh. The consistency of the mixture should be such as to allow it to be dipped up with the platinum wire loop if a smooth surface is to be expected. Only a few minutes' heating in a Fischer burner flame is necessary to bake the bead.

This apparatus is inexpensive, is far less subject to disaster than an Orsat or Burrell, and requires but a fraction of the time to conduct an analysis, yet accuracy is not sacrificed. The operator may sit at a table while conducting analyses.

Acknowledgment

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Determination of Rubber in Rubber-Bearing Plants

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THE determination of the true rubber content of both raw and manufactured rubber has been the subject of extensive investigation. Search has failed to reveal any corresponding record covering studies applicable to rubber-bearing plants. The authors' investigations, covering such methods as have been published, demonstrate their inaccuracy and inadequacy for practical use. There has never been published, as far as the authors have been able to determine, any thorough, systematic study of the factors which determine the value and accuracy of any method for the quantitative determination of the pure caoutchouc contained in a given specimen of plant tissue.

The work embodied in the present communication was undertaken as an essential step towards the solution of some of the complex problems in the production of rubber from the guayule shrub. Without some method for determining with completeness and accuracy in terms of pure caoutchouc[1] the value of any given sample it would have been fruitless to proceed to studies of the metabolism of the plant. The equally important problems in the control of commercial operations, both in field and factory, hinged at the outset on the development of an accurate means to determine the rubber content of the plant.

The authors' method, while primarily developed for the analysis of guayule, has been applied with success to the investigation of other rubber-producing plants. The difficulties encountered and overcome in developing the method for guayule shrub are no different from those which will arise, to a greater or less extent, in the investigation of rubber-bearing plants in general. The authors are indebted to the Intercontinental Rubber Company for permission to make public the results of two years of intensive study of this problem.

At the outset the investigation was limited to methods involving solvent extraction of the rubber from the plant tissue and the direct gravimetric determination of the product. Past experience of the senior author in this field had conclusively demonstrated inherent inaccuracies and uncertainties in alternative methods, such as the determination of the rubber as tetrabromide.

Factors Affecting Accuracy

From the results of study of existing methods it became evident that the problem of the complete extraction of the rubber hydrocarbon from vegetable tissue was not nearly as simple as it might seem (*2, 3, 5, 6*). The methods described in the literature (*1, 7*) resulted either in incomplete extraction with losses from one source or another, or in contamination of the extracted rubber by impurities present in the raw material. The alcohol precipitation method of Fox (*1*), for example, was found to give, with guayule shrub, films contaminated in some instances with as much as 25 per cent of benzene-insoluble impurities. Furthermore, some of the most important factors affecting the accuracy of rubber determinations as applied to plant products have been entirely overlooked. Among those of major importance are:

Respiration changes occurring in the plant tissue after harvesting and before analysis.

The influence of colloidal, protective materials in the plant structure upon the extraction of the rubber.

The effect of the type of rubber solvent used.

The oxidation which occurs during the drying of films of extracted rubber.

Much attention has been directed by Hall and Goodspeed (*2*), Fox (*1*), and others to the influence of fine grinding of the sample upon the completeness of extraction. In the authors' early work considerable time was devoted to an investigation of this question. Later, however, they were able to show that the degree of fineness of grinding of the material for analysis is of relatively minor importance when account is taken of other factors, more particularly of the breaking down and removal of the protective colloids before extraction of the pure rubber. The finest of grinding is no substitute for this.

That changes are continually going on in plant products after harvesting is generally recognized. In some fields these changes have been studied in great detail and are of the utmost importance, but in the handling of rubber-bearing plants for analysis they have apparently been overlooked. Many of the anomalous results of past analyses may be traced, without doubt, to the failure to appreciate the extent of such respiration changes.

The evolution of carbon dioxide and water vapor, with consequent loss of dry weight, which takes place in the ordinary course of respiration in plant products stored under favorable conditions, results in fictitiously high values for the rubber content of the parent material. Losses of more than 15 per cent in the dry weight of the original material have been found to occur in the few days elapsed between pulling and analysis of guayule shrub.

This emphasizes the necessity for careful storage prior to analysis. The authors' studies have shown that desiccation to less than 9 per cent moisture content or storage of the freshly ground material, ready for analysis, in tightly packed and stoppered jars, is an effective means for preventing this loss in weight.

In addition to the apparent increase in rubber in the sample, brought about by the more or less rapid disappearance of materials other than rubber by decomposition in storage, there may be a real increase in the amount of rubber extracted by the published methods of analysis from shrub in which such changes have taken place. But this, again, is due entirely to the inadequacy of the analytical methods in use. These methods have not taken into account the influence of materials present in the plant which seriously interfere with the extraction of the rubber itself. The decomposition of these plant materials by respiration in storage facilitates the subsequent extraction of the rubber by solvents.

It is obvious that if account is not taken of this fact, the rubber value of a sample will depend upon the time and conditions of storage. This was the situation found in connection with guayule. Years of recorded results obtained by the older methods of analysis tended to show consistently that the percentage of rubber in the guayule plant increased by storage after harvesting. Similarly, the increase in the rubber content of Chrysothamnus plants during storage, reported by Hall and Goodspeed (*2*), will undoubtedly find its true explanation in

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[1] The terms "pure caoutchouc" or "pure rubber" used throughout refer to the ultimate product of analysis which not only resembles rubber in all its physical characteristics but also bears the empirical formula $(C_5H_8)_n$, as determined by analysis.

changes and losses in materials other than rubber brought about by respiration processes going on in the sample before analysis.

The influence of other plant products (hemicellulose, pectins, proteins, etc.) within and without the cell wall upon the extractability of the rubber has nowhere been given sufficient consideration. Acetone extraction to remove fats, resins, etc., has been generally applied. But the authors' studies have shown that the presence of these other materials has a much more profound influence upon the completeness of extraction than the constituents of the acetone extract. Mere water leaching, as suggested by Whittlesey (*7*), is entirely inadequate. A slow hydrolysis in fact occurs during the leaching operation, but the complete removal of water-soluble materials from the plant by such means is a matter of months and quite impossible as a practical matter.

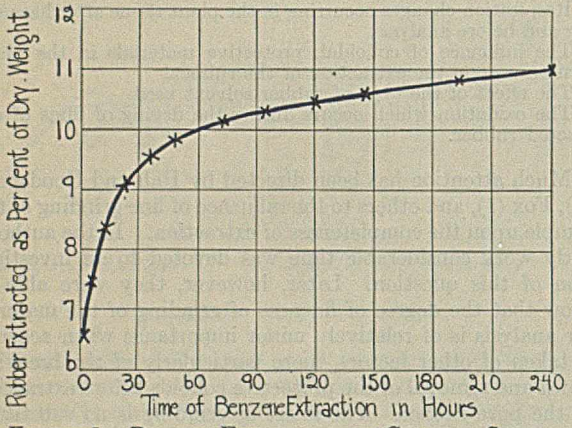

FIGURE 1. RUBBER EXTRACTION OF GUAYULE SHRUB

Samples extracted with water and acetone before determination of rubber.

Very drastic treatment is required to break down those materials which prevent the complete extraction of the rubber itself. Much time was devoted to the study of this problem before a satisfactory method, involving hydrolysis by dilute acid under steam pressure, was evolved. Even this is insufficient unless followed by a thorough removal of all the products of hydrolysis prior to extraction of the rubber.

The results in this connection all tend to show that the difficulties in the way of complete extraction of rubber from plants are not due, as has been at times thought, to either cell wall hindrance or to insoluble modifications of rubber. Rather it is the presence of other materials, colloidal in character, which seems to prevent the solution of the rubber. This is somewhat analogous to the effect of gelatin in raw rubber, 10 per cent of which mechanically incorporated (by milling) renders raw rubber very difficult of solution in benzene.

The choice of solvent used for rubber extraction has generally been left entirely open. The authors' experience has proved, however, that this is a matter of no small importance. Carbon tetrachloride is a conspicuous example of a solvent which has been widely advertised and much recommended for extraction purposes in general because of its noninflammability. But the decomposition to which it is subject, in the presence of light, makes it entirely unsuitable for accurate quantitative work (*4*). Chlorination of the rubber in the process of extraction takes place accompanied by the formation of nonvolatile residues from the solvent itself, which are an even more serious source of error. The use of so-called pure carbon tetrachloride for extraction purposes over some period of time resulted in values for the authors' rubber estimations which were never less than 10 and sometimes 15 per cent too high.

These same errors are introduced in varying degree by all the chlorinated hydrocarbon solvents investigated. With the more stable ones, such as dichloroethane, the errors are reduced, but in all cases the uncertainty involved makes the use of a stable solvent such as benzene strongly recommended.

The universal practice in all published methods of rubber determination of this class includes drying the film of extracted rubber in the air. The error due to oxidation of the rubber under these conditions has been more or less ignored. But such thin films of rubber, being free from the protective agents present in the plant, are extremely susceptible to oxidation. An increase of more than 10 per cent in the weight of a film may easily be due to this source.

Neither vacuum drying nor the use of inert gases offers a solution of the difficulty in practical routine work. The former is excessively slow and the latter exceedingly cumbersome.

Experience with antioxidants suggested their possible application to analytical practice to overcome this difficulty. The authors have been able to show that antioxidants of the proper type are very effective in preventing the oxidation of thin films of pure rubber obtained from plant extracts by their method. Very small amounts of dimethyl-*p*-phenylenediamine, for example, are capable of protecting the rubber during the severest overdrying. Added in a standard benzene solution to the rubber extract before evaporation, this offers a convenient means for eliminating the oxidation error.

It is the authors' belief that such use of antioxidants in analytical procedure should be capable of wide application in other fields of research where organic compounds of great susceptibility to oxidation are encountered.

With the foregoing major explanations the reasons for the various steps in the authors' method of analysis for rubber-bearing plants will be at once clear. Simplification has been sought wherever possible without sacrifice of accuracy, but in the case of guayule shrub, attempted short cuts have been fatal from the standpoint of complete extraction. Laborious fine grinding has been eliminated. An analysis may be completed in 48 hours and in routine work two men may handle fifty analyses daily.

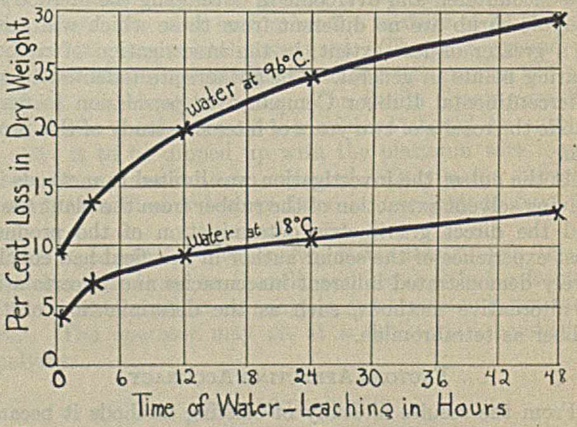

FIGURE 2. RATE OF WATER EXTRACTION OF GROUND GUAYULE SHRUB

The accuracy of the method is shown by repeated treatments of the extracted residues from the first analysis, which fail to show the slightest trace of residual hydrocarbon, attesting the completeness of extraction; by tests on a large number of samples by independent workers, which have given results agreeing within 0.2 per cent; and by the purity of the extracted rubber.

That the material extracted from the plant tissue by this method is pure rubber is indicated not merely by its physical characteristics (a colorless, transparent, elastic film) but also by its chemical reactivity toward sulfur, bromine, etc. The figures for analysis (by combustion) of the extracted films point clearly to a hydrocarbon of the composition $(C_5H_8)_n$ of India rubber. The rather remarkable absence, in fact, of any appreciable amount of oxygen and the complete absence of nitrogen in the films of rubber obtained in daily practice from guayule shrub make both material and method ready means for the preparation of pure, protein-free rubber.

EXPERIMENTAL

It should be unnecessary to point out that proper precautions to insure a uniform and representative sample precede any analytical work. As the authors were confronted with sampling problems ranging from two or three irreplaceable plants to fields of hundreds of acres, the difficulties in this phase of the subject were forcibly impressed upon them. The work involved in developing accurate methods which would give the true rubber content for such cases has no place in the present discussion. It is mentioned merely to emphasize the fact that with variable plant products the method of sampling is of equal importance with the subsequent analytical procedure.

PREPARATION OF SAMPLE

Certain precautions are necessary in the handling of rubber-bearing plants if respiration losses are to be prevented where there is, for any reason, a delay between harvesting and analysis. The importance of this is well illustrated in Table I.

TABLE I. EFFECT OF RESPIRATION LOSSES UPON THE EXTRACTABLE RUBBER IN GUAYULE SHRUB

(5-gram samples leached with hot water and acetone, then extracted 24 hours with benzene)

TREATMENT OF SHRUB	TIME OF TREATMENT	LOSS IN DRY WEIGHT IN TREATMENT	CO_2 EVOLVED DURING TREATMENT	MOISTURE CONTENT WHEN ANALYZED	RUBBER EXTRACTED Actual dry basis	RUBBER EXTRACTED Original[a] dry basis
	Days	%	%	%	%	%
Analyzed immediately	None	None	None	39.5	9.2 9.2	9.2 9.2
Same, chopped plants kept in flask covered with watch glass at room temperature	4	4.7	Not determined	42.4	11.0 11.4 11.4	10.5 10.9 10.9
Chopped plants kept in flask at 40° C. and slow current of moist air passed through	5	16.0	7.2	41.0	14.0 14.1	11.8 11.8
Finely ground shrub kept in open at room temperature	7	1.1	Not determined	18.8	9.3 9.5	9.2 9.4
Same packed tightly in glass-stoppered bottle and kept at room temperature	89	None	None	35.3	8.9 9.3	8.9 9.3
Finely ground shrub, vacuum dried, kept in open jar at room temperature	89	None	None	8.6	9.1 9.2	9.1 9.2

[a] After correction for loss in dry weight.

The differences between the results in the last two columns of Table I represent the increase in the per cent of rubber resulting from the loss through respiration of non-rubber materials in varying amounts brought about by different conditions of storage. This table also shows how the usual methods of analysis, in which no provision is made for the complete removal of all colloidal materials interfering with the extraction of the rubber, may give real increases in the amount of rubber extracted from shrub stored prior to analysis. These increases are a function of the respiration changes as measured by the loss in dry weight of the samples. When such elimination of extraction-inhibiting materials is provided for in the method of analysis, no increase in rubber is obtained by aging, as shown by Table II.

TABLE II. COMPARATIVE EFFECT OF RESPIRATION AND STEAM HYDROLYSIS IN INCREASING THE EXTRACTABILITY OF RUBBER FROM GUAYULE SHRUB

TREATMENT OF SAMPLE BEFORE ANALYSIS	METHOD OF ANALYSIS	LOSS OF DRY WEIGHT IN TREATMENT	EXTRACTED RUBBER Actual dry basis	EXTRACTED RUBBER Original dry basis
		%	%	%
Analyzed at once	Water, acetone, and benzene extraction	None	10.4 9.7	10.4 9.7
Same; chopped plants incubated at 40° C. in saturated atmosphere with slow current of air for 7 days.	Same	5.1	12.9 12.7	12.3 12.1
Analyzed at once	Hydrolyzed by steaming 3 hours at 30 lbs. pressure, then extracted as above	None	13.2 13.3	13.2 13.3
Incubated 7 days at 40° C. in slow current of saturated air	Same	6.4	14.4 14.5	13.4 13.5
Same, except hydrolyzed before incubation	Same, except incubated between hydrolysis and extraction	None	13.0 13.2	13.0 13.2

The increasing amounts of rubber extracted from samples of increasing fineness by the usual published methods of analysis are shown by Table III.

TABLE III. EFFECT OF FINENESS OF GRINDING UPON THE EXTRACTION OF RUBBER FROM GUAYULE SHRUB

(5-gram samples leached with hot water and acetone, then extracted with benzene for 24 hours)

FINENESS OF GRINDING	BENZENE EXTRACT (Per cent of dry weight of shrub) Without hydrolysis	BENZENE EXTRACT (Per cent of dry weight of shrub) Acid hydrolysis under steam pressure
Coarse. Slivers about 9.5 mm. long ranging down to pieces 1.6 mm., with many lumps.	10.1 10.7	14.5 14.4
Medium. A few slivers 6.4 mm. long but most pieces about 3.2 mm. ranging down to some very fines. (All pass 14 mesh.) No lumps.	11.9 12.3	14.2 14.3
Fine. A very few slivers 3.2 mm. long but most pass 30 mesh. Some lumps of rubber.	12.8 13.0	14.1 14.3
Regrinding. Residue from fine grinding above; reground after first analysis until all passes 50 mesh.	0.6 0.8	None
Total for fine sample, reground, average	13.6	14.2

Even with the finest grinding practicable with guayule shrub, more and more rubber may be removed by increasing the time of extraction, as is clearly brought out by Figure 1. But such extremes of fine grinding are unnecessary when the proper analytical procedure, involving hydrolysis, is followed, as demonstrated by Table III. Moreover, owing to the high rubber content of guayule shrub, extremely fine grinding is impractical because of the tendency of the rubber to agglomerate under mechanical working. For this reason a fineness of about 14 mesh which gives a uniform sample has been adopted. With other plants of lower rubber content, the hydrolysis process will eliminate the tedious grinding to 100 mesh or more which has been recommended.

REMOVAL OF COLLOIDAL PROTECTIVE MATERIALS

It has already been pointed out that drastic treatment is necessary to insure the complete breaking down and removal of materials which otherwise interfere with the accuracy and completeness of the rubber extraction. The slow hydrolysis which goes on in the ordinary water-leaching of guayule shrub is shown in Figure 2. The relationship between the removal of materials which are water-soluble or which may be rendered so and the rubber extracted is brought out by Table IV.

Table IV. Relation between Water-Soluble Material Removed and Rubber Extractable from Guayule Shrub

(Acetone extraction 12 hours, benzene extraction 24 hours)

Method of Removing Water-Soluble Material	Water-Soluble Materials Removed (By difference)	Acetone Extract	Benzene Extract
	%	%	%
2 hours' leach with water at 60° C.	6.2	5.9 6.0	8.5 8.6
3 hours of steaming at 30 lbs. pressure (2.1 kg. per sq. cm.) followed by leaching as above	23.1	6.4 6.6	8.7 9.0
Steaming as with preceding sample, followed by 6 hours of leaching at 132° C.	30.7	6.0 6.3	9.2 9.4
Same as preceding, except 1% sulfuric acid used for leaching	49.4	6.9 7.0	10.0 10.3

All results based on dry weight of sample

Some of the studies made to determine the optimum conditions of acid concentration, and time and temperature of steaming required for complete rubber extraction are shown in Tables V and VI. It was from such results as these that 3 hours of boiling with 1 per cent sulfuric acid followed by 3 hours of steaming at 122° C. was adopted for the hydrolysis treatment in the final method.

Table V. Effect of Acid Concentration and Time in the Hydrolysis of Guayule Shrub Prior to Rubber Extraction

(All samples steamed 6 hours at 30 pounds per sq. in. pressure (2.1 kg. per sq. cm.) after acid treatment and then extracted with hot water 3 hours, acetone 12 hours, and benzene 24 hours)

Concentration of Sulfuric Acid	Time of Boiling with Acid	Rubber Extracted (Based on dry weight of sample)
%	*Hours*	%
None	None	8.31–8.74
0.5	3	9.44–9.47
0.5	6	10.04–10.11
1.0	1	9.81–9.99
1.0	2	10.63–10.85
1.0	3	10.76–10.90
1.0	6	10.75–10.88
2.0	1	10.01–10.53
2.0	3	10.62–10.90
2.0	6	10.77–10.95
3.0	1	10.58–10.76
3.0	3	10.70–10.92
3.0	6	10.68–10.82

That the complete removal of such materials after they have been rendered water-soluble is absolutely necessary for complete rubber extraction is illustrated by Table VII. Clearly it is not only the hydrolysis which is important but the removal of materials which interfere with the extraction of the rubber. This has been provided for in the analytical method finally adopted by 3 hours of leaching with hot water after hydrolysis.

Table VI. Effect of Time and Temperature of Steaming on Extractability of Rubber from Guayule Shrub

(All samples treated with boiling 1 per cent sulfuric acid for 3 hours before steaming and after steaming extracted with hot water 3 hours, acetone 12 hours, and benzene 24 hours)

Temperature of Steaming	Time of Steaming	Rubber Extracted (Based on dry weight of sample)
° *C.*	*Hours*	%
...	None	8.0–8.1
98	3	10.2–10.4
	6	10.0–10.1
	9	11.5–11.5
	12	11.5–11.7
122	1	10.1–10.3
	2	10.0–10.5
	3	11.3–11.6
	6	11.1–11.4
153	3	11.6–11.6
	6	11.4–11.5
162	1	11.2–11.4
	3	11.4–11.5

Table VII. Effect of Presence of Water-Soluble Materials upon Extractability of Rubber from Guayule Shrub

(All samples extracted 12 hours with acetone and 24 hours with benzene)

Treatment of Samples	Rubber Extracted (Based on dry weight of sample) After leaching 3 hours with hot water	Without water leach	Difference Due to Removal of Water-Solubles
	%	%	%
No hydrolysis	7.9–8.2	8.0–8.3	1
Steam hydrolysis	9.5–9.8	8.6–8.4	10

Choice of Rubber Solvent

The error introduced by the use of such solvents as carbon tetrachloride may be clearly seen from Table VIII.

In the decomposition of carbon tetrachloride which takes place in the light in the presence of air the odor of carbonyl chloride was detected. The chlorination of the rubber produced by the more stable dichloroethane clearly indicates the advisability of using benzene as a solvent for accurate quantitative work unless the determinations are carried out in the dark.

Prevention of Oxidation

The importance of protecting the rubber after extraction against oxidation, during drying, in preparation for weighing has been emphasized. The extent of the error introduced by the usual air-drying is shown by Table IX which also illustrates the way in which dimethyl-*p*-phenylenediamine may be used to overcome this difficulty. Details of procedure

Table VIII. Effect of Solvent on the Rubber Values of Guayule Shrub

(All samples boiled 3 hours with 1 per cent sulfuric acid and steamed 3 hours at 30 pounds per sq. in. (2.1 kg. per sq. cm.) pressure, then extracted with hot water 3 hours, acetone 12 hours, rubber solvent 24 hours)

Solvent Used (150 cc. in each case)	Method of Extraction	Total Weight of Extract	Weight of Residue from Solvent (Determined in blank) Before extn.	After extn.	Chlorine in Rubber (approx.)	Rubber Extract (Based on dry weight of shrub sample) No corrections	Corrected for residue from solvent
		Mg.	*Mg.*	*Mg.*	%	%	%
Carbon tetrachloride (purified)	In the dark	424 433	000	000	..	11.2 11.5	11.2 11.5
Same	In diffused light	443 452	000	19	0.9 1.1	11.8 12.1	11.2 11.5
Same	In direct sunlight	469 481	000	42	Not estimated	12.4 12.7	11.3 11.6
Same, except crude from reagent bottle	In dark	460 462	30	30	Not estimated	12.3 12.3	11.4 11.4
Same	In diffused light	459 470	30	39	2.9 3.5	12.1 12.4	11.1 11.4
Same	In direct sunlight	506 521	30	82	Not estimated	13.4 13.8	11.2 11.6
Dichloroethane (from reagent bottle)	In diffused light	442 450	...	...	0.21 0.23	11.7 11.9	..
Benzene (c. p.)	In diffused light	422 428	000	000	0.0	11.2 11.4	11.2 11.4

adopted to this end are to be found in the description of the method given below.

TABLE IX. OXIDATION OF RUBBER FILMS DURING DRYING

(All samples obtained by standard acid hydrolysis and steaming treatment of guayule shrub followed by extraction with hot water, acetone, and benzene)

	TIME OF DRYING			
	24 HOURS		48 HOURS	
METHOD OF DRYING	Weight of film	Extraction (Based on dry shrub)	Weight of film	Extraction (Based on dry shrub)
	Mg.	%	*Mg.*	%
In flask open to air in oven at 105° C.	674 676	15.0 15.0	701 705	15.6 15.7
In closed flasks through which current of nitrogen at 105° C. was passed	629 637	14.0 14.1	634 639	14.1 14.2
In flask open to air in oven at 105° C. but in presence of 7 mg. of dimethyl-*p*-phenylene diamine. (Results corrected as determined in blank)	628 632	14.0 14.1	631 638	14.1 14.2

ACCURACY OF METHOD

The two criteria of accuracy in the determination of the true rubber value of a plant product are both met by the present method. First, the extraction of the rubber is complete as evidenced by the failure of repeated treatments, even after regrinding of the sample to a fine mesh, to remove the slightest trace of additional rubber. This is to be contrasted with the results obtained with the usual methods which do not include hydrolysis treatment as shown in Figure 1 and Table III. Second, the rubber extracted and weighed in the final determination is entirely free from impurities. The unusually good agreement between the carbon and hydrogen values for the rubber extracted by this method from guayule shrub (when dried in nitrogen), with the theoretical values for C_5H_8, is shown by Table X. In addition, qualitative tests gave negative results for nitrogen, sulfur (thought possible as a result of the acid hydrolysis treatment), and ash.

TABLE X. COMBUSTION OF RUBBER OBTAINED FROM GUAYULE SHRUB BY ACID HYDROLYSIS, STEAMING AND EXTRACTION WITH BENZENE

(Rubber films dried in a current of pure dry nitrogen)

	CARBON	HYDROGEN	TOTAL
	%	%	%
Theory (C_5H_8)	88.22	11.78	100.0
Sample A	88.00	11.75	99.75
Sample B	88.09	11.68	99.77
Sample C	88.15	11.41	99.56

DESCRIPTION OF METHOD

The following is a detailed description of the method as finally adopted for the routine handling of as many as fifty samples a day of guayule shrub by two experienced operators:

PREPARATION OF SAMPLE. The plants to be analyzed, washed free of adhering soil, are first coarsely crushed by two passes through corrugated differential laboratory mill rolls set up as tightly as possible. This material is then ground successively with a Universal grinder and a corn mill. (Made by Landers, Frary, and Clark, New Britain, Conn. The use of an attrition-type mill operated with a reciprocating motion for the finer stages of grinding has proved effective in preventing the agglomeration of the rubber in guayule shrub.) After each stage of grinding the shrub is thoroughly mixed and quartered by means of Jones ore samplers of various sizes. The final quarter is divided into two lots of a little more than 5 grams each and one lot of approximately 10 grams. The remaining shrub is preserved, packed tightly in an airtight glass jar, in case of emergency.

Duplicate 5-gram samples are then weighed out on the analytical balance from the small samples divided out with the sampler. These are transferred to Coors porcelain extraction thimbles, which for convenience are 22 mm. in diameter by 70 mm. high, inside measurements, with 2-mm. perforations in the bottom. A thin layer of wool batting is placed below and above the shrub to prevent loss.

The moisture content of the sample is determined at the same time by vacuum-drying the 10-gram sample at 110° C. in a Petri dish.

REMOVAL OF WATER-SOLUBLES. The samples in the porcelain thimbles are boiled in a 1 per cent solution of sulfuric acid for 3 hours. For this operation it has been found convenient to use a monel metal bath provided with a water-sealed lid and water-cooled condenser outlet to maintain the acid concentration. A punched plate is employed to hold the thimbles upright on a monel metal screen. After 3 hours the samples, still saturated with acid, are transferred, along with the supporting tray, to an autoclave where they are steamed for 3 hours at 30 pounds per sq. in. (2.1 kg. per sq. cm.) pressure.

For the subsequent operation of leaching to remove the materials rendered water-soluble by the preceding treatments, a copper bath has been found convenient in which the thimbles are held upright by holes in the lid and are supported on a wire screen 4 cm. from the bottom. Water at 60° C. from a storage-type electric water heater is run through each thimble individually in a slow stream. Three hours of leaching are sufficient completely to remove all water-soluble materials. The amount of material thus removed can be determined quantitatively with fair accuracy, by difference, by weighing the thimbles before and after the completed analysis.

ACETONE EXTRACTION. After water-leaching, the thimbles are immediately placed in siphon cups of the Underwriters' Laboratories type and are extracted for 12 hours (on an electric hot plate) using about 150 cc. of acetone. If the water-solubles are to be determined, as above, this extraction must, of course, be made in a tared flask.

EXTRACTION OF RUBBER. The acetone left in the sample from the preceding operation is first removed by heating the thimbles in the vacuum oven for about half an hour. The rubber is then extracted with 150 cc. of benzene in the usual way. At least 16 hours are required for this operation.

DRYING OF RUBBER. The benzene extract of the shrub is evaporated, dried, and weighed in the same tared flask used for the extraction. Before evaporation 5 cc. of a 0.1 per cent solution of dimethyl-*p*-phenylenediamine in benzene is pipetted into the rubber solution. A correction, based upon a blank determination, is made for this material in calculation of the results. The rubber solution is evaporated on a water bath and then dried to constant weight in a Freas oven at 105° C. Overnight drying has been found very convenient for this last step. The flask is finally weighed to three decimal figures. Accuracy to three significant figures in the final result expressed as a percentage of the dry weight of the sample has been found sufficient for all purposes.

ACKNOWLEDGMENTS

The authors desire to express indebtedness to R. D. Gibbs, W. J. McCallum, and J. L. Rysko for their assistance in carrying out many of the studies herein outlined, on which the method depends.

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INCREASED TRADE IN TANNING EXTRACTS. That the trend in international trade in tanning products is toward increased purchases of tanning extracts and reduction in purchases of raw products is revealed in a survey recently completed by the Commerce Department. International trade in tanning extracts during 1932 totaled nearly 310,000 tons as compared with 270,000 tons in the preceding year. Quebracho continued to be the most important tanning extract in international trade, accounting for approximately 75 per cent of total exports of tanning extracts. Argentina supplied almost the entire amount of this item, making shipments to all parts of the world, with the United States the chief purchaser.

Evaluation of Textile Penetrants

An Improved Centrifugal Method

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An improved centrifugal method for the evaluation of textile penetration assistants is described. The advantages of this method as compared with the sinking-time method for the quantitative evaluation of wetting-out agents are pointed out. It is shown that the surface tension of a solution toward air is no criterion of its penetrating ability toward textile fibers. Measurements of the efficiency of a variety of textile assistants as penetrating agents over a range of concentrations and temperatures are given.

THE recent wide use of a variety of synthetic organic chemical products, as assistants in the penetration of textile fibers by liquids, has led to a considerable interest in the quantitative evaluation of the efficiency of these substances. The penetration of textile fibers is assisted by two classes of materials, solvents which remove the obstructions to penetration, and surface-active materials which greatly reduce the tension at interfaces and act as colloidal penetrating assistants. This paper is concerned only with the surface-active materials. The action of solvent penetration assistants in aiding in the entrance of solutions into fibers requires no discussion, but the action of the colloidal penetrants is complicated by a number of factors which require study. No attempt is made to throw light on the mechanism of the action of penetrants, but a method for the practical evaluation of surface-active, or colloidal, textile penetrants is described.

It is necessary to examine a system in which the textile fiber, surrounded by oils and waxes together with a layer of sorbed gases, is in contact with a solution of the penetration assistant. If the solution is to penetrate the fiber it must displace this gas, emulsify the waxes and oils sufficiently to gain access to the material, and diffuse throughout the fiber by means of capillary forces. The evaluation of a penetration assistant is an evaluation, directly or indirectly, of the tension of the solution at the interface liquid–adsorbed gas, as well as of the tension at the interface liquid-solid (fiber); and of the emulsifying action of the solution on the waxes and oils of the fiber.

A number of methods for the evaluation of textile penetration assistants have been reported in the literature, but many are obviously capable of giving only a qualitative measure, while others are limited through their failure to measure all the factors involved. The methods may be divided roughly into three groups:

1. Measurements of the forces acting at the surface of the solutions.
2. Determinations of the time taken for a substance to wet-out and sink in a solution.
3. Measurement of the quantity of liquid absorbed during a given period of time by the fiber.

Kind and Auerbach (*7*) made comparisons of wetting agents by measuring the drop number of solutions of the assistants. Herbig and Seyferth (*6*) made observations of the capillary rise in threads of yarn suspended under standard conditions in solutions of the wetting assistants. Auerbach (*1*) used as a method of evaluation the measure of the time required for a square of fabric floating on the surface of the liquid to become wet-out and sink. Ristenpart and Petzold (*9*) measured the time required for a submerged strand of the fiber to become sufficiently wet-out to sink, while Draves and Clarkson (*2*) measured the time required for a submerged skein to become sufficiently wet-out to sink when attached to a 1.5-gram weight. Herbig and Seyferth (*4, 5*) wet-out yarn and centrifuged it under standard conditions in order to obtain a measure of the amount of water absorbed. Seck and Lachmann (*10*) immersed a weighed piece of cloth in a solution for a definite time, and after draining calculated the amount of solution absorbed from the gain in weight of the cloth.

Comparisons of wetting assistants based on determinations of the surface tension of their solutions do not take into consideration the interfacial tension and the forces of capillary attraction involved. Methods based on the capillary rise in a thread dipping into a solution of the assistant are stated by Herbig and Seyferth (*6*) to lead to conclusions contradictory to observations made in actual commercial practice. Methods which involve sinking-time measurements are frequently erratic in their performance since they depend upon the interface liquid–adsorbed gas, the behavior of which may be readily influenced by both the temperature and the viscosity of the solution. A method involving the use of a centrifuge to remove extraneous solution from the wet fibers appears much more likely to give uniformly reproducible results than does a method which relies upon the draining of the liquid from the fabric.

The method of Herbig and Seyferth (*4, 5*) has certain defects which tend to render questionable any conclusions of a quantitative nature based on its use. Stöcker (*11*) has pointed out that large errors are introduced as a result of the procedure employed by Herbig because of the relatively long time interval between the wetting of the yarn and the subsequent centrifuging process. He also states that Herbig's immersion time is too short to give results of any significance. The work reported in this paper has eliminated the source of error pointed out by Stöcker, placed the method on a sound basis, and established a method of testing that will be of significance in industrial problems.

The primary function of any good textile penetration assistant is the production of a thorough and rapid penetration of fibers by a solution. It is of importance in the evaluation of textile penetration assistants to know the actual degree of saturation of the fiber with a solution—i. e., the extent to which the solution has penetrated into the fiber—at various time intervals during the wetting-out process, as well as to know the moisture content of a fiber when it is wet-out. These data, together with stability data, are needed to evaluate the worth of penetration assistants.

Outline of Method

Textile penetration assistants are most widely used in the processing of cotton. Most of the work with the centrifugal method has been confined to a study of cotton yarn. However, the method is applicable to other vegetable and to animal fibers. The cotton fiber used was in the form of skeins prepared from unbleached, unboiled-out cotton yarn (40/2) of the type which is extensively used in the testing of dyestuffs. This yarn contained moisture which had been absorbed from the atmosphere, but several months' experience indicated that the validity of the results was not seriously impaired by the initial quantity of moisture present in the air-dry yarn provided the yarn was of uniform quality.

A skein of the raw cotton yarn, approximately 5 grams in weight, was weighed to the nearest centigram. The yarn was pulled tight several times in order to line up the strands, then doubled to form a loop of half the original length, and attached to an anchor. The skein was cut open at the top of the loop by means of shears and struck on the palm of the hand 8 to 10 times in order to separate and free the individual strands. This preparation produces uniformity in the physical condition of the skeins, while the shearing of the yarn facilitates the rapid expulsion of adsorbed air by the solution as it penetrates the fibers. The skein and anchor were dropped into a cylinder containing a solution of the penetration assistant at a known concentration. The yarn was immersed in this solution for a time, measured on a stop-watch graduated to read to fifths of a second, and was then transferred to the slowly revolving basket of a centrifuge by pouring the entire contents of the cylinder into the basket. The centrifuge used was a hand machine with a gear ratio of 1 to 36 and a basket radius of 5.5 cm. Since the time of contact of the yarn with the liquid is an important factor in this test, care was taken that the skein dropped from the cylinder into the basket with a variation of only a few fifths of a second from the desired wetting-out time. Within one second after the transfer of the skein, the speed of the slowly rotating basket was brought to approximately 2160 r. p. m. and the extraneous solution was removed. The basket was revolved at this velocity for the desired time and then stopped quickly by means of a braking force. The skein was removed, detached from the anchor, and weighed in a weighing bottle. The quantity of solution retained by the yarn was expressed in terms of the initial weight of the skein.

The amount of solution in the yarn after this treatment is indicative of the amount of water absorbed. The percentage of moisture absorbed is a relative figure which depends entirely upon the length of the wetting-out time and the conditions employed in the centrifuging procedure. For this reason it is necessary to adopt a standard procedure that will give results which can be reproduced with reasonable accuracy and which at the same time will remove a minimum quantity of the solution actually absorbed by the fibers. To study the various conditions which can be employed and to select a proper testing procedure, a series of tests were made with solutions of a commercial alkylated naphthalene sodium sulfonate (product A) over a range of concentrations with a variation in the immersion time of from 15 to 60 seconds and in the centrifuging time of from 10 to 30 seconds. Five determinations were made at each concentration for each specified variation. Summary of the data is given in Table I.

Table I. Penetration Tests on Cotton with Product A Solutions in Water at 25° C.

	Water Absorbed				
Concn., *G./l.*	%	%	%	%	%
Immersion time, seconds:	60	30	30	15	15
Centrifuging time, seconds:	30	30	10	30	15
0.0	27.4	21.1	24.6	..	..
0.1	29.6	29.5	27.5	23.5	25.6
0.2	36.1	34.0	33.1	29.8	29.5
0.5	50.1	45.0	48.9	38.1	41.5
1.0	64.9	55.8	68.8	50.1	53.2
2.0	68.3	64.0	80.3	62.5	71.7
3.0	65.1	66.1	86.2	67.4	78.2
5.0	69.9	66.1	88.3	72.4	82.7

As a result of the above tests a standard wetting time of 15 seconds and a standard centrifuging time of 15 seconds were adopted. The immersion time of 15 seconds is sufficiently long for a good wetting agent to show pronounced activity at concentrations ordinarily used in commercial practice, while the results obtained by centrifuging the yarn for 15 seconds are sufficiently reproducible to permit a definite distinction to be made in the activity of the solutions at different concentrations of the penetration assistant. To illustrate the variation to be expected between individual determinations, detailed information on experiments at four different concentrations of product A is given in Table II.

While the individual determinations of a given series in Table II show considerable variation, the mean averages obtained represent reasonably accurate evaluations of the quantity of solution retained by the cotton fibers. The probable error in the mean average of a series has been determined by the equation (*3*)

$$\text{Probable error} = 0.6745\sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

where Σd^2 is the sum of the squares of the deviations of the single observations from the mean. It was found that the probable error in the mean average was in each case less than 1.5 per cent. The results are represented graphically in Figure 1 with logarithms of the concentrations plotted as abscissas and logarithms of the average per cent absorption plotted as ordinates. It is observed that a smooth curve can be drawn through the points plotted.

Table II. Penetration Tests with Solutions of Product A in Water at 25° C.

Trial	Weight of Skein	Water Absorbed	
	Grams	*Grams*	%
	Concentration 1.0 gram per liter		
1	5.05	2.59	51.3
2	5.00	2.71	54.2
3	5.09	2.64	51.9
4	5.07	2.73	53.8
5	5.11	2.80	54.7
		Av.	53.2
	Concentration 2.0 grams per liter		
1	5.11	3.53	69.1
2	5.09	3.89	76.4
3	5.19	3.79	73.0
4	5.11	3.48	68.1
5	5.15	3.71	72.0
		Av.	71.7
	Concentration 3.0 grams per liter		
1	5.04	3.67	72.8
2	5.11	3.71	72.6
3	5.11	4.22	82.6
4	4.97	4.03	81.1
5	5.10	4.18	81.9
		Av.	78.2
	Concentration 5.0 grams per liter		
1	5.15	4.45	86.4
2	5.14	4.00	77.9
3	5.11	4.37	85.4
4	5.08	4.32	85.0
5	5.00	3.95	79.0
		Av.	82.7

Application of Method

The method was applied to a study of a variety of chemical types of penetration assistants which represent the most important commercial products on the market at present.

Product A is a dialkylated naphthalene sodium sulfonate of 85.25 per cent strength.

Product B is a sodium lauryl sulfate product of 71.1 per cent strength prepared from technical lauryl alcohol.

Product C is a sodium oleyl sulfate product of 48.4 per cent strength prepared from technical oleyl alcohol of iodine number 50.

Product D, which contains 39.7 per cent of active constituent, is a condensation product of oleic acid or oleyl acid chlorine with taurine.

The soap used was a sodium oleate soap containing 79.4 per cent of fatty acid salts.

Penetration Efficiency of Water Solutions

Tests of the wetting-out efficiency of solutions of these products were made over a range of concentrations at 25°, 49°, and 93° C. A summary of the results obtained is given in Table III, while graphical representations of the data at 25° and 49° C. are given in Figures 2 and 3. Each value given in this table represents an average of five experimental determinations.

The data given in Table III show that, with the exception of solutions of product C, the actual efficiency of the solutions

TABLE III. WATER ABSORBED BY COTTON YARN AT 25°, 49°, AND 93° C. FROM SOLUTIONS OF TEXTILE PENETRATION ASSISTANTS

CONCN.	PRODUCT A			PRODUCT B			PRODUCT C			PRODUCT D			SOAP		
	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.
G./l.	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
0.0	24.0	20.9	67.5	..	23.1	..	..	..	..	..	19.2	..	..	25.5	..
0.1	25.6	27.8	..	27.4	31.9	..	..	..	..	..	22.5	..	27.9	34.3	..
0.2	29.5	36.3	..	33.2	40.6	..	..	..	..	30.9	28.8	..	33.6	35.0	..
0.5	41.5	44.2	69.0	52.2	55.6	64.4	36.3	50.8	70.1	43.1	48.7	62.1	50.8	52.1	64.9
1.0	53.2	52.6	..	69.1	68.9	68.3	45.6	61.0	..	55.0	57.4	..	66.4	60.1	..
1.5	..	..	..	..	..	..	..	..	..	..	..	..	..	72.0	..
2.0	71.7	64.0	..	81.2	73.1	68.9	..	73.9	..	68.7	69.0	..	79.5	73.9	..
3.0	78.2	70.6	65.1	83.6	74.4	67.3	59.4	74.6	72.9	..	..	65.4	85.2	81.5	75.9
4.0	..	..	..	..	..	..	..	..	..	74.8	..	..	..	..	..
5.0	82.7	71.5	..	81.5	73.3	..	66.1	77.0	..	..	70.8	..	94.1	88.9	..
6.0	..	..	..	..	..	..	..	..	..	78.0	..	..	..	..	..
7.5	..	..	..	..	..	..	..	..	..	..	69.4	..	94.7	87.0	..
8.0	..	..	..	..	..	..	..	..	..	79.4	..	..	..	..	..
10.0	..	72.3	..	..	..	..	77.9	75.2	..	82.0	73.0	..	90.7	85.9	..

of wetting-out agents studied decreases with increase in temperature. The surface activity of these solutions decreases as the temperature increases and this decrease in surface activity leads to the conclusion that these colloidal penetration assistants pass into molecular solution as the temperature is increased. On the other hand, solutions of product C are shown to exhibit decidedly superior penetrating qualities at the higher temperatures. Solutions of product C are particularly effective at 49° C. but still show some superiority even at 93° C. Lenher (*8*) has shown that the micelles of product C are too large to produce their maximum effect at 25° C. A dispersion of the micelles at high temperatures into more effective sizes would account for the marked increase noted in the surface activity and the resultant penetration of the fiber by the solution.

The indicated lack of efficiency of most penetration agents at elevated temperatures was checked in the following way:

Weighed skeins of cotton yarn were wet out at 93° C. by the method of Draves and Clarkson (*2*). The skeins were then subjected to the standard centrifugal procedure and it was shown that the average amount of water retained by the skeins was 82 per cent of the weight of the dry cotton. Further tests on this point were made by submerging weighed skeins of unbleached cotton yarn in boiling water for a period of 10 minutes. The skeins were removed and subjected to the standard centrifugal procedure. The amount of water retained by the skein was 90 per cent of the weight of the yarn.

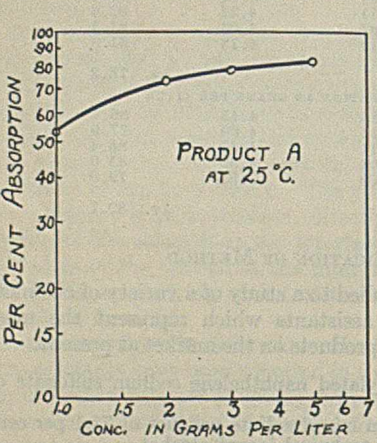

FIGURE 1. PENETRATION WITH SOLUTIONS OF PRODUCT A IN WATER AT 25° C.

These data add further proof that the lack of efficiency at elevated temperatures, observed in the solutions of the wetting-out agents, is not due to unexpected changes in the nature of the fiber or to a variable expulsion of the liquor at varying temperatures.

The ease of removal of the absorbed solution from yarn is obviously related to the viscosity of the solution. With the exception of soap solutions, the viscosities of the solutions of penetration assistants used in the experimental work reported in this paper are approximately that of water. It was observed from the data reported in Table III that the maximum apparent absorption of water by cotton yarn immersed in soap solutions is uniformly greater at the higher concentrations than the indicated absorption from the solutions of the other assistants. The following tests show that in general this apparent difference is due to a difference in the relative viscosity of the solutions: A stock solution of product B with gelatin was prepared, such that the solutions of product B and soap at 25° C. possessed the same relative viscosities at a concentration of 5 grams per liter of the assistant. Tests of the amount of solution retained by the yarn after being run through the standard centrifugal procedure were made over a range of concentrations. Comparisons of the quantity of solution retained by cotton yarn when immersed in solutions of product B, product B plus gelatin, and soap are made in Table IV.

TABLE IV. RELATIONSHIP OF VISCOSITY TO RETENTION OF SOLUTION IN PENETRATION TESTS

CONCN.	PRODUCT B	PRODUCT B + GELATIN	SOAP
G./l.	%	%	%
1.0	69.1	68.5	66.4
2.0	81.2	84.1	79.5
3.0	83.6	88.5	85.2
5.0	81.5	87.5	94.1

The data in Table IV show that solutions prepared from the same assistant but with different viscosities at comparable concentrations differ appreciably from each other in the values which they give for retention of the solution.

While the apparent greater absorption of water from soap solutions is accounted for at most concentrations on the basis of the greater viscosity of the soap solutions, this explanation does not apply at a concentration of 5 grams per liter. The concentration of soap micelles on the cotton fiber might be advanced as an explanation. However, at concentrations below 1 per cent the soap micelles are very small and it is to be expected that they will not concentrate on the fiber to a greater extent than they are absorbed with the solution during a 15-second contact.

PENETRATION OF HARD WATER SOLUTIONS

One of the outstanding advantages of the various penetration assistants as compared with soap is the ability of solutions of the products to effect penetration in hard water solutions under conditions where soap is coagulated. Tests were made of the penetration efficiency of products A, B, and D in a solution containing 400 p. p. m. of calcium chloride. This concentration of calcium chloride is above the limit of the hardness of the water ordinarily encountered in industrial practice. A summary of the data obtained is given in Table V.

TABLE V. SOLUTION RETAINED BY COTTON YARN AT 25° C. FROM SOLUTIONS OF TEXTILE ASSISTANTS IN PRESENCE OF CALCIUM CHLORIDE (0.4 g./l.)

CONCN.	PRODUCT A	PRODUCT B	PRODUCT D
G./l.	%	%	%
0.1	25.5	29.5	..
0.2	31.2	33.8	22.2
0.5	43.8	47.9	35.1
1.0	60.5	55.6	52.5
2.0	76.9	75.2	66.9
3.0	79.9	84.0	..
5.0	80.2	83.2	80.2
7.5	..	..	84.2
10.0	..	..	81.1

It is evident from a comparison of the data in Tables III and V that the efficiency of products A and D as penetration assistants is actually increased in calcium chloride solutions as compared with distilled water solutions. On the other hand the efficiency of solutions of product B decreases slightly under the same conditions. However, the general order of effectiveness remains product B > product A > product D.

APPLICATION TO WOOL AND SILK

The centrifugal method has been applied in this laboratory for the evaluation of the effects obtained by the use of penetration assistants with wool and silk as well as with cotton. The wool skeins used in these tests were prepared from scoured wool yarn (30/2), while the skeins of silk were prepared from Spanish floss silk in the gum (2 ply). The tests were made in distilled water solution at 25° C. A comparison of the data obtained by immersing skeins of cotton, wool, and silk in the gum, in solutions of product B over a range of concentrations is given in Table VI.

TABLE VI. WATER ABSORBED BY COTTON, WOOL, AND SILK FROM SOLUTIONS OF PRODUCT B

CONCN. G./l.	COTTON %	WOOL %	SILK %
0.0	24.0	54.4	40.0
0.5	52.2	52.0	45.7
1.0	69.1	51.8	48.5
3.0	83.6	52.7	58.8

The maximum amount of water retained by unboiled-out cotton yarn has been shown to be 90 per cent. Wool yarn, after immersion for 180 seconds in a solution of product B of 5 grams per liter concentration, retains 56 per cent of its weight of moisture, while silk in the gum after immersion under similar conditions retains 77 per cent of its weight of water.

The tests summarized in Table VI show that well-scoured wool wets out readily in water. The results obtained with the silk in the gum are interesting since they show that while the rate of penetration is entirely different from that observed with cotton, a very definite effect can be evaluated by the centrifugal method.

RELATIONSHIP OF SURFACE TENSION TO PENETRATION OF TEXTILE FIBERS

Measurements of the surface tension of solutions of several assistants were made over a range of concentrations in order to determine whether or not a definite relationship can be established between penetration and surface tension. The measurements were made with the du Noüy ring type of tensiometer. The instrument was calibrated against distilled water and the values given in Table VII are corrected on the basis of the calibration. The surface tensions of solutions of products A, B, C, and D, and soap at 25° C. are given. Each value given in the table represents an average of five experimental determinations.

TABLE VII. SURFACE TENSIONS OF SOLUTIONS OF TEXTILE ASSISTANTS

CONCN. G./l.	PRODUCT A Dynes/cm.	PRODUCT B Dynes/cm.	PRODUCT C Dynes/cm.	PRODUCT D Dynes/cm.	SOAP Dynes/cm.
0.0	72.0	72.0	72.0	72.0	72.0
0.1	..	43.3	41.8	33.0	33.9
0.2	..	33.3	..	31.5	30.6
0.5	51.5	28.3	35.3	31.6	26.9
1.0	44.8	27.9	34.5	32.0	26.7
2.0	..	27.0	34.7	31.6	26.7
2.5	38.2	..	..	..	..
3.0	..	26.7	..	31.6	26.9
5.0	34.1	28.9	32.8	31.4	27.3
10.0	32.6	..	34.0	31.1	..

These data show that the presence of soap, product B, and product D produces marked lowering in the surface tension of water. While the surface tensions of product A solutions are relatively quite low, product A produces the least effect of the five assistants. These data show that while there is the expected general increase in penetration ability with a decrease in the surface tension there is no general quantitative relationship. For example, solutions of product A at a concentration of 5 grams per liter show a surface tension of 34.1 dynes per centimeter, a value which is higher than that found for solutions of product D or soap at a concentration of 0.1 gram per liter. However, data obtained by the centrifugal method (Table III) show that cotton yarn absorbs 83 per cent of its weight of a solution containing 5 grams per liter of product A, while the quantity of liquid absorbed from a solution of soap at a concentration of 0.1 gram per liter is less than 28 per cent. It is evident from this and other comparisons which can be made from the data in Tables VII and III that there is no quantitative relationship between the surface tension of a solution of a textile assistant and its ability to penetrate textile fibers.

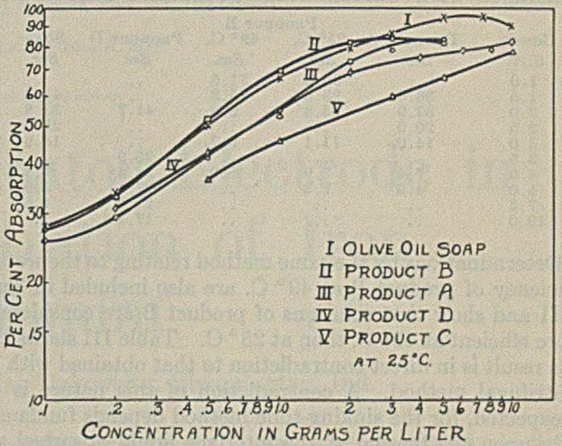

FIGURE 2. WATER ABSORBED BY COTTON YARN AT 25° C. FROM SOLUTIONS OF TEXTILE PENETRATION ASSISTANTS

CRITICAL SURVEY OF METHODS BASED ON SINKING TIMES

The most satisfactory sinking-time method is that of Draves and Clarkson (*2*). Data have been accumulated in this laboratory which make possible a comprehensive comparison between the sinking-time method as developed by Draves and Clarkson and the centrifugal method described in this paper.

The sinking-time method, as applied by Draves and Clarkson, measures the time required for an aqueous solution of the textile assistant to wet a submerged 5-gram skein of unbleached cotton yarn to an extent such that its weight plus the weight of absorbed liquid, together with that of an attached 1.5-gram sinker will overcome the buoyant force of the wetting solution and cause the skein with its attached weight to sink to the bottom of a cylindrical container. This method can give only a measure of the time required for a textile fiber to reach a certain unknown degree of saturation with a solution containing a known concentration of wetting assistant.

Tests made of the wetting-out efficiency at 25° C. of aqueous solutions of products A, B, and D, and soap by the sinking-time method are summarized in Table VIII, and a graphical representation of the data is given in Figure 4. Each value given in Table VIII represents an average of seven experimental determinations, made with skeins of raw cotton yarn (40/2).

An examination of the data in Table VIII and of the graphical representation in Figure 4 shows that the sinking-time method appears to give uniformly good results with solutions of products B and A, but very erratic results with solutions of soap and of product D. Very definite experimental difficulties were encountered in observations of the wetting times of both the soap and the product D solutions and these difficulties are reflected in the data.

TABLE VIII. WETTING-OUT TIME OF SOLUTIONS OF TEXTILE ASSISTANTS WITH COTTON YARN BY SINKING-TIME METHOD

CONCN.	PRODUCT A	PRODUCT B 25° C.	PRODUCT B 49° C.	PRODUCT D	SOAP
G./l.	Sec.	Sec.	Sec.	Sec.	Sec.
1.0	..	35.0	31.5	..	..
1.5	86.0	23.6	15.3	..	43.2
2.0	32.9	15.8	9.3	41.7	33.8
2.5	20.9	..	..	..	25.6
3.0	14.0	11.1	6.2	..	15.6
3.5	..	..	..	25.9	..
4.0	7.4	7.9	5.0	28.4	7.1
5.0	4.9	7.3	..	27.1	5.9
7.5	..	..	..	21.0	4.6
10.0	..	..	..	17.1	..

Determinations by the same method relating to the wetting efficiency of product B at 49° C. are also included in Table VIII and show that solutions of product B are considerably more efficient at 49° C. than at 25° C. Table III shows that this result is in direct contradiction to that obtained with the centrifugal method. A contradiction of this nature is not unexpected, for the sinking-time method depends fundamentally upon the tension at the interface liquid–adsorbed gas. It is obvious that this tension is extremely sensitive to variations in temperature. On the other hand the centrifugal method depends basically upon the tension at the interface fiber-liquid and it is this interface that is of fundamental importance in the penetration of the fiber. The data in Tables III and VIII give additional proof that the quantitative evaluation of a penetration assistant by means of the sinking-time method alone may easily give misleading results and lead the investigator to erroneous conclusions. The centrifugal method of testing shows that solutions of soap are considerably superior to those of product A as penetrating agents in distilled water while the sinking-time method would indicate that solutions of soap are slightly inferior. This discrepancy probably lies in the difficulty of obtaining satisfactory determinations of the wetting-out times in soap solutions by the sinking-time method. The sinking-time method shows that concentrations of 2 grams per liter of product B and 12 grams per liter of product D in distilled water solution are required to produce wetting out of cotton yarn in a 15-second wetting time. This indicates that product B is six times as efficient as product D in producing this degree of effectiveness. On the other hand, according to the centrifugal method a concentration of 2.4 grams per liter of product B produces 82 per cent absorption in cotton yarn during an immersion time of 15 seconds, while a concentration of 10 grams per liter of product D is required to produce the same effect. Product B is only four times as effective as product D on this basis.

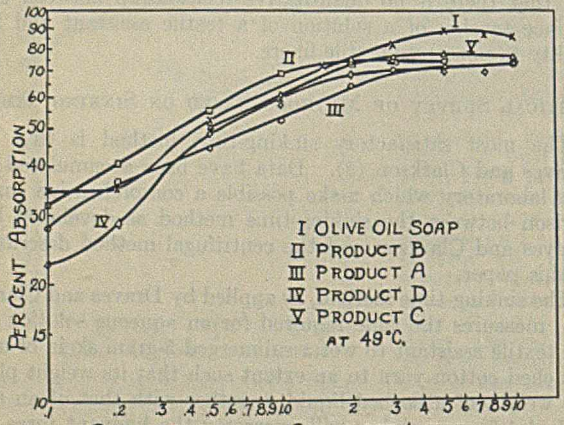

FIGURE 3. WATER ABSORBED BY COTTON YARN AT 49° C. FROM SOLUTIONS OF TEXTILE PENETRATION ASSISTANTS

The sinking-time method for the evaluation of wetting agents is quite limited in the range of concentrations over which it may be employed. In the evaluation of agents with which this method has been successfully used the results are erratic when the actual time measured is greater than 40 to 50 seconds. Thus the lowest concentration of penetration assistant which can be evaluated is approximately 0.1 per cent or 1 gram per liter. However, with many agents of excellent wetting power the method breaks down when the concentration is from 2 to 3 grams per liter. The sinking-time test cannot be used for a quantitative comparison of the efficiencies of penetration assistants of different types or for the comparison of the relative efficiency at different temperatures. On the other hand the sinking-time method has been found to be decidedly valuable in the standardization of the alkylnaphthalenesulfonic acid type of penetration assistants. This is largely because slight changes in concentration cause relatively large variations in the sinking time as observed in a logarithmic plot of concentration against sinking time. As a result the actual strength of the wetting assistant present can be determined within an experimental error of 5 per cent even though the values for the sinking time may be in error by a considerably greater figure.

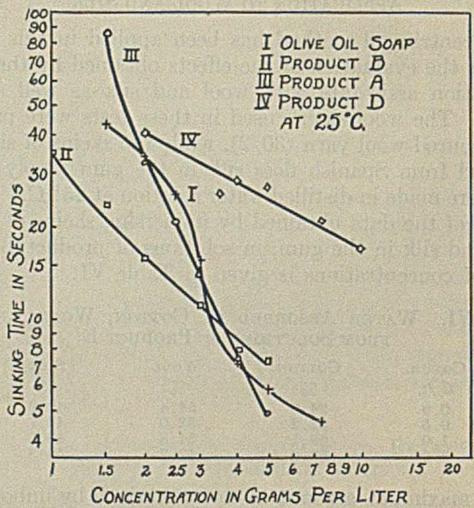

FIGURE 4. WETTING-OUT EFFICIENCY OF PRODUCTS A, B, AND D, AND SOAP AT 25° C.

ADVANTAGES OF CENTRIFUGAL METHOD

The centrifugal method is of value for the comprehensive evaluation and comparison of textile assistants. Evaluations made by this method give a direct measure of the most important factor in the penetration of textile fibers—i. e., a measure of the quantity of a solution absorbed by the fiber. The amount of solution absorbed at the end of any time at any desired concentration of wetting agent can be determined regardless of the degree of saturation which the fiber has reached. The centrifugal method makes possible a determination of the maximum absorption of liquid by a fiber in solutions of all textile assistants. Measurements may be made at any temperature with the assurance that the results obtained are comparable with those obtained at any other temperature. The method can be applied to cotton, wool, or silk fibers.

The technic involved in the use of the centrifugal method can be readily mastered by any person experienced in laboratory methods. The time required for a test compares favorably with the sinking-time method. A series of five individual determinations, required for the determination of the efficiency at a given concentration, may be made in 15 to 20 minutes, depending naturally upon the length of the actual sinking-time observed.

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Antimony as an Indicator Electrode in Potentiometric Titration of Iron and Aluminum

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The antimony electrode is applied as indicator electrode to the direct titration of ferric chloride and aluminum chloride with sodium hydroxide solution. Data are given which show the general suitability of the antimony electrode for the titration of aluminum and iron chlorides. The method also affords an approximate analysis of mixtures of the two salts.

ANTIMONY has been found by many investigators to be well adapted as an indicator electrode to the potentiometric titrations of acids and bases and to the determination of the pH of various solutions. The antimony electrode has also found application in a number of titrations involving precipitation reactions.

In the titration of aluminum and magnesium chlorides with sodium hydroxide solution, Treadwell and Bernasconi (*3*) have found that in the titration of aluminum chloride two jumps in the antimony electrode potential occur, one when the aluminum hydroxide has been quantitatively precipitated, and one, which is less pronounced, when the aluminate has been produced. In the titration of mixtures of aluminum and magnesium chlorides with sodium hydroxide, jumps in the electrode potential occur at the precipitation of aluminum and magnesium hydroxides, respectively, the second jump being too early, causing an error of from 1 to 2 per cent.

The antimony electrode has been found by Malvea and Withrow (*2*) to be satisfactory to indicate the end points in the titration of mixtures of calcium and magnesium with sodium hydroxide solution.

An abnormal titration curve occurs, according to Elder (*1*), for the antimony electrode in acid solutions of ferric chloride, probably because of the presence of pentavalent antimony in solution.

The purpose of this investigation is to show the application of antimony as an indicator electrode in the precipitation of ferric iron and aluminum from neutral solutions of their chlorides by the addition of sodium hydroxide solutions.

PROCEDURE

The titrations were carried out using antimony as the indicator electrode. The electrode was prepared from electrolytically refined antimony by casting in a carbon mold, and undoubtedly contained some oxide; however, no precaution was taken to exclude the oxide from the cast metallic rod. The electrode had a length of 4.5 inches (11.25 cm.) and a diameter of 0.25 inch (0.63 cm.). In all the titrations the potential of the indicator electrode was measured against the saturated calomel electrode. The titration vessel consisted of an open 400-cc. beaker. The potential of the electrode combination was measured by means of a students' type Leeds and Northrup potentiometer, No. 7651, in conjunction with a Leeds and Northrup galvanometer No. 2310. In all cases, unless otherwise indicated, the solutions were kept continually agitated by means of a current of air bubbling through the solution in the titration vessel. All experiments were carried out at room temperature, which varied from 24° to 28° C.

Three stock solutions of ferric and aluminum chloride were prepared having the following normalities with respect to iron and aluminum: ferric chloride, 0.3146 *N*, 0.9969 *N*, and 0.1000 *N*; aluminum chloride, 0.2968 *N*, 1.0045 *N*, and 0.1000 *N*. The aluminum chloride solutions were standardized gravimetrically and the ferric chloride solutions by reduction with stannous chloride and titration with potassium bichromate solution. A determination of the chloride content of the ferric and aluminum chlorides used in preparing the stock solutions indicated that the error encountered in the calculation of the theoretical quantity of the sodium hydroxide solutions required for the samples of ferric and aluminum chlorides titrated was of little consequence, since the commercial preparations of ferric and aluminum chlorides used contained an undeterminable amount of basic salts.

Titrations of various quantities of ferric and aluminum chlorides, both separately and as mixtures, were carried out using sodium hydroxide solutions approximately 1 *N*, 0.5 *N*, and 0.1 *N*. These solutions were prepared from carbonate-free sodium hydroxide and carbon dioxide-free water and were standardized against pure recrystallized succinic acid, using phenolphthalein as indicator. The strengths of the various sodium hydroxide solutions are shown in the tables.

Three series of experiments were carried out, involving sodium hydroxide solution approximately 0.5 *N*, and 1 *N*, and 0.1 *N*, respectively. In the first series the effect of the presence of sodium and ammonium sulfate was also determined.

Because of the difference in solubilities of ferric and aluminum hydroxide, the ferric hydroxide was found to be quantitatively precipitated first, giving rise to a jump in the potential of the antimony electrode at the iron equivalence point.

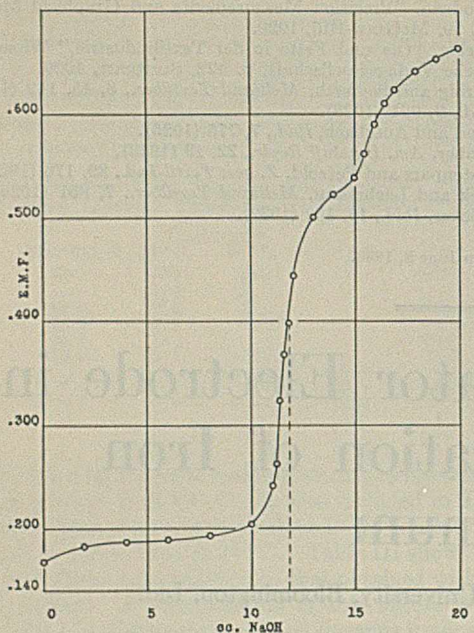

Figure 1. E. m. f.-Volume Curve for Titration of Aluminum Chloride with Sodium Hydroxide Solution (Experiment 3, Table I)

The precipitation of the aluminum hydroxide followed and the second jump in the potential appeared at the quantitative formation of aluminum hydroxide. In the case of the titration of aluminum chloride alone, two jumps in the potential appeared, as found by Treadwell and Bernasconi, one when aluminum hydroxide was quantitatively precipitated, and a second less pronounced jump when the aluminate was produced. The second jump appeared to be rather indistinct and unsuitable for accurate determinations. In the case of the titration of ferric chloride alone, only one jump in the potential occurred, the one at the quantitative precipitation of ferric hydroxide.

Table I. Series 1 of Titrations

Expt.	Vol. of Soln.	Present FeCl$_3$	Present AlCl$_3$	Vol. of NaOH[a] Theoretically Required FeCl$_3$	Vol. of NaOH[a] Theoretically Required AlCl$_3$	Vol. of NaOH[a] Actually Used FeCl$_3$	Vol. of NaOH[a] Actually Used AlCl$_3$	Error FeCl$_3$	Error AlCl$_3$
	Cc.	*Grams*	*Grams*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%	%
1	50	0	0.3297	0	11.78	0	11.80	....	+0.17
2	75	0	0.3297	0	11.78	0	11.70	....	−0.68
3	125	0	0.3297	0	11.78	0	11.80	....	+0.17
4	50	0.4250	0	12.49	0	12.40	0	−0.72	....
5	75	0.4250	0	12.49	0	12.50	0	+0.08	....
6	125	0.4250	0	12.49	0	12.40	0	−0.72	....
7	150	0.4250	0.3297	12.49	11.78	12.40	11.80	−0.72	+0.17
8	150	0.8500	0.3297	24.98	11.78	24.98	11.90	0.00	+1.02
9	150	0.4250	0.6594	12.49	23.56	11.90	24.00	−4.72	+1.87
10[b]	150	0.4250	0.6594	12.49	23.56	11.80	23.40	−5.52	−0.67
11[c,d]	125	0	1.8275	0	27.00	0	26.60	....	−1.48
12[e]	125	0	1.8275	0	27.00	0	26.60	....	−1.48
13[c]	125	1.3519	0	28.60	0	29.00	0	+1.39	....
14[c]	125	0.6759	0.9137	14.20	13.50	13.00	15.00	−8.45	+11.11
15[f]	125	0.6759	0.9137	14.20	13.50	12.80	13.40	−9.85	−0.74

[a] 0.6297 N NaOH used.
[b] 25 cc. of 15 per cent NH_4Cl solution added.
[c] 2 grams of Na_2SO_4 added.
[d] In experiments 11 to 15, inclusive, 0.5059 N NaOH was used.
[e] 1 gram of Na_2SO_4 added.
[f] 2 grams of $(NH_4)_2SO_4$ added.

In order to determine the end point of each reaction, curves were constructed with e. m. f. of the electrode combination plotted as ordinates and volume of sodium hydroxide solution as abscissas. The definite location of the point of maximum increase in potential was determined from these curves by means of the oscillatory tangent to the curve and also from differential curves in which the volume of sodium hydroxide solution was plotted against the change of potential with unit change of volume of sodium hydroxide ($\Delta E/\Delta V$). Curves for the titrations in this first series of experiments, which are typical of the curves in all the titrations in this investigation, are shown in Figures 1, 2, 3, and 4. The determination of the end points is shown and it is seen that the accuracy of the end point is largely dependent upon the correct interpretation of the curve. The differential curve gives a much more definite determination of the end points, since it brings out more clearly the points of maximum increase in potential of the indicator electrode.

Table II. Series 2 of Titrations

Expt.	Present[a] FeCl$_3$	Present[a] AlCl$_3$	Vol. of NaOH[b] Theoretically Required FeCl$_3$	Vol. of NaOH[b] Theoretically Required AlCl$_3$	Vol. of NaOH[b] Actually Used FeCl$_3$	Vol. of NaOH[b] Actually Used AlCl$_3$	Error FeCl$_3$	Error AlCl$_3$
	Grams	*Grams*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%	%
16	0.5390	0.4460	11.10	11.19	11.20	11.20	+0.90	+0.08
17	1.0780	0.4460	22.20	11.19	21.60	11.40	−2.70	+1.84
18	0.5390	0.8920	11.10	22.38	11.00	22.50	−0.90	+0.52
19[c]	1.0780	0.8920	22.20	22.38	21.60	22.70	−2.70	+1.41
20	0.2695	1.1150	4.52	22.80	4.40	22.40	−2.70	+2.23
21	1.3475	0.2230	22.62	4.56	22.50	5.00	−0.55	+9.67
22[d]	0.5390	0.4460	9.05	9.12	10.30	11.30	−13.80	+23.90

[a] In all cases volume of titration solution was 100 cc. at the start.
[b] 0.8972 N NaOH used.
[c] In experiments 19 to 21, inclusive, 1.1012 N NaOH was used.
[d] Hydrogen electrode used.

Table III. Series 3 of Titrations

Expt.	Present[a] FeCl$_3$	Present[a] AlCl$_3$	Vol. of NaOH[b] Theoretically Required FeCl$_3$	Vol. of NaOH[b] Theoretically Required AlCl$_3$	Vol. of NaOH[b] Actually Used FeCl$_3$	Vol. of NaOH[b] Actually Used AlCl$_3$	Error FeCl$_3$	Error AlCl$_3$
	Gram	*Gram*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%	%
23	0.0540	0.0444	10.00	10.00	10.10	10.10	+1.00	+1.00
24	0.0270	0.1111	5.00	25.00	4.80	25.20	−4.00	+0.80
25	0.1352	0.0222	25.00	5.00	26.00	5.30	+4.00	+6.00
26[c]	0.1081	0.0889	20.00	20.00	19.90	20.20	−0.50	+1.00
27[d]	0.1081	0.0889	20.00	20.00	19.80	20.70	−1.00	+3.50

[a] Volume of solution at start of titration, 100 cc.
[b] 0.1 N NaOH used.
[c] Agitated with a stream of hydrogen bubbling through solution.
[d] Hydrogen electrode used in this experiment.

In the second series of experiments the titrations were made with sodium hydroxide of approximately normal strength. More ferric and aluminum chlorides were present than in the first series of experiments. In this series of titrations, various mixtures of ferric and aluminum chloride were used, and the data in Table II show the results obtained.

The third series of experiments was carried out with 0.10 N sodium hydroxide solution and more dilute solutions of ferric and aluminum chlorides. As in the second series, one titration was made using the hydrogen electrode in order to make a comparison with the antimony electrode. Table III gives the data for the titrations in series 3.

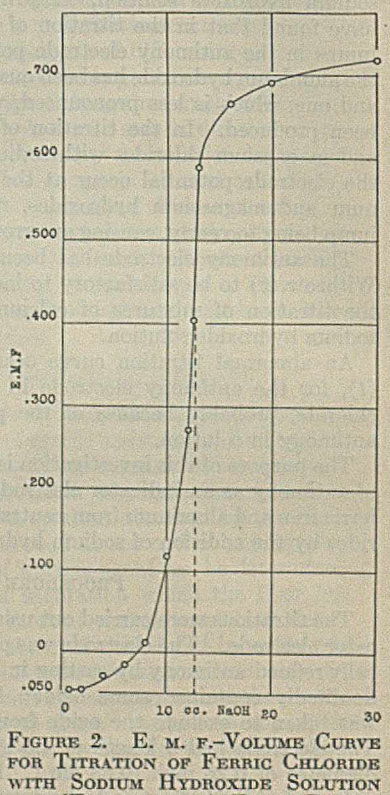

Figure 2. E. m. f.-Volume Curve for Titration of Ferric Chloride with Sodium Hydroxide Solution (Experiment 6, Table I)

RESULTS

The data given in the tables indicate that antimony is suitable as an indicator electrode in the potentiometric titration of either aluminum or ferric chloride with sodium hydroxide solution. The end point is clearly defined and accurately located by the jump in the electrode potential at the quantitative precipitation of the hydroxides. The slight jump in potential (Figure 1) at the equivalence point for the aluminate formation is less distinct and practically imperceptible in the case of mixtures of aluminum and ferric chlorides and is not satisfactory, under the conditions of these experiments, for the determination of the end point. Dilution seems to have little effect upon the accuracy of the method.

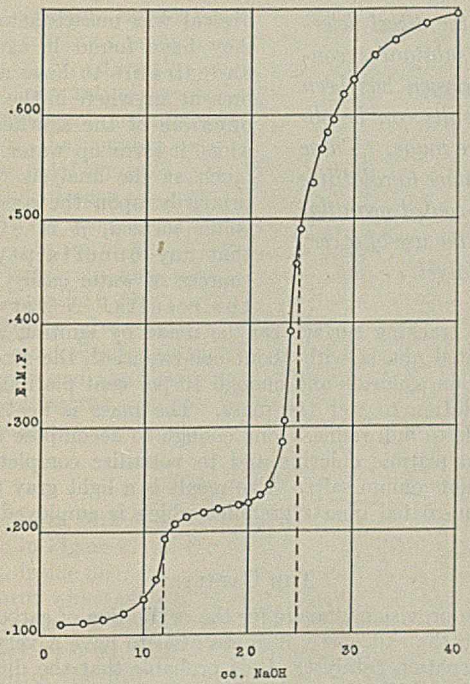

FIGURE 3. E. M. F.–VOLUME CURVE FOR TITRATION OF MIXTURE OF ALUMINUM AND FERRIC CHLORIDE WITH SODIUM HYDROXIDE SOLUTION (EXPERIMENT 7, TABLE I)

In general it was found that in the titrations involving mixtures of aluminum and ferric chlorides, the end point indicating the equivalence point for ferric hydroxide was too early and the end point for aluminum hydroxide too late. In all cases the jump in the electrode potential at the ferric hydroxide equivalence point was less pronounced.

The potentiometric titration of mixtures of ferric and aluminum chlorides with sodium hydroxide, using an antimony indicator electrode, affords a method for an approximate analysis. Titration errors occur which prohibit a more accurate analysis. The accuracy is greater when nearly equal proportions of the two salts are titrated, probably because the titration curves can be more easily interpreted. The accuracy is no doubt impaired by the formation of basic salts at the location of the jump in potential, since no precautions were taken to prevent this difficulty at the end point. Evidence of the formation of basic salts is clearly indicated by the small jump in potential immediately before the aluminum end point in Figure 4.

The presence of sodium sulfate in the solutions of either aluminum or ferric chloride caused an increased error, as is seen from Table I. In the case of mixtures of aluminum and ferric chlorides, the presence of sodium sulfate caused errors of from 8 to 11 per cent, making the method prohibitive in the presence of this alkali sulfate. The presence of ammonium sulfate had an effect similar to that of sodium sulfate. Normal titration curves were obtained in the experiments in which sodium and aluminum sulfate was added.

The strength of the sodium hydroxide solution used for the titrations and the amounts of ferric and aluminum chlorides present in the solutions to be titrated seem to have, in general, little effect on the suitability of antimony as the indicator electrode (Table I).

The hydrogen electrode was found to be inferior to the antimony electrode for the direct titration of iron and aluminum by sodium hydroxide, especially in concentrated solutions, probably because the platinized surface is poisoned by the salts in solution. In more dilute solutions, the hydrogen electrode behaves in the same manner as the antimony electrode but exhibits no advantages.

Stirring by means of air was found to be a suitable method of causing agitation during the titrations. There was no perceptible difference in the action of the antimony electrode where hydrogen was used in place of air.

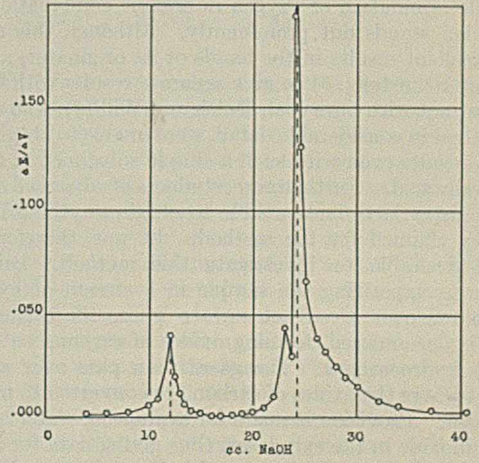

FIGURE 4. DIFFERENTIAL CURVE FOR TITRATION IN FIGURE 3

The potential of the antimony electrode reached equilibrium rapidly, except at the very start of the titrations. The presence of a relatively large quantity of iron in the solution seemed to affect the electrode, causing it to be covered with a dark coating. When most of the iron had been precipitated, the dark coating disappeared and the potential of the electrode thereafter reached equilibrium almost immediately after the successive additions of sodium hydroxide solution. In contrast to this, when the hydrogen electrode was used equilibrium was reached only after 10 to 15 minutes throughout the entire titration. This fact, together with the other factors above mentioned, points favorably to the use of the antimony electrode for the titration of ferric and aluminum chlorides with sodium hydroxide.

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AB C♂

ter Meulen Method for Direct Determination of Oxygen in Organic Compounds

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The method of ter Meulen for the direct determination of oxygen in organic substances containing carbon, hydrogen, and oxygen has been examined. Very satisfactory results can be obtained if certain modifications are made. These involve primarily the use of a furnace to volatilize the sample, the use of platinum-coated granular quartz as a cracking surface, and the use of a very active, thoria-promoted, nickel catalyst.

ALTHOUGH methods for the direct determination of oxygen in organic compounds have been studied for over eighty years, it is probable that oxygen is still most frequently determined by difference. The defects of the indirect method are obvious in that it is time-consuming and subject to accumulated errors, if not gross error—e. g., where complete combustion is difficult. The need of a rather simple, reliable, direct method is apparent. Among the methods proposed during the past decade (*1–3, 6–10*) for the direct determination of oxygen in organic combination, that of Meulen stands out prominently. Although this method gave excellent results in the hands of its originator, and was found by Schuster (*15*) to give accurate results with benzoic acid, but not with pure coal, Dolch and Will (*2*), who studied the method in considerable detail, were unable to obtain satisfactory results even with such a simple substance as crystallized oxalic acid. Furthermore, students of advanced analytical chemistry have been unable to obtain anything like the accuracy claimed for the method. It was therefore considered desirable to investigate this method. Briefly it consists in vaporizing the sample in a stream of hydrogen which flows over a red hot surface where the organic substance is decomposed, forming oxides of carbon, water, and gaseous hydrocarbons. The gases then pass over a nickel catalyst where the oxides of carbon are converted to methane and water. Provision is made for evaluating water and any carbon dioxide in the exit gases, thus giving data for the calculation of the oxygen present. In the present work certain modifications of this method have been found desirable in order to obtain consistently good results.

Vaporization of Sample

As Meulen points out (*9*), the success of the method depends largely upon vaporizing the sample very slowly and uniformly. This necessitates very careful manipulation with a microburner for a half hour or more. If the sample is heated in an electric furnace, however, it may be easily vaporized at the desired rate and a tedious and uncertain operation avoided. While the temperature to be employed in the furnace varies with the substance undergoing analysis, it is usually best to heat rapidly to the melting point of the substance and then to raise the temperature just fast enough to avoid any appreciable condensation of water in the side arm of the first calcium chloride tube. Too rapid heating causes poor results because of incomplete methanation, sublimation of the sample through the absorption train, etc. While with substances like β-naphthol especial care is necessary in order to avoid sublimation, in most cases 20 to 30 minutes suffice to vaporize 200 to 300 mg. of sample.

The Cracking Surface

Various hot "cracking" surfaces have been proposed by Meulen (*6, 7, 9*), such as fine nickel wire, platinized asbestos, and pure asbestos. The authors' experience with iron or nickel was unsatisfactory and they have found it extremely undesirable to have asbestos present anywhere in the system because of the slowness with which it gives up water. Inasmuch as the analysis depends primarily upon the amount of water formed, it is obvious that any uncertainty about sources of water easily vitiates the results. A very satisfactory cracking surface can be made by igniting 20-mesh granulated quartz with about one-twentieth the amount of ammonium chloride and enough 10 per cent platinum chloride solution to wet the mass. The mass is heated in a casserole to dull redness long enough to decompose the ammonium platinic chloride and to volatilize completely the excess ammonium salts. The result is a light gray mass of platinum-coated quartz granules which is employed at red heat.

The Catalyst

As no provision is made for the evaluation of carbon monoxide in the exit gases, it is essential to have a very active hydrogenation catalyst. It is probable that the difficulties of Dolch and Will (*2*) were in part due to an inactive catalyst although they used the asbestos-supported nickel recommended by Meulen. Very active methanation catalysts (*5, 14*) can be prepared by using thoria as a promoter for nickel. Rugged catalysts of high activity were prepared in the present work by dissolving pure thorium nitrate in pure nickel nitrate melted in its water of crystallization, in amounts necessary to give 2 per cent thorium oxide on the nickel present. The mass was stirred continuously, while igniting over a Bunsen burner, to a fine gray powder. To insure complete destruction of the nitrates, the mass may well be cooled and finely ground once during the ignition. Because the thoria acts also as a support, the oxide may be reduced with hydrogen at 350° and finally at 400° C. While the initial reduction required, to give a blank of about 1 mg. of water per hour at the rates of hydrogen flow used, occupied 2 to 3 days, subsequent reductions could be carried out overnight at 400° C. To avoid delays extra catalysts may be reduced independently and sealed off in glass tubes in an atmosphere of hydrogen. Such catalysts may be transferred to the analysis system with only superficial oxidation if a rapid stream of hydrogen is issuing from it. Thoria-promoted catalysts are pyrophoric and so become incandescent when air is drawn through the analysis tube, as is necessary when carbon deposited on the cracking surface must be burned off. With continued use they become less active and may then be heated slightly during the burning-out process in order to remove any deposited carbon or volatile poisons. If the samples analyzed contain no catalyst poisons, such as mercury, sulfur, halogens, etc., one charge of 5 to 10 grams of catalyst may serve for 10 to 15 analyses before requiring reactivation. Substances such as anthraquinone, which clog by depositing much carbon on the first portions of the platinized quartz, necessitate burning out carbon after 4 to 5 analyses.

In order to have a quantitative removal of the oxides of carbon, it is essential that conditions be such that the following reactions go very near completion:

$$CO + 3H_2 = CH_4 + H_2O$$
$$2CO + 2H_2 = CO_2 + CH_4$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

While there is evidence that the equilibrium constants for these reactions reach a maximum between 300° and 400° C., other reactions probably intrude and complete equilibrium data (*4*, *11*, *12*) in this temperature region are not available. The temperature range of 350° to 420° C. proposed by Meulen seems unnecessarily high and 300° to 350° C. has proved satisfactory with the active catalysts used here. Using a large excess of hydrogen the authors have found 350° C. to be the most generally applicable temperature because of the faster rate of reaction. The relatively high rate of hydrogen flow employed in the present work—90 cc. per minute—is advantageous too because it tends to prevent the deposition of carbon (*13*) on the catalyst, and also shortens the time of analysis by allowing the system to be rapidly swept out at the end.

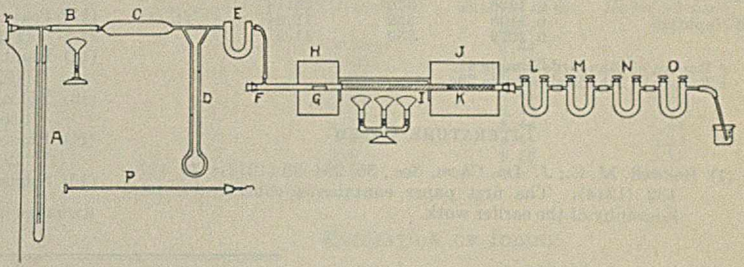

Figure 1. Diagram of Apparatus

The Apparatus

A quartz tube is an indispensable part of the apparatus shown in Figure 1. It should be about 1 meter long, about 1 cm. in inside diameter, and preferably provided with a small side arm which greatly facilitates the safe introduction of the sample. If desired, the plain tube suggested by Meulen (*9*) may be used. While it is desirable to have at least the portion of the tube which holds the sample boat made of transparent quartz, the whole tube may be of opaque material if the platinum boat *G* is provided with an eyelet into which the hook of the loading rod *P* fits, so that the sample cannot be overturned when inserted. The substitution of an opaque quartz tube removes the only expensive part of the apparatus. About 5 cm. from the exit end of the tube *F* a plug of glass wool is inserted, followed by 5 to 10 grams of the prepared oxides *K*. A perforated platinum disk is slipped in and then enough of the platinized quartz *I* to fill the tube about two-thirds full. Another perforated platinum disk may now be inserted if desired, but the tube must not be packed too tightly. The filled tube is conveniently placed in an ordinary organic combustion set-up in which the smallest furnace, *H*, is used to volatilize the sample, and the medium-sized unit, *J*, to heat the catalyst. The largest furnace may be used to heat the granulated quartz to redness but this may be conveniently and efficiently done, as has been the practice in most of the present work, by using the full temperature of 3 ordinary Bunsen burners. In the latter case, 2 shields and a light covering of asbestos paper are sufficient to retain the heat. The ends of the tube *F* are flared out to receive rubber stoppers snugly. The U-tubes *L* and *M* contain calcium chloride, and *N* contains ascarite and calcium chloride, while *O* is a calcium chloride guard tube. Electrolytic hydrogen is freed from oxygen by passing over hot palladized asbestos in *B*, dried over calcium chloride in *C*, measured in the flowmeter *D*, and finally dried over calcium chloride in *E*.

The Method

Having in the system a reduced catalyst, its temperature is brought to 400° C. and a rapid stream of hydrogen is passed for at least a half-hour interval. This is necessary even though the system is always kept under a positive pressure of hydrogen when not in use. During this interval the granulated quartz should be at full heat and the U-tubes may well be in place in order to flush them with hydrogen. The catalyst temperature is then lowered to just 350° C. and the recently weighed tubes *L*, *M*, and *N* are placed in the train. Hydrogen is passed at 90 cc. per minute for half an hour in order to obtain the blank which is by no means negligible. Since results are desired to 0.1 mg., the blank must be carefully determined—e. g., temperature and rate of hydrogen flow kept constant, and in case of doubt another should be taken after the analysis. Having ascertained the blank, the U-tubes are again attached but not opened. The hydrogen tank valve is opened so that 100 to 150 cc. per minute pass out through *A* and the weighed sample quickly inserted in *F*. Having placed the sample about 5 cm. from the hot cracking surface by means of the rod *P*, the solid rubber stopper is tightly replaced. The U-tubes are now opened, the hydrogen rate is adjusted to 90 cc. per minute, and *H* rapidly raised to the desired temperature. The sample is slowly and uniformly volatilized during the course of half an hour and then the temperature of *H* raised to 300° to 400° C. The furnace is then slid back and the tube holding the sample boat heated with the full heat of a blow torch. Strong heating is especially necessary with substances like sugars which leave a voluminous carbon in the boat. The greater portion of the second half hour is allotted to sweeping out the system. Thus the analysis proper usually takes an hour. One analysis can be immediately followed by another, with occasional blanks, until the tube becomes choked with carbon. With an active catalyst and following the above procedure, all the oxygen will be found as water in the first calcium chloride tube. The tubes *M* and *N* are therefore useful mainly as guard tubes. When it becomes necessary to remove the carbon from *I*, the quartz tube *F* is evacuated on a good water pump and air drawn over the hot quartz. When this operation is complete, the air is evacuated and replaced by hydrogen which starts reduction of the catalyst again. This procedure avoids the use of an inert gas like carbon dioxide and also does not disturb the set-up. Directions have been given in some detail in order to avoid ambiguity (*2*).

Results

The results of analyses made upon high-grade organic chemicals by the modified Meulen method are given in Table I. These results were obtained using an ordinary analytical balance and it is felt that by the use of semi-microtechnic somewhat better accuracy could be obtained, or smaller samples might be satisfactorily employed. The analyses made substantiate the soundness of the basic principles of the Meulen method for representative substances containing only carbon, hydrogen, and oxygen. While Meulen gives procedures by which materials containing also nitrogen, sulfur, chlorine, bromine, and iodine (*7*) can be handled, such substances have not been dealt with in the present work. It is hoped to report on these at a later date.

TABLE I. RESULTS OF ANALYSES BY MODIFIED MEULEN METHOD

SUBSTANCE	WEIGHT OF SAMPLE	TEMPERATURE OF CATALYST	OXYGEN Found	OXYGEN Calculated
	Gram	° *C.*	%	%
Succinic acid	0.1289	300	54.22	54.21
	0.1621	300	54.24	
	0.1830	350	54.26	
	0.1480	380	54.14	
Oxalic acid	0.1940	325	76.15	76.16
	0.1053	350	76.24	
Dextrose[a]	0.2566	300	53.39	53.31
	0.1293	350	53.30	
Cane sugar	0.2855	300	51.59	51.44
Benzoic acid[b]	0.2650	325	26.31	26.22
	0.2315	350	26.24	
Anthraquinone	0.2716	350	15.50	15.38
	0.2108	350	15.38	
Quinhydrone	0.1601	350	29.57	29.35
	0.1906	350	29.18	
β-Naphthol	0.2108	350	11.04	11.11
	0.2029	350	11.21	

[a] Bureau of Standards sample 41.
[b] Bureau of Standards sample 39c.

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Volumetric Determination of Small Quantities of Inorganic Iodine

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RECENT attempts to increase the accuracy of the determination of iodine in biological material have been largely directed toward improvements in the procedure for destruction of organic matter. Though most methods described have employed the Winkler procedure (*25*) for the final estimation of the iodine, little attention has been given to the investigation of the accuracy of the procedure when applied to the small quantities of iodine dealt with in biological material. Recently several investigators (*2, 17*) have held this procedure to be defective because of the risk of decomposition of iodides in acid solution. It is the purpose of this contribution, first, to show that under conditions to be described the estimation of small amounts of iodine, 1 mg. or less, by the Winkler procedure is both accurate and trustworthy; second, to report a study of the interference by other substances; and third, to make a practical application—namely, the determination of iodine in iodized salt.

REAGENTS AND APPARATUS

STANDARD IODATE SOLUTION. An exactly 0.1 *N* iodate solution was prepared according to the directions of Jamieson (*9*), using Kahlbaum's purest potassium iodate. The solution so obtained was further diluted to give an exactly 0.005 *N* reagent.

THIOSULFATE. Thiosulfate solutions 0.005 *N* seemed to be more stable if they contained 3.8 grams of crystallized borax ($Na_2B_4O_7.10H_2O$) per liter (*15*). The solution was standardized immediately before use, employing the optimum concentrations of acid and potassium iodide mentioned below.

STANDARD POTASSIUM IODIDE SOLUTION. The iodine content of a specimen of potassium iodide was accurately determined by precipitation with silver nitrate, using the precautions recommended by Hillebrand and Lundell (*7*). The requisite amount of the salt was dissolved in water to give a solution so dilute that small quantities of iodine could be measured with sufficient accuracy.

BROMINE. Iodine-free bromine was prepared by repeated washings of the C. P. product with water in the manner suggested by Karns and Donaldson (*11*). Early in the work it was found that the use of bromine water for oxidation purposes was inadvisable. Therefore, the following procedure, slightly modified from Schockaert and Foster (*22*), was employed: Bromine vapor, obtained by blowing air (washed with water and dried by calcium chloride) through a gas-washing tube containing bromine, was delivered just above the surface of liquid in a flask. Upon swirling the contents of the flask, sufficient bromine was dissolved to give a yellow color to the liquid. To prevent the expulsion of too large quantities of bromine it is wise to draw out to a capillary both the inlet and outlet tubes of the gas-washing tube.

STARCH INDICATOR. This reagent containing salicylic acid for a preservative as recommended by Nichols (*19*) was found to be very satisfactory as to sensitivity and keeping qualities. A solution kept at room temperature with no aseptic precautions for over 6 months showed no deterioration in quality.

OTHER REAGENTS AND APPARATUS. Iodine-free water was produced by redistilling water from an alkaline permanganate solution. Pumice stone used for the prevention of bumping was prepared by boiling millimeter cubes in dilute nitric acid and, after washing thoroughly with water, igniting to a bright red heat in a porcelain crucible. All volumetric glassware was carefully calibrated. Titrations were carried out with 1-, 5-, and 10-ml. microburets.

SENSITIVITY OF END POINT

In order to gage the accuracy of a volumetric method, it is essential to know the sensitivity of the end point. Accordingly, experiments were carried out to ascertain the smallest quantity of iodine necessary to give a perceptible blue color to a solution 50 ml. of which contained 0.1 gram of potassium iodide, 1 ml. of 2 *N* sulfuric acid, and 1 ml. of starch indicator. Potassium iodate (0.001 *N*) was added from a micropipet in successive 0.002-ml. portions to the first appearance of a blue color. At 31° C. (room temperature in Baltimore in the summer of 1932), the following amounts of iodate iodine were necessary: 1 ml. volume, 0.08 γ; 10 ml.

volume, 0.5 γ; 100 ml. volume, 4 γ (1 γ = 0.001 mg.) Six times this amount of free iodine would be necessary for the production of a blue color, but the authors have chosen to express the results in terms of iodate iodine in order to define the sensitivity in terms of the amount of iodine present in the original material under analysis. The Erlenmeyer flasks employed for the experiments were respectively 25, 50, and 200 ml. At a temperature of 17° C., only 2 γ iodine was necessary to impart a blue color to 100 ml. of solution—that is, half the quantity required at 31° C. Therefore, the temperatures at which the thiosulfate solution is standardized and the actual determination is made should be approximately the same. Since completing this work a paper has appeared by Allott, Dauphinee, and Hurtley (*1*) reporting values very similar to those given here, though the authors fail to state the temperature in their experiments.

Since the sensitivity of the starch indicator when the total volume is 1 ml. is 0.08 γ of iodate iodine at 31° C., the determination at this temperature of quantities of iodine less than 8 γ would theoretically be subject to errors greater than 1 per cent. The authors have therefore confined their attention in this paper to quantities no smaller than 20 γ. It would appear that the titration of quantities of iodine smaller than this can be carried out more accurately at low temperatures where the sensitivity of the starch indicator is increased.

EFFECT OF ACIDITY AND IODIDE CONCENTRATION

Acid solutions of iodides decompose with greater or less rapidity according to their H^+ concentration to liberate free iodine. Upon this fact—namely, the oxidation of hydriodic acid by atmospheric oxygen—are based the objections to the titrimetric method for iodine determination. Since the reaction (formulistically)

$$H^+ + I^- \rightleftharpoons HI \qquad (1)$$

is reversible, it should be possible to have a minimum of hydriodic acid formed if both the acid and iodide concentrations are as low as possible. On the other hand, the solution should possess the requisite acidity and iodide content for the reaction

$$IO_3^- + 5\,I^- + 6\,H^+ \rightleftharpoons 3\,I_2 + 3\,H_2O \qquad (2)$$

to go to completion.

If the titration were carried out under an inert gas such as nitrogen or carbon dioxide, there should be no appreciable oxidation of hydriodic acid and the acid concentration could be neglected. This procedure, however, is burdensome in routine laboratory work, so efforts were made to determine the effect of acid and iodide concentrations on titrations carried out in the presence of atmospheric oxygen.

Consideration of the effect of pH on the titration of free iodine with thiosulfate at the acid concentrations to be employed can be neglected, since Reith (*20*) has shown that the reaction is quantitative at pH values below 6.

It was found that variation of the iodide concentration within certain limits did not markedly affect the procedure. Optimum conditions were obtained when 0.1 gram of potassium iodide was present in 50 ml. of solution.

The effect of acidity, however, was more striking. It can be seen from the data given in the third column of Table I that the acid normality of the solution must be 0.02 or higher in order to carry Reaction 2 rapidly to completion. In the presence of air there is a marked increase in titer as the acid strength becomes greater than 0.1 N. This increase is presumably due to the oxidation by air of the larger amount of hydriodic acid formed according to Equation 1, since no such increase is noted in the absence of oxygen (column 4). Therefore, if the titration of small quantities of iodine is to be made in the presence of air, the pH of the solution must be between 1.0 and 2.0 if serious errors are to be avoided. Solutions of potassium iodide with a pH between 1.0 and 2.0 show no appreciable oxidation by air even after standing 0.5 hour. The rate of air oxidation appears to decrease with temperature. It is therefore possible that titrations could be carried out in higher acid concentrations than those recommended here if lower temperatures were employed.

TABLE I. EFFECT OF ACIDITY

(5 ml. of 0.005 N KIO_3 titrated with $Na_2S_2O_3$. 0.1 gram of KI present, total volume 50 ml. Room temperature 20° ± 2° C.)

EXPERIMENT	ACID NORMALITY	THIOSULFATE TITER Exposed to air	THIOSULFATE TITER Under nitrogen
		Ml.	Ml.
1	0.0005	2.44	..
2	0.005	4.42[a]	..
3	0.02	4.42	..
4	0.04	4.43	4.40
5	0.05	4.44	..
6	0.10	4.44	4.42
7	1.0	4.49	4.41
8	2.0	4.53	4.42
9	4.0	..	4.43

[a] Very slow end point.

ESTIMATION OF IODINE

Because the use of chlorine water in Winkler's method has several disadvantages, chief among which is the fact that high results (*8*, *12*, *13*, *21*, *23*) may be obtained, the employment of bromine as originally proposed by Bugarszky and Horwath (*3*) has been instituted for purposes of oxidation.

An accurately measured portion of the potassium iodide solution was transferred to a 125-ml. Erlenmeyer flask. After the addition of 1 ml. of 2 N sulfuric acid and sufficient water to give a total volume of 50 ml., bromine vapor was added as previously described. A few glass beads were introduced and the contents of the flask boiled briskly over a thin sand bath. After the yellow color due to bromine had disappeared, the boiling was continued for 2 minutes in order to insure complete removal of that element. Upon cooling to room temperature, the sides of the flask were washed down with sufficient water to replace that lost by boiling. One milliliter of a freshly prepared 10 per cent potassium iodide solution was added, the flask was gently swirled, and the liberated iodine immediately titrated with thiosulfate.

Table II gives the result of a typical experiment and shows that the Winkler procedure gives satisfactory results when the precautions given here are followed.

TABLE II. DETERMINATION OF IODINE

EXPERIMENT	TOTAL VOLUME	2N H_2SO_4	KI ADDED	0.00512 N $Na_2S_2O_3$	0.001024 N $Na_2S_2O_3$	IODINE TAKEN	IODINE FOUND	DIFFERENCE
	Ml.	Ml.	Gram	Ml.	Ml.	Mg.	Mg.	Mg.
1	50	1	0.1	9.25	...	1.000	1.002	+0.002
2	25	0.5	0.05	4.64	...	0.501	0.502	+0.001
3	25	0.5	0.05	1.845	...	0.1995	0.200	+0.0005
4	10	0.2	0.02	...	4.54	0.1000	0.0983	−0.0017
5	10	0.2	0.02	...	2.27	0.0500	0.0492	−0.0008
6	10	0.2	0.02	...	0.915	0.0200	0.0198	−0.0002

USE OF SALICYLIC ACID. It is the practice of some workers to add salicylic acid or phenol directly after boiling the solution in order to destroy any traces of residual bromine. This procedure was apparently substantiated by the observation that determinations of iodine in which salicylic acid was added were invariably lower than in those to which the compound was not added. Later, however, this interpretation was shown to be incorrect by subjecting iodate solutions to the same treatment. A lowering of titer manifested itself in those cases where salicylic acid had been introduced even though no bromine was present in the solution prior to this mode of treatment. Moreover, titrations of iodate solutions in which bromine had been added (no salicylic acid added) and then boiled off did not differ from those in which none of this element had been present. Salicylic acid, therefore, apparently offers a reducing action and must not be added.

The small amount of salicylic acid present as a preservative in the starch solution has no harmful effects.

INTERFERENCE BY OTHER SUBSTANCES

Experiments on interference with the proposed procedure by certain elements and compounds were carried out according to the technic given above. In brief, the substance to be tested for its effect on the determination was added to 50 ml. of a solution containing 1 mg. of iodine and 1 ml. of 2 *N* sulfuric acid. The estimation of iodine was carried out in the usual manner.

IRON. When 0.1 mg. of iron was present, the results obtained were about 1 per cent too high, indicating that the added potassium iodide was being oxidized by the ferric salt. Correct figures were had when less than 0.1 mg. of iron was present. If the determination of iodine is carried out in the presence of larger amounts of iron, phosphoric acid should be added to remove the ferric ion.

BROMIDES. Since the oxidation of iodides by bromine is a reversible reaction, bromides may be expected to have some effect. It was found that no more than a twenty-fold excess of bromine over iodine could be present. When 30 mg. of bromine (as Br^-) were introduced, a 1 per cent loss of iodine took place and as much as a 30 per cent loss was observed when 50 mg. were present. Reith (*21*), on the other hand, has reported that a four hundred fold excess of the bromide ion may be present with no deleterious effects. This disagreement is probably due to the fact that he worked with quantities of 1 to 10 γ of iodine.

NITRITES. There should be little or no nitrites present. As small a quantity as 1 mg. of nitrous acid caused a 2 per cent loss of iodine. The azide method of Reith (*21*) was found to be highly effective in destroying even as much as 100 mg. of nitrous acid present in a determination.

CHLORIDES. Only large quantities of chlorides interfere.

OTHER SUBSTANCES. Sulfates interfere only when present in a nearly saturated solution. Ammonium salts and nitrates apparently have no effect if present in moderate amounts. Mercury does not interfere until sufficient quantities (30 to 50 mg.) are contained in solution and precipitate as mercuric iodide when potassium iodide is added, thus obscuring the end point. Only traces of alcohol may be present; in the extraction of iodides with this substance care must be taken, therefore, that all alcohol is evaporated off.

ANALYSIS OF IODIZED SALT

The use of iodized salt for the prevention of endemic goiter (*14*, *16*) is well known and various methods, both volumetric (*4*, *5*, *18*) and colorimetric (*6*, *24*), have been devised for the estimation of iodides in this product. The volumetric methods of Dunn and von Fellenberg were tested, but the results obtained were not satisfactory with iodine and sodium chloride mixtures comparable to the iodized salts as sold in America. Indeed, using the procedure of Dunn, losses of iodine as high as 50 per cent were experienced.

TABLE III. DETERMINATION OF IODINE IN PRESENCE OF SODIUM CHLORIDE

EXPERIMENT	NaCl PRESENT[a]	0.00500 *N* $Na_2S_2O_3$	IODINE ADDED	IODINE FOUND	DIFFERENCE
	Gram	*Ml.*	*Mg.*	*Mg.*	*Mg.*
1	20	5.37	1.000	0.568	−0.414
2	20	8.04	1.000	0.850	−0.150
3	10	9.40	1.000	0.994	−0.006
4	10	9.32	1.000	0.986	−0.014
5	5	9.45	1.000	0.999	−0.001
6	5	4.74	0.501	0.501	0.000
7	5	1.89	0.199	0.200	+0.001
8	5	0.95	0.100	0.101	+0.001

[a] Volume, 100 ml.

EFFECT OF CHLORIDES. The estimation of iodides in iodized salt resolves itself to a matter of determination of iodine in the presence of large amounts of chlorides. Accordingly, experiments were carried out to ascertain the interference, if any, of salt on the determination. Sodium chloride (C. P.) was carefully recrystallized from alcohol and weighed portions were added to solutions containing a known amount of iodine and 2 ml. of 2 *N* sulfuric acid in a volume of 100 ml. The iodine was then determined by the procedure given above.

Results obtained (Table III) show that no more than 5 grams of sodium chloride should be present in 100 ml. of solution if accurate results are desired. It is to be noted that the methods of Dunn and von Fellenberg depend upon determination of the iodine in a 20 per cent solution of iodized salt. Doubtless this high salt concentration accounts for failure to obtain correct figures with their analytical procedure.

ANALYSIS OF IODIZED SALT. The method finally adopted for the determination of iodine in iodized salt is as follows:

A 5-gram portion of the salt and 100 ml. of water were transferred to a 200-ml. Erlenmeyer flask and the contents of the vessel mixed until solution of the sodium chloride had taken place. Methyl orange indicator was added and 2 *N* sulfuric acid was introduced drop by drop until a pink color resulted which persisted on standing. (This treatment is necessary since table salts usually contain calcium phosphate or certain carbonates which are insoluble in neutral solution.) After the addition of 2 ml. of 2 *N* sulfuric acid and bromine vapor, a few glass beads were added and the solution boiled until the yellow color due to bromine had disappeared and then for 2 minutes longer. Upon cooling, the sides of the flask were washed down with approximately the amount of water lost by boiling, 2 ml. of a 10 per cent potassium iodide solution (freshly prepared) were added, the contents of the flask were gently swirled, and the liberated iodine was immediately titrated with 0.005 *N* thiosulfate, adding 2 ml. of starch indicator near the end point.

Analyses were made on several representative brands of iodized table salt as purchased on the open market. The results obtained are summarized in Table IV, and it can be seen that salts A, B_1, and B_2 contain an amount of potassium iodide which is far below their stated value. This is probably due to loss, since it has been shown by several investigators (*5*, *10*, *18*) that iodized salts may lose their iodine content with greater or less rapidity according to the form of the iodine compound contained, the presence of certain other elements in the salt, and the mode of storage.

TABLE IV. DETERMINATION OF POTASSIUM IODIDE IN IODIZED SALT

EXPERIMENT	BRAND	WEIGHT OF SAMPLE	0.00500 *N* $Na_2S_2O_3$	KI FOUND	KI CLAIMED[a]
		Grams	*Ml.*	%	%
1	A	5.18	0.63	0.00168	0.01
2	A	5.40	0.64	0.00164	0.01
3	B_1	5.29	5.08	0.0133	0.023
4	B_1	5.42	5.10	0.0130	0.023
5	B_2	5.14	4.96	0.0133	0.023
6	B_2	5.05	4.91	0.0134	0.023
7	B_3	5.00	7.64	0.0211	0.023
8	B_3	5.00	7.64	0.0211	0.023
9	C	5.13	7.37	0.0199	0.02
10	C	5.12	7.42	0.0200	0.02

[a] Label statement.

As a final verification of the procedure, determinations of iodine recovery were carried out. Twenty-five grams of iodized salt (sample B_3) were dissolved in water and the volume was made up to 500 ml. after total solution by careful acidification as given above. Aliquot portions of 100 ml. were taken for analysis and are represented by experiments 7 and 8 in Table IV. To each of two other aliquot portions was added 0.501 mg. of iodine. After estimations of the total iodine present, it was found that 0.503 and 0.502 mg., respectively, of iodine were recovered.

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Errors in Determination of Carbonate in Boiler Waters

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From the results of adsorption tests on the Winkler method it is apparent that the method is susceptible to serious errors in the presence of sulfate. It will not prove satisfactory for boiler waters where the sulfate ion is present in appreciable concentrations.

The phenolphthalein–methyl orange titration is not accurate in solutions whose concentrations of carbonate are below 60 parts per million. At 30 parts per million of carbonate, the minimum possible error which may be expected is 26 per cent.

Methods have been suggested for improving the accuracy of this determination of carbonate. It is advised, however, that any method used for the determination of carbonate be checked by the evolution method (13) which is known to be accurate in practically all cases.

THE concentration of carbonate present in a boiler water is ordinarily determined, in plant practice, by either the modified Winkler method (*9*) or the phenolphthalein–methylorange method (*1*). Like most analytical procedures for boiler waters, these two methods have been taken from the field of analysis of natural waters, and without material modification or very extensive checking have been applied directly to boiler waters. Between natural waters and boiler waters there are very material differences; and these differences are especially great in the case of the carbonate. In natural waters an extremely low concentration of hydroxide and a comparatively high concentration of carbonate are ordinarily found. In samples removed from a boiler the reverse is usually true.

The carbonate concentrations in a boiler treated with sodium carbonate for the prevention of scale usually run from 5 or 6 to 50 or 60 parts per million. In most natural waters the concentration of carbonate is above 60 parts per million. The extension of an analytical method to lower concentrations than those for which it has been designated will often cause the method to be inaccurate or perhaps fail altogether. As a considerable amount of previous work has shown (*13, 17*), and as will be shown in the present paper, the Winkler method and the phenolphthalein–methyl orange method for the determination of carbonate become inaccurate at low concentrations, but for different reasons. The Winkler method has been found to be inaccurate in the presence of sulfate; the phenolphthalein–methyl orange method because it has been extended to carbonate concentrations which are too low.

WINKLER METHOD

The Winkler method, as applied to the determination of the carbonate concentration of a sample containing hydroxide and carbonate, consists in the titration of one sample directly to the phenolphthalein end point; a second sample, after the precipitation of the carbonate by the addition of barium chloride, is also titrated to the phenolphthalein end point. The difference in the amount of acid used in these two titrations is equivalent to the carbonate present.

The presence of sulfate in the samples causes the precipitation of the barium sulfate before barium carbonate is precipitated, because the sulfate is considerably more insoluble than the carbonate. The fact that the sulfate causes errors in the Winkler method has been definitely shown (*10, 13*). It seems desirable to ascertain whether the errors in the presence of sulfate are due to the occlusion or adsorption of hydroxide by the precipitate of barium sulfate. This would seem to be highly probable, since both barium sulfate and carbonate have been shown to occlude or adsorb many compounds (*2, 4, 5, 7, 8, 12, 14*).

EXPERIMENTAL METHOD. The method used consisted essentially in making up solutions of accurately known concentrations of hydroxide which contained sulfate, precipitating the sulfate as barium sulfate, and then titrating back the hydroxide to find how much was still present in the solution. This back-titration was performed both on the solution containing the precipitate and on an aliquot portion after the precipitate had been filtered off.

All the solutions used were made up with boiled distilled water and great care was exercised to keep them carbonate-free throughout the duration of the test. The carbonate-free sodium hydroxide was made up with sodium metal in the manner described by Clark (*3*). The sodium hydroxide solution was standardized against potassium acid phthalate. The hydrochloric acid solution was standardized against the hydroxide solution. An evolution analysis for carbonate was run on all the solutions and the distilled water used. This indicated that the maximum amount of carbonate which could be present in any of the samples titrated was less than 0.8 part per million. The sodium sulfate and the barium chloride solutions used were neutralized until the maximum possible error they could cause was less than 0.01 cc. of the titrating acid.

For those samples in which an aliquot was titrated the apparatus shown in Figure 1 was used. It consists essentially of a tower filled with soda lime and ascarite for removing carbon dioxide from the air which was to come in contact

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with the sample; the sample with the precipitate was held in the 100-cc. volumetric flask shown; this sample filtered down through the crucible into the lower suction flask. The crucible used had a porous bottom and over this were placed four layers of fine filter paper. After 10 minutes for precipitation at room temperature, a 100-cc. sample could be readily filtered in this equipment in 10 or 20 minutes, without having a chance to come in contact with the carbon dioxide of the air.

In the actual filtration of the sample the first 10 or 20 cc. were discarded to allow the filter paper to come to equilibrium with the solution, or the filter paper itself might have adsorbed hydroxide. The aliquot was then taken from the remainder. No correction was made for the change in the volume of the solution during precipitation. Some tests indicated that this change was about 0.25 cc., which would produce a difference of about 0.03 cc. on the titrating acid used. This was about within the limits of accuracy of the experiments on these titrations of the aliquots.

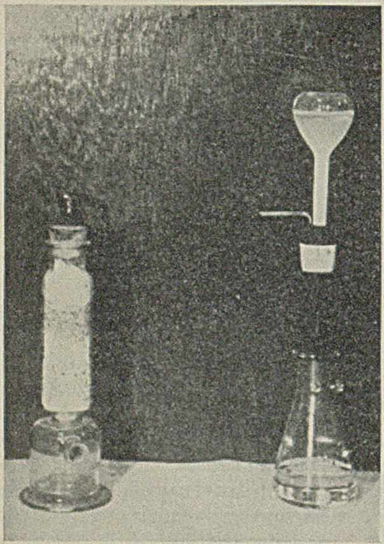

FIGURE 1. APPARATUS FOR FILTERING OFF BARIUM SULFATE PRECIPITATE

All pipets and burets used were calibrated and the measurement of the volume of the titrating acid used was made accurate within 0.02 cc.

RESULTS OF TITRATIONS. Table I shows the results secured for a series of samples which were titrated back with acid in the presence of the barium sulfate precipitate. This represents, of course, the procedure generally used in the Winkler method where the precipitate is not filtered off.

TABLE I. TITRATION OF HYDROXIDE IN PRESENCE OF BARIUM SULFATE PRECIPITATE

SAMPLE	OH	SO_4	NaOH	HCl REQUIRED	HCl USED	CO_3 EQUIVALENT
	P. p. m.	*P. p. m.*	*Cc.*	*Cc.*	*Cc.*	*P. p. m.*
5	102	300	10.00	12.35	12.10	7.3
	102	300	10.00	12.35	12.13	6.4
3	102	500	10.00	12.35[a]	12.13	6.4
	102	500	10.00	12.35	12.10	7.3
4	102	1500	10.00	12.35	11.87	13.9
	102	1500	10.00	12.35	11.86	14.2
6	254	500	25.00	30.94[a]	30.43	14.8
	254	500	25.00	30.94	30.43	14.8
7	254	1500	25.00	30.94	30.05	25.8
	254	1500	25.00	30.94	30.08	25.0

[a] Values determined by titration of a 100-cc. sample.

5 minutes for precipitation at room temperature. Stoppered.
10 cc. neutralized 10 per cent $BaCl_2$ added.
NaOH solution 0.05986 *N*.
HCl solution 0.04837 *N*.
100-cc. samples.

Since the hydrochloric acid required is the amount of acid necessary to titrate the sodium hydroxide added to the sample, the difference between this value and the hydrochloric acid used represents the amount of hydroxide which was occluded or adsorbed during the precipitation of the barium sulfate. This difference in the amount of acid used has been converted into carbonate equivalent in parts per million, exactly as if this analysis were being applied to the determination of carbonate. This carbonate equivalent really represents the positive error in the carbonate concentrations when the Winkler method is being applied to solutions of these concentrations of hydroxide and sulfate. As is seen, this error runs from about 7 to 25 parts per million of carbonate and, since in boiler waters we are usually dealing with concentrations from about 5 to 60 parts per million, this may cause an extremely large error. The error also tends to increase with increase in either the hydroxide or sulfate concentration.

Table II shows the results secured in titrating a 50-cc. aliquot after filtering off the precipitate of barium sulfate.

TABLE II. TITRATION OF 50-CC. ALIQUOT AFTER FILTERING OFF BARIUM SULFATE

SAMPLE	OH	SO_4	NaOH	HCl REQUIRED	HCl USED	CO_3 EQUIVALENT[a]
	P. p. m.	*P. p. m.*	*Cc.*	*Cc.*	*Cc.*	*P. p. m.*
8	102	500	10.00	6.18[b]	5.74	25.6
	102	500	10.00	6.18	5.75	25.0
9	102	1500	10.00	6.18	5.57	35.4
	102	1500	10.00	6.18	5.66[c]	30.2
10	254	500	25.00	15.47[b]	14.83	37.2
11	254	1500	25.00	15.47	14.62	49.4

[a] Calculated on the basis of 100-cc. sample.
[b] Values determined by titration.
[c] Faint turbidity present in filtrate.

10 minutes for precipitation at room temperature.
10 cc. neutralized 10 per cent $BaCl_2$ added.
NaOH solution 0.05986 *N*.
HCl solution 0.04837 *N*.
100-cc. samples.

The fifth and sixth columns apply to the 50-cc. aliquot; twice the difference between the two would represent the amount of hydroxide adsorbed or occluded in the 100-cc. sample, the value used in the carbonate equivalent. This makes the last column in Tables I and II directly comparable and, as shown, the error is much larger in the filtered sample. This indicates that when the Winkler method is applied to solutions containing sulfate a larger error for adsorption or occlusion will occur when the precipitate is filtered off than when it is not. It is very possible that some of the adsorption of the hydroxide occurs on the surface of the barium sulfate precipitate and that, when the precipitate is left in the solution which is being titrated, a portion of the hydroxide on the surface may enter into the back-titration.

The adsorption or occlusion of hydroxide by the barium sulfate precipitate will, of course, cause some error in the determination of the hydroxide concentration as well as the carbonate. Since the hydroxide in boiler waters is usually high, and since an error of 10 parts per million in the carbonate corresponds to an error of only 3.5 parts per million of hydroxide, this will not be important in routine work. Where a high degree of accuracy is required for the hydroxide determination it may become important.

Straub has indicated (*16*) that the precipitation of sulfate in an alkaline solution does not produce serious errors in the determination of sulfate. This checks well with the present work which indicates that to some extent the hydroxide is adsorbed on the surface and this might be removed by exposure of the material to wash water, especially that containing carbon dioxide. The precipitates from the six filtered samples in Table II were washed with carbon dioxide–free water until the wash water was acid to phenolphthalein and were then placed in a solution of excess standard acid and allowed to stand, with occasional shaking, for 24 hours. On back-titration it was found that practically none of the excess acid was neutralized by the precipitate. This would indicate that the wash water may have, to a considerable extent, removed the hydroxide adsorbed on the surface and that the rest of the hydroxide was occluded in such a manner that it could not react with the acid.

Since the work which has been done shows that the Winkler method for carbonate is susceptible to large errors in the presence of sulfate, it would seem desirable to consider ways of removing this error. The use of strontium chloride instead of barium chloride for the precipitation of the carbonate has been found satisfactory; when strontium is used it is not necessary to precipitate the sulfate at all, and the strontium carbonate precipitated does not occlude or adsorb enough hydroxide to produce a measurable error (*15*). The chief disadvantage with the use of strontium is that the sample in which the precipitation is carried out has to be boiled. At the present time this seems, however, to be the most satisfactory method for carbonate unless it is possible to use the evolution method (*13*).

PHENOLPHTHALEIN–METHYL ORANGE METHOD

The application of the phenolphthalein–methyl orange method to a solution containing hydroxide and carbonate assumes that at the phenolphthalein end point all the hydroxide has been titrated and the carbonate has been titrated to bicarbonate; at the methyl orange end point the bicarbonate is assumed to have been converted to carbonic acid. From this reasoning the amount of acid used between the phenolphthalein and methyl orange end points is equivalent to the carbonate present in the sample. Several investigators have found that this method is not reliable at low concentrations of carbonate (*13*, *17*) and it has been found especially inaccurate in actual boiler-water samples. It seems desirable to ascertain if there is anything fundamentally wrong with this method at low concentrations of carbonate, and to determine at which concentrations it may be expected to become reasonably accurate. In order to do this, a series of titration curves for mixtures of hydroxide and carbonate were calculated.

DERIVATION OF EQUATIONS. The equation for the titration curve—that is, the curve of pH against cubic centimeters of acid required to reach a given pH—is derived very simply by writing all the fundamental equations for the sample involved. Assuming a solution containing hydroxide, carbonate, sodium, and the indicators phenolphthalein and methyl orange which is being titrated with hydrochloric acid, the following equations may be written:

$$H_2CO_3 + HCO_3^- + CO_3^{--} = c_2 \qquad (1)$$

$$Na^+ + H^+ = OH^- + HCO_3^- + 2(CO_3^{--}) + Cl^- + (In^-)_p + (In^-)_m \qquad (2)$$

$$(H^+)(OH^-) = K_w = 10^{-14} \qquad (3)$$

$$Na^+ = c_1 + 2c_2 \qquad (4)$$

$$K' = \frac{(H^+)(HCO_3^-)}{H_2CO_3} = 3 \times 10^{-7} \qquad (5)$$

$$K'' = \frac{(H^+)(CO_3^{--})}{HCO_3^-} = 6 \times 10^{-11} \qquad (6)$$

$$K_p = \frac{(H^+)(In^-)_p}{(HIn)_p} = 1 \times 10^{-10} \qquad (7)$$

$$K_m = \frac{(H^+)(In^-)_m}{(HIn)_m} = 5 \times 10^{-4} \qquad (8)$$

Where c_1 = moles per liter of NaOH added
c_2 = moles per liter of Na_2CO_3 added
c_3 and c_4 = moles per liter of phenolphthalein and methyl orange added, respectively
HCO_3^- = moles per liter of HCO_3 ion in the solution, etc.
In = indicator

Equation 1 states that the sum of all the carbonate in the solution is equal to the total carbonate; 2 is the equation for the electroneutrality of the solution; 4 defines the total sodium present; 3, 5, and 6 are the equations for the dissociation of water, the first dissociation constant of carbonic acid, and the second dissociation constant of carbonic acid, respectively; and 7 and 8 are the dissociation constants of phenolphthalein and methyl orange, respectively.

Substituting in 2 so as to eliminate all the variables except Cl^-, which represents the mole per liter of acid added, and H^+ Equation 9 is obtained. The values for the various dissociation constants have also been inserted.

$$Cl^- = c_1 + 2c_2 + H^+ - \frac{K_w}{H^+} - 3c_2 \times 10^{-7}\left[\frac{H^+ + 1.2 \times 10^{-10}}{(H^+)^2 + 3 \times 10^{-7}(H^+) + 1.8 \times 10^{-17}}\right] - \frac{6 \times 10^{-15}}{H^+ + 10^{-10}} - \frac{5 \times 10^{-10}}{H^+ + 5 \times 10^{-4}} \qquad (9)$$

This equation assumes that all the hydroxide has been added as sodium hydroxide and all the carbonate as sodium carbonate. The hydrolysis of the sodium carbonate is negligible because of the high initial pH of the samples dealt with. The concentration of phenolphthalein was assumed to be about that obtained when 4 drops of a 1 per cent solution are added to a 100-cc. sample ($c_3 = 6 \times 10^{-5}$); and of methyl orange that obtained when 4 drops of a 0.02 per cent solution are added to the same sample ($c_4 = 1 \times 10^{-6}$). The activity coefficients are used as unity and the effect of dilution due to the addition of the titrating acid is neglected. The effect of dilution, as will be shown later, is very small in such samples as are usually dealt with.

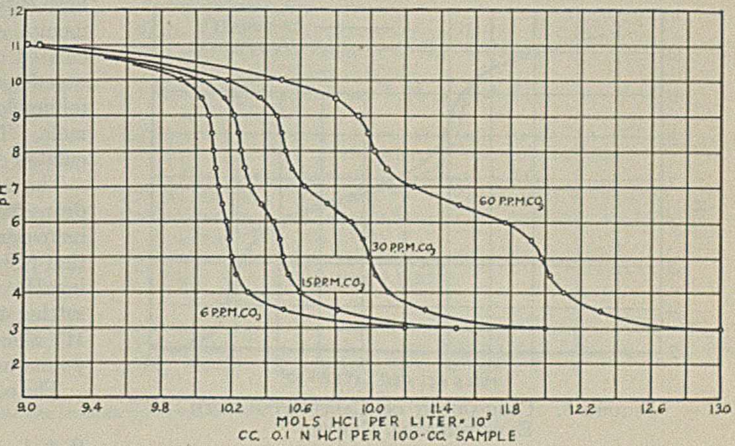

FIGURE 2. TITRATION CURVES FOR SOLUTIONS CONTAINING 170 P. P. M. HYDROXIDE AND VARIOUS CONCENTRATIONS OF CARBONATE

By selecting values for H^+ corresponding to every 0.5 pH and substituting them in Equation 9, the corresponding amount of acid (Cl^-) required to reach this pH is obtained. Using $c_1 = 10^{-2}$ (170 p. p. m. of OH) and $c_2 = 1 \times 10^{-4}$; 2.5×10^{-4}; 5.0×10^{-4}; and 1×10^{-3}; (6, 15, 30, and 60 p. p. m. of CO_3, respectively) a series of curves was calculated in the manner described.

TITRATION CURVES. The curves secured are shown in Figure 2. In the case of the phenolphthalein end point it is evident that the reversal of the direction of the curve (inflection point) for the four curves shown always comes between a pH of 8 and 8.5. This inflection point comes sufficiently close to the colorless point of phenolphthalein (pH of about 8) so that the end point should be satisfactory. At higher concentrations of carbonate the slope of the curve in the region of the inflection point is less, and this causes a slow color change which will make an accurate determination of the end point somewhat difficult. For the concentrations shown on this figure the phenolphthalein end point should be fairly satisfactory.

In the case of the methyl orange end point a number of difficulties appear. The methyl orange end point may be taken as a pH of 3.9 corresponding to 20 per cent converted to the acid form. This is about the pH that would ordinarily be attained in routine practice when a color comparison solution is not used. It is seen from Figure 2 that the lower inflection points occur at a much higher pH than this value of 3.9 for the methyl orange end point. At a pH of 3.9 the curves are very flat. This will make the color change extremely slow and the end point difficult to detect. It is apparent in this region that a considerable amount of acid may be added with only a small change in the pH.

A more startling fact appears, however, if the amount of acid which should be required to titrate the carbonate in the 6 parts per million sample, on the basis of the regular phenolphthalein–methyl orange calculations, is compared to the amount actually used for this titration as shown by the curve. Six parts per million of carbonate are 0.1 millimole per liter. By the usual phenolphthalein–methyl orange calculations this would require 0.10 millimole of hydrochloric acid per liter for titration or on this plot would require from 10.10 to 10.20 millimoles of hydrochloric acid. Actually, to go from pH 8.3 to 3.9 requires from 10.1 to 10.32 millimoles of acid; 0.22 millimole has been used instead of the required 0.10 millimole. This is an error of 120 per cent. The rest of the curves show similar errors, the percentage error decreasing, however, as the carbonate increases. To a large extent this error is due to the presence of the water in the sample which is not taken account of in the assumptions on which the phenolphthalein–methyl orange method is based.

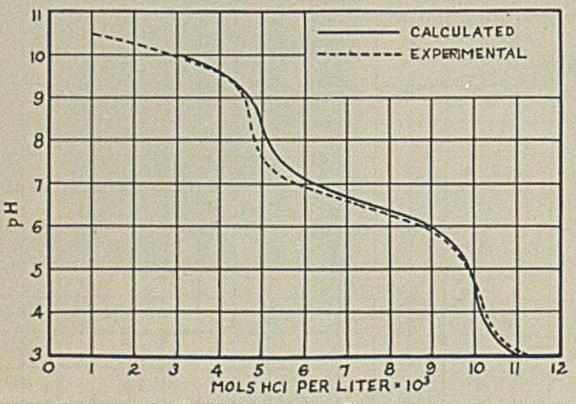

Figure 3. Comparison of Calculated with Experimental Curve

Table III shows the millimoles per liter of acid which would be required to titrate the carbonate present in these four samples between the phenolphthalein and methyl orange end points according to the usual calculations, the millimoles per liter of acid used according to the curves, and the per cent error in the carbonate. The conclusion that the phenolphthalein–methyl orange method is too inaccurate to be used for even routine work on samples containing less than 60 parts per million of carbonate is inescapable.

Table III. Error in Determination of Carbonate Using Phenolphthalein–Methyl Orange Titration

CO_3	HCl Required[a]	HCl Used[b]	CO_3 Error
P. p. m.	*Millimoles/l.*	*Millimoles/l.*	%
6	0.10	0.22	120
15	0.25	0.37	48
30	0.50	0.63	26
60	1.00	1.14	14

[a] Based on usual phenolphthalein–methyl orange calculations.

[b] Determined from acid required to titrate between pH 8.3 and 3.9 according to curves in Figure 2.

Moreover, the errors shown represent the absolute minimum error that may be expected. The effect of dilution and loss of carbon dioxide during the titration, the possibility of the samples picking up carbon dioxide when it is alkaline, and the effect of organic matter or buffer salts in the solution will all tend to increase the size of this error.

In order to demonstrate the accuracy of the method of calculation used, a calculated curve was compared with an experimental curve as shown in Figure 3. These curves are for 300 parts per million of carbonate. The experimental curve was taken from the curves published by Greenfield and Buswell (*6*), and is for 0.01*M* solution, using a rocking hydrogen electrode. The values secured using the bubbling hydrogen electrode (*11*) cannot be compared with the calculated curve, because the flow of hydrogen removes too much carbon dioxide from the sample.

Figure 3 shows extremely good agreement, the maximum deviation being only 0.3 millimole. The inflection points on both curves occur at the same pH. As predicted, the experimental curve actually shows a larger error than the calculated curve. The effect of dilution by the titrating acid was determined for this calculated curve and is less than 0.02 millimole except at a pH of 3.0 where it becomes 0.10 millimole. The effect tends to bring the experimental and calculated curves into slightly better agreement.

The curve in Figure 2 shows that the lower inflection point drops from a pH of about 5.3 to about 4.60 as the carbonate increases from 6 to 60 parts per million. The upper inflection point remains almost constant at about 8.3. Substituting $H^+ = e^{-2.303n}$ in Equation 9, differentiating twice, and setting the second derivative equal to zero an equation in H^+ alone may be secured from which the actual inflection points may be accurately calculated.

The equation finally secured is the following:

$$0 = 1 - \frac{K_w}{(H^+)^2} - c_2 \times \left[\frac{(H^+)^4 - 3 \times 10^{-7}(H^+)^3 + 5.4 \times 10^{-24}(H^+) - 3.24 \times 10^{-34}}{[(H^+)^2 + 3 \times 10^{-7}(H^+) + 1.8 \times 10^{-17}]^3}\right] \qquad (10)$$

Using different values of c_2 (the carbonate concentration) this equation may be solved for H^+. The upper inflection point—that is, the phenolphthalein end point—will be found to be independent of concentration of carbonate and always occurs between a pH of 8.36 and 8.37.

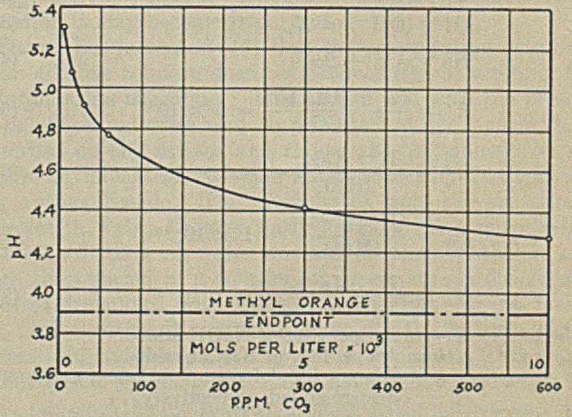

Figure 4. Change of Methyl Orange Inflection Point with Concentration of Carbonate

The position of the lower inflection point, which is supposed to be measured by the methyl orange end point, as was indicated by Figure 2, is dependent on the concentration of carbonate present. Figure 4 shows how the position of the inflection point varies with carbonate concentration. The position of the methyl orange end point (pH of 3.9) is marked on this chart and deviates most widely from the inflection point at low carbonate concentrations. This shows, again, why the phenolphthalein–methyl orange titration is so inaccurate at low concentrations. The curve shown crosses the pH of 3.9 around 6000 parts per million of carbonate (0.10 *M*) and at this point the titration should be quite accurate. This is found to be true experimentally.

Calculations were made to see if the position of the inflection points agreed with the stoichiometric values for the titration of bicarbonate to carbonic acid as assumed in the phenolphthalein–methyl orange method. At the upper pH the position of the inflection point was always within 0.02 per cent of the correct position. At the lower pH the maximum deviation was 0.4 per cent. These errors are not serious and it is not the deviation of the inflection point from the stoichiometric equivalent point that causes the errors, but the fact that the pH of the lower inflection point changes with concentration and that in low concentrations of carbonate the indicator is not properly selected to give the correct end point.

The accuracy of the method might be improved by using an indicator which changes color at a higher pH than methyl orange. If such an attempt is made, it is absolutely necessary that accurate color comparison blanks should be prepared which will indicate the correct end points. One difficulty with such a method is the necessity of knowing the approximate carbonate concentration in order to select the correct end point. Another possible source of error that will have to be guarded against is salt errors in the indicators. If an attempt is made to use different indicators on boiler waters, it seems absolutely necessary that the method should be checked at least occasionally (*13*).

ACKNOWLEDGMENT

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Composition of Fatty Acid Mixtures

I. Relation of Composition to Dalican's Curve

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IN THE manufacture of commercial fatty acids, it is customary to estimate cold press yields from the titers of pressroom products by making use of a table of empirical data showing the percentages of commercial oleic acid and commercial stearic acid in mixtures of different titer. Such data are extremely useful in the control of plant operations, but their purely empirical nature and correspondingly limited applicability must always be kept in mind. Thus, while it is perhaps generally recognized as hazardous to apply the same set of data to stocks differing widely in source, it is not as generally realized that, even in the case of a single stock, such calculations give no reliable information whatever regarding the actual percentages of saturated and unsaturated fatty acids present.

There are two important considerations involved here, neither of which must be lost sight of. In the first place, when a solid fraction is separated from a fatty acid mixture by cooling, both fractions are solutions and each contains all components present in the original mixture. The solid which separates, considered apart from any entrained or adsorbed liquid, is a solid solution—that is, a wholly solid phase containing, however, components that are themselves (when alone, but not now) liquids, just as a solution of salts in water is wholly liquid although it contains components that are, when alone, solids. Similarly, the liquid fraction contains solid fatty acids in solution and, as will be seen, a considerable percentage of these dissolved solid acids can never be separated, even theoretically, by chilling.

A second and more important consideration is the fact that the customary analytical methods applied to the original mixture and to the end products are themselves impossible of interpretation, in any exact way, in terms of fatty acid composition. The free fatty acid value assumes an average molecular weight which is purely arbitrary or involves assumptions as to composition. The iodine value assumes the presence of only mono-unsaturated acids unless combined with the thiocyanogen iodine value which has brought a notable advance in analytical procedures by providing an index to more highly unsaturated acids. In either event, the analytical results are controlled by the purely empirical time factor involved in the iodine value. This reaction time was established originally by working with some known product and assuming that the proper time for the method is the time in which, in this case, the amount of substitution that one does get just makes up for enough of the addition at double bonds that one does not get, to give, as a result, exactly the iodine value that one started out to get. And, in the reaction mixture in which this time was thus determined, the highly sensitive and all-important reaction velocities were necessarily different than in the case of the mixtures later analyzed, because of considerable differences in chemical environment.

It is the writer's conviction that only by perfecting methods that determine individual fatty acid components directly can fatty acid and soap chemists hope to build up reliable conceptions of the composition and changes of composition of their stocks in process. Because of the closely similar chemical properties of the fatty acids, such methods are certain to be physical-chemical methods. One of these is the mixed-melting point method developed by Twitchell (*7*) and later used by McGregor and Beal (*6*) in their study of the composition of menhaden oil. Further improvements in this method have more recently been made and will be described in a later communication.

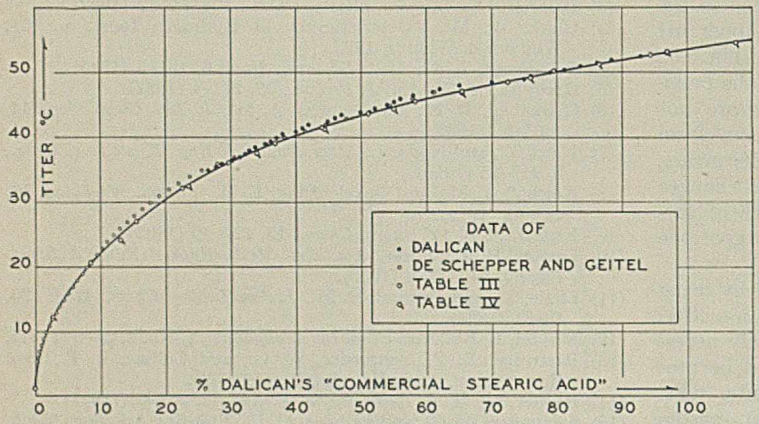

Figure 1. Dalican Curve Showing Titers of Fatty Acid Mixtures as a Function of Their Content of Commercial Stearic Acid

The present paper discusses the use of a table of data published originally in 1868 by Dalican, who devised the titer test itself, and still used to determine yields in the pressing operation. Dalican's data, modified to apply to the fatty acids rather than to their glycerides, and extended to lower titers by means of similar data published by de Schepper and Geitel (*2*), are presented graphically and compared with titers obtained from present-day commercial stocks. The important relation between the composition of fatty acid mixtures and their melting points, or titers, is also shown graphically for the simple palmitic-stearic-oleic system in a way which makes clear the effect of the presence of linolic acid in such a system and just how Dalican's curve fits into this picture.

Dalican's Table

In the separation of solid from liquid fatty acid by pressing, it is obvious that if the percentages of stearic acid in the stock charged, in the oil and in the press cake, can be estimated from their respective titers, then the yield follows at once from the fact that the amount of stearic acid in the two fractions must equal that in the original mixture before pressing.

Data for this purpose are furnished by Dalican's table as printed in Lewkowitsch (*4*). This table shows yields of commercial stearic acid and commercial oleic acid obtainable from fats of different titer. The figures are based on the glycerides and thus add in each case to 95 per cent. By dividing by 0.95, yields on the free fatty acid basis are obtained.

For lower titers, extension can be made on the basis of a similar table by de Schepper and Geitel (*2*), also reproduced in Lewkowitsch (*5*). This table is not directly comparable with Dalican's, since it gives percentages of "stearin" of solidifying point 48° C., whereas Dalican's stearic acid was evidently of about 54° C. titer. According to Dalican's data, a stock of 48° C. titer contains 65 per cent commercial stearic acid. The data of de Schepper and Geitel can, therefore, be expressed in terms of Dalican's stearic acid by multiplying by 0.65.

Dalican's data and those of de Schepper and Geitel, thus converted to the same basis, are given in Tables I and II.

It should, of course, be apparent from the fact that stocks of widely different chemical composition might have the same titer, that the data of Dalican and of de Schepper and Geitel cannot hold in any absolute way. For stocks that are fairly uniform as to source and are blended according to a fixed formula, however, an empirical relationship of that sort should hold with but little variation. De Schepper and Geitel stress this point particularly. They show the wide difference in the curves for palm oil, for tallow, and for mixtures of the two and they recommend that works chemists establish their own data with their own stocks.

The following experiments constitute such a check with commercial fatty acid stocks:

A sample of 1842 grams of run-off fatty acids, titer 38.95° C., was pressed at 24° C. for 10 minutes at 5000 pounds per square inch in a laboratory press; 569.5 grams (38 per cent) of pressed cake were obtained, having a titer of 50.15° C. The titer of the oil was 20.70° C. Samples of the oil and cake were then recombined in accurately weighed proportions and the titers of the mixtures recorded.

By pressing at 32.2° C., 357.2 grams of cake from the above experiment were further separated, giving a cake of 52.80° C. titer and an oil of 36.00° C. titer. The yield of cake here was 77.2 per cent.

Four hundred grams of the cold pressed oil were cooled in a refrigerator overnight and then placed in an ice bath while 30.5 grams of oil were drawn off from the semisolid mass through a cloth filter. The titer of this oil was 1.1° C., while that of the remaining 92.4 per cent was 21.45° C.

Table I. Dalican's Table

Titer	Commercial Stearic Acid	
	Fat basis	Fatty acid basis
° *C.*	%	%
35	25.20	26.53
35.5	26.40	27.79
36	27.30	28.74
36.5	28.75	30.26
37	29.80	31.37
37.5	30.60	32.21
38	31.25	32.90
38.5	32.15	33.84
39	33.44	35.20
39.5	34.30	36.10
40	35.15	37.00
40.5	36.10	38.00
41	38.00	40.00
41.5	38.95	41.03
42	39.90	42.00
42.5	42.75	45.00
43	43.70	46.00
43.5	44.65	47.00
44	47.50	50.00
44.5	49.40	52.00
45	51.30	54.00
45.5	52.25	55.00
46	53.20	56.00
46.5	55.10	58.00
47	57.95	61.00
47.5	58.90	62.00
48	61.75	65.00
48.5	66.50	70.00
49	71.25	75.00
49.5	72.20	76.00
50	75.05	79.00
50.5	77.10	81.16
51	79.50	83.69
51.5	81.90	86.21
52	84.00	88.42
52.5	88.30	92.95
53	92.10	96.95

Table II. Data of de Schepper and Geitel Converted to Basis of Dalican's Table

Solidifying Point	Stearin of Solidifying Pt. 48° C.	Dalican's Com'l Stearic Acid
° *C.*	%	%
6	0.3	0.2
7	0.8	0.5
8	1.2	0.8
9	1.7	1.1
10	2.5	1.6
11	3.2	2.1
12	3.8	2.5
13	4.7	3.1
14	5.6	3.6
15	6.6	4.3
16	7.7	5.0
17	8.8	5.7
18	9.8	6.3
19	11.1	7.2
20	12.1	7.9
21	13.2	8.6
22	14.5	9.4
23	15.7	10.2
24	17.0	11.0
25	18.5	12.0
26	20.0	13.0
27	21.7	14.1
28	23.3	15.1
29	25.2	16.4
30	27.2	17.7
31	29.2	19.0
32	31.5	20.5
33	33.8	22.0
34	36.6	23.8
35	39.5	25.7
36	43.0	28.0
37	46.9	30.5
38	50.5	32.8
39	54.5	35.4
40	58.9	38.3
41	63.6	41.4
42	68.5	44.5
43	73.5	47.8
44	78.9	51.3
45	83.5	54.3
46	89.0	57.9
47	94.1	61.1
48	100.0	65.0

According to the data of Tables I and II, the cold pressed cake, having a titer of 50.15° C., contained 79.6 per cent commercial stearic acid, and the cold pressed oil, titer 20.7° C., contained 8.4 per cent. If we accept these two values, the composition of the other samples, in terms of Dalican's "commercial stearic acid," is determined by the percentages of the intermediate mixtures and the yields obtained in the hot pressing and chilling experiments. The results are given in Table III.

Table III. Titers of Technical Fatty Acid Mixtures of Varying Commercial Stearic Acid Content

Sample	Cold Pressed Oil	Cold Pressed Cake	Titer	Dalican's Commercial Stearic Acid
	%	%	° C.	%
1	100.0	..	20.70	8.4
2	90.0	10.0	27.05	15.5
3	80.0	20.0	32.20	22.6
4	70.0	30.0	36.20	29.8
5	60.0	40.0	39.10	36.9
6	50.0	50.0	41.60	44.0
7	40.0	60.0	43.70	51.1
8	30.0	70.0	45.60	58.2
9	20.0	80.0	47.10	65.4
10	10.0	90.0	48.65	72.5
11	..	100.0	50.15	79.6
12	Hot pressed cake		52.80	94.4
13	Chilled oil		1.10	−0.1

A second series of values was obtained by determining the titers of mixtures made up from commercial grades of double-pressed distilled stearic acid and double-distilled red oil. These results are given in Table IV. Conversion to the basis of Dalican's commercial stearic acid was made by accepting the published data for mixtures having the titers of samples 1 and 10. Sample 11 is thus found to contain 107.5 per cent of Dalican's stearic acid, a figure which results from the fact that it has a higher titer than the sample Dalican used.

Table IV. Titers of Mixtures of Commercial Stearic Acid and Red Oil

Sample	Commercial Stearic Acid	Commercial Red Oil	Titer	Dalican's Commercial Stearic Acid
	%	%	° C.	%
1		100.00	12.25	2.5
2	10.00	90.00	24.25	13.0
3	20.00	80.00	32.53	23.5
4	30.00	70.00	37.72	34.0
5	39.97	60.03	41.19	44.5
6	50.00	50.00	44.29	55.0
7	60.00	40.00	46.92	65.5
8	70.00	30.00	49.26	76.0
9	79.96	20.04	51.29	86.5
10	89.96	10.04	53.11	97.0
11	100.00	...	54.70	107.5

In taking the titers the standard procedure was carefully followed. The thermometer used was standardized by comparison with a thermometer certified by the U. S. Bureau of Standards and corrections were made for the temperature of the emergent stem.

The results of these experiments, together with the data of Dalican and de Schepper and Geitel, are shown graphically in Figure 1.

Titers of Fatty Acid Mixtures

The relation of titer to composition in technical fatty acid mixtures is most readily visualized by considering the three-dimensional diagram, Figure 2.

Here the actual situation is simplified by considering all mixtures as composed of only palmitic, stearic, and oleic acids. The base, *P′ S′ O′*, is the familiar triangular composition diagram within which any point represents a definite mixture of three components, in this case palmitic, stearic, and oleic acids. Titers are laid out on the vertical, temperature scale. The titers of all possible mixtures thus determine a surface, *OASJPBO*, with peaks at the three points *P*, *S*, and *O*, representing the individual acids and a minimum at some point, *C*. Contours of this surface, such as shown at *TUV*, if projected onto the base, give lines of constant titer on the composition diagram. Data giving the position of such lines have been published by Carlinfanti and Levi-Malvano (*1*). The intersections of the titer surface with the sides of the triangular prism are titer curves for the three binary mixtures and have the shapes indicated.

The lowest region of this titer surface is of particular interest. The position of the point *B* has been carefully investigated by Lapworth and Pearson (*3*), using highly purified palmitic and oleic acids, and found to be at 7.2 per cent palmitic acid. This means that crystallization and pressing of mixtures of oleic and palmitic acids containing more than 7.2 per cent palmitic acid to begin with, can never produce an oil carrying less than 7.2 per cent palmitic acid. The corresponding point, *A*, on the stearic-oleic curve has apparently never been investigated. It is apparent, however, that whatever the composition at *A*, the oil which is saturated with palmitic acid at *B* would take up still more solid acid at that temperature if the added acid were stearic. Addition of stearic acid to the mixture at *B* would change the composition along the line *BX*. The mixture would then be unsaturated and remain liquid until it again met the titer surface at *W*.

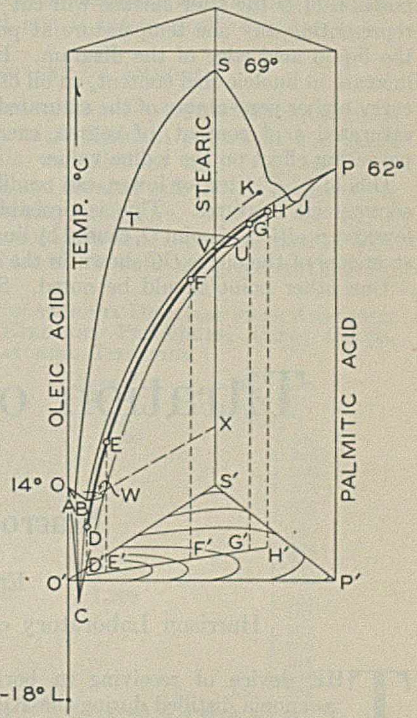

Figure 2. Titer Diagram for System Palmitic Acid–Stearic Acid–Oleic Acid

Addition of stearic acid to the mixture at *B*, or palmitic acid to that at *A*, would cause a further depression of the crystallizing point until finally a ternary eutectic would be encountered at *C*. The position of this point has never been established. It might require less than 7 per cent of solid acids or it might require considerably more.

It is interesting to note that Carlinfanti and Levi-Malvano did not encounter the eutectics *A* and *B* at all when they mixed their oleic acid with palmitic and with stearic. As pointed out by Lapworth and Pearson (*3*), this can only mean that their supposedly pure oleic acid contained more than 7 per cent of palmitic acid and an unknown amount of stearic acid dissolved in it. Their diagram of solidifying points for ternary mixtures is therefore also in error to that extent.

Dalican Curve on Titer Surface

Consider now the curve *DEFGH* which corresponds to the Dalican curve. The upper point *H* represents the composition and titer of the commercial stearic acid used, the point *D* that of the red oil. Neither is a fixed point. *H* will be closer to *SJP* the more completely the liquid acids are removed. It will shift back and forth with the ratio of palmitic to stearic in the solid acids and this ratio may vary considerably in the different stocks. If it takes up a new position, as at *K*, this will involve a change in both position and shape of the entire curve.

So also with the lower point *D*. At this end of the curve, wide variation in position is possible because of variation in the amount of linoleic acid present with the oleic. For oleic acid the position of *O* would be at +14° C., for linoleic it would be at −18° C., and for intermediate proportions it might be anywhere between, or even considerably lower because a curve for these two acids would drop to a minimum of its own.

It is particularly to be noticed that with a drop in the position of *O* the titer surface will cut the horizontal plane representing any one temperature at positions farther from the liquid acid edge of the diagram. In other words, with increase in linoleic acid content, an oil of 10° C. titer will also carry higher percentages of the saturated acids. This higher saturated acid content, of course, exerts a partially compensating effect on the iodine value.

Oils of 0° C. titer, or lower, can readily be obtained from commercial mixtures. This is probably due more to the lowered position of point *O*, caused by linoleic acid, than to the steepness of the curve *OC* shown in the diagram.

One other point should be noted. Since Dalican's mixtures are all made up from the two stocks *D* and *H*, they all have compositions which can be represented on the triangular diagram by a straight line, *D'H'*. This is not necessarily true of the stocks actually handled in the plant to arrive at the products *D* and *H*, since these two cannot exist as liquid and solid phase in equilibrium with each other in any mixture and so can only be arrived at by a series of operations.

Enough has perhaps been said to show that the Dalican curve is at best only an approximation which must be handled with considerable caution even in its proper application, which is the estimation of probable yields of commercial products. It can contribute no evidence of an exact quantitative nature regarding the actual content of saturated fatty acids in any technical mixture.

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Titration of Ammonia in Presence of Boric Acid

Macro- and Micro-Kjeldahl Procedures

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THE device of receiving in boric acid solution the ammonia distilled during the Kjeldahl analysis, suggested in 1913 by Winkler (*11*), has been reported upon favorably by several workers (*1, 2, 7, 8*), and especially by Markley and Hann (*5*). That this procedure does not more rapidly displace the less convenient excess-acid method is perhaps due in part to difficulty with the end point, for the indicators recommended—e. g., bromophenol blue, methyl red, methyl orange, and congo red—are not very satisfactory when used in the ordinary manner in presence of boric acid, the color changes being too gradual or too slight to be perceived sharply except after practice or by use of special light. Bromophenol blue has been considerably used, as in the extensive trials of the boric acid absorption method by Scales and Harrison (*7*), Spears (*8*), and Markley and Hann (*5*), with empirical correction (included in the over-all blank) for the effects of boric acid and dilution upon the indicator, but apparently none for any effect due to ammonium salt, reported by Kolthoff (*4*) and by Stover and Sandin (*9*) to be marked.

Preliminary trials suggested the probable advantage in the use of an indicator which in presence of boric acid develops its acid color in an intermediate intensity which within a limited range is proportional to the acidity, and which is suitable for accurate color-matching. With such an indicator the end point of the titration can be detected by matching the color of a control liquid which contains the same quantity of boric acid and the same amount of indicator in the same volume. The titration will thus be completed in the acid region, but always at the pH of the diluted boric acid solution. The effect of the boric acid upon the indicator is the same in the color standard and the analysis, and therefore cancels out.

Methyl red fully meets the requirements mentioned, and in addition its salt error is negligible, as was shown by Thomson (*10*) and in the course of the present study. Its suitability for the color-matching titration was demonstrated some years ago, and the resulting procedure has been used successfully in numerous Kjeldahl analyses, many by inexperienced students. Recently Stover and Sandin (*9*) reported the use of a color-matching titration in the micro-Kjeldahl method with boric acid absorption, the preferred indicators being a mixture of tetrabromophenol blue and methyl red, and of methylene blue and methyl red. There is described below a titration procedure like that of Stover and Sandin, but extended to both macro- and microtitrations. Methyl red is used as indicator, and gives an end point which is definite and unmistakable without use of special light.

MACROTITRATION IN PRESENCE OF BORIC ACID

Erlenmeyer flasks of 500 cc. capacity are used. The color control is prepared by dilution (with carbon dioxide-free water) of 50 cc. of 4 per cent boric acid solution to a volume equal to or slightly greater than the final volume of the distillate liquid at the end of the titration of ammonia (about 250 cc.), and addition of 2 to 4 drops of 0.1 per cent solution of methyl red in 95 per cent alcohol. The control liquid should be clear pink or red; a moderately pronounced red color seems best, very pale or very deep colors being less easily matched. If the flask is tightly stoppered the color standard can be used for a day or more. For absorption of ammonia 50 cc. of the same 4 per cent boric acid solution and as many drops of indicator as were added to the color control are taken. After distillation of the ammonia the cold liquid is titrated with 0.1 *N* acid, with the color control beside the distillate liquid, both flasks resting upon a white surface. The first faint orange or pink color which persists signals the approach of the end point. The titration is continued slowly until the colors of the two liquids are identical in intensity, the volumes being equalized (±10 cc.) if necessary by addition of water (best carbon dioxide–free if considerable is required). If the matching is properly done, 0.5 drop more of acid will markedly increase the intensity of the color as compared with that of the control. The color-matching can be accomplished with ease and precision, a variation of 0.01 to 0.02 cc. of 0.1 *N* acid being readily detectable. The addition (to the color control) of pure ammonium salt approximately equal to that formed in the titration is optional, but its effect is so small as to be negligible.

MICROTITRATION IN PRESENCE OF BORIC ACID

The procedure is that given for the macrotitration, with suitable reduction in scale. There are used 100-cc. Erlenmeyer flasks with like dimensions and prepared as described by Pregl (*6*), 5 cc. of 4 per cent boric acid solution (measured with a pipet), and about 2 drops of 0.05 per cent methyl red indicator (enough to yield in the control liquid a distinct pink color), in a final volume of 35 to 40 cc. Water used in the color control and for volume adjustment should be free from carbon dioxide. The end point can be located within 0.01 cc. of 0.01 *N* acid.

STANDARDIZATION OF ACID FOR TITRATION

The 0.1 *N* and 0.01 *N* acids were standardized against sodium carbonate (De Haen's guaranteed, previously gently ignited), using methyl red indicator. Standardizations were made both by the color-matching titration in presence of boric acid, and by the usual procedure in its absence. In every case the liquid was boiled just before the true end point, then cooled rapidly and the titration completed. The color controls were likewise boiled. Normalities by the two methods were identical, showing that the titration of alkali in presence of boric acid by the color-matching procedure described is accurate, and that acid to be used in this procedure may be standardized in either way. Some results appear in Table I, which includes also values obtained by use of methyl red–methylene blue indicator, recommended by Johnson and Green (*3*) and tested by Stover and Sandin (*9*).

TABLE I. STANDARDIZATION OF 0.1 *N* AND 0.01 *N* HYDROCHLORIC ACID WITH SODIUM CARBONATE IN PRESENCE AND ABSENCE OF BORIC ACID

INDICATOR	NORMALITY OF ACID	
	In presence of boric acid, by color-matching titration	In absence of boric acid, by usual standardization procedure[a]
Macro:		
Methyl red	0.12615	0.12615
	0.12620	0.12620
	Av. 0.12618	Av. 0.12618
Micro:		
Methyl red	0.01189	0.01188 (first pink)
	0.01188	0.01188
	0.01188	Av. 0.01188
	Av. 0.01188	
Methyl red–methylene blue	0.01188	0.01188 (first violet)
	0.01189	0.01189
	0.01188	Av. 0.01189
	Av. 0.01188	

[a] Color blanks deducted.

DETERIORATION OF BORIC ACID SOLUTION

Freshly prepared boric acid solution, diluted as specified above, gives with methyl red a pronounced acid color. Upon storage for some time the solution affects methyl red less strongly, and eventually fails to yield a red color. The explanation for this change is being sought; it may be the passage of alkaline constituents from the glass container into the boric acid solution, which may thus be partially buffered. While it is perhaps best to use an undeteriorated solution, it has been found that one which has deteriorated can be made usable by treating the whole stock solution with 0.1 *N* or 0.5 *N* acid until a portion properly diluted yields with methyl red an approximately normal red color. The color need not be exactly that imparted by a fresh boric acid solution; it need only be some tone of red which is suitable for color-matching. Since the restored solution will be used in equal amounts in both color standards and analyses, the total effect of the boric acid, etc., is automatically compensated.

RECOVERY OF AMMONIA

Aliquots of a standard solution of pure ammonium chloride were transferred to a micro-Kjeldahl apparatus and made alkaline; the ammonia was distilled into 5 cc. of 4 per cent boric acid solution and titrated with 0.01 *N* hydrochloric acid by the color-matching procedure. Methyl red and a mixture of methyl red and methylene blue were used as indicators, in two series of trials. Results are given in Table II.

TABLE II. RECOVERY OF AMMONIA DISTILLED FROM AMMONIUM CHLORIDE BY MICRO-KJELDAHL PROCEDURE, USING COLOR-MATCHING TITRATION

INDICATOR	NITROGEN TAKEN[a]	NITROGEN FOUND
	Mg.	*Mg.*
Methyl red	1.209	1.210
		1.208
		1.208
		1.207
		1.208
		1.207
		1.208
		1.208
		1.207
		Av. 1.208
Methyl red–methylene blue	1.209	1.208
		1.207
		1.207
		1.208
		1.208
		1.208
		Av. 1.208

[a] 10-cc. aliquots of solution of 0.4619 gram of ammonium chloride (De Haen's guaranteed) in 1000 cc.

The results in Table II represent a recovery of 99.9 per cent of the ammonia, using either indicator. Results with the two indicators are in better agreement than was found by Stover and Sandin. While both indicators are satisfactory, and even though the mixed indicator signals the approach of the end point earlier, it is thought that the color-matching at the end point is sharper and more certain with methyl red. The final colors of the mixed indicator are composites of the increasingly strong red of the methyl red and the color of the methylene blue, and these intermediate tones are less easy to match.

In Table III are collected results of some nitrogen analyses by both macro- and micromethods using the boric acid modification described. A number of results by the excess-acid procedure are included for comparison. Methyl red was used as indicator. In all cases over-all blanks were run, using sucrose, and suitable corrections applied.

As shown by the results in Tables II and III, ammonia distilled by the macro- or micro-Kjeldahl method and absorbed in boric acid solution can be titrated accurately with methyl red indicator, the end point being recognized by matching the color of a control liquid of the same volume and containing the same quantities of boric acid and of indicator. The titration can be made with normal rapidity.

The advantages of the proposed color-matching titration are the following: (1) the end point in presence of boric acid is sharp and unmistakable, and can readily be tested

Table III. Nitrogen Analyses by Boric Acid Modification of Kjeldahl Method, Using Color-Matching Titration with Methyl Red Indicator

		Nitrogen Found			
		Macromethod[a]		Micromethod[b]	
Compound	Nitrogen Calc.	Excess-acid procedure	Boric acid absorption	Boric acid absorption	
	%	%	%	%	%
Urea	46.66	46.60 46.51 46.65 46.80 Av. 46.64	...	46.5 46.2 46.8 46.3 Av. 46.5	
p-Aminophenol–hydrochloride (Cl = 24.0%; calc. 24.4%)	9.62	9.45 9.45 Av. 9.45	9.48 9.44 9.49 9.50 9.46 Av. 9.47	9.37 9.47 9.48 Av. 9.44	Excess-acid 9.47 9.46 9.45 Av. 9.46
Glycine	18.67	18.73 18.79 18.78 Av. 18.77	18.51 18.78 18.69 18.73 Av. 18.68	18.6 18.6 Av. 18.6	
Uric acid (commercial)	By Dumas 33.0	32.86 32.94 33.05 32.87 Av. 32.93	32.87 32.83 Av. 32.85	33.2 33.2 Av. 33.2	
Acetanilide	10.37	10.17 10.34 Av. 10.26	10.31 10.21 Av. 10.26		
Metol, recryst.	8.19		8.14 8.18 Av. 8.16		
Amyl-*p*-toluidine–hydrochloride (Cl = 16.59%; calc. 16.60%)	6.56		6.55 6.56 Av. 6.56		
p-Nitrophenol (zinc reduction)	10.08		10.08 10.09 10.14 Av. 10.10		

[a] Used 25 cc. sulfuric acid, $CuSO_4$-$HgSO_4$ catalyst, 10 grams sodium sulfate; digestion about 1 hour after clearing.
[b] Used Pregl procedure for digestion, with selenium catalyst. Results rounded off to three significant figures.

by a half-drop overtitration; (2) the end point is visible by daylight or by ordinary electric light, making available the advantages of boric acid absorption without need for special light equipment; (3) the color-matching titration can be used equally well in the macro- and the micro-Kjeldahl methods.

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Flask Oxidation in the Determination of Sulfurous Acid by Distillation

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In the determination of sulfurous acid by distillation from dried fruits and other products two difficulties have long been recognized. First, some of the sulfurous acid may be oxidized before it reaches the receiver. Second, especially in volumetric methods, reducing substances other than sulfurous acid may react in the receiver and give too high results. Among the means that have been recommended or adopted to overcome the first difficulty are steam distillation, distillation in a stream of carbon dioxide, rapid boiling, and the addition of sodium bicarbonate together with extra acid to the sample before distillation. Among the means used for overcoming the second difficulty are the substitution of iodine for bromine in the receiver, the use of gravimetric methods, the benzidine gravimetric method, and the use of cold hydrogen peroxide as a selective oxidant.

In a previous paper (*2*) the authors have reported a study of some phases of the problem, in which dried fruits and other products were used, and a few observations with sulfurous acid solutions made by passing sulfur dioxide gas from a cylinder through distilled water were included. When the available methods are used the true sulfurous acid content of dried fruit samples is to some extent uncertain. No entirely satisfactory reference substance has been found. In the authors' experience sulfurous acid solutions were less susceptible to oxidation and hence more satisfactory than solutions of sulfites or bisulfites.

In the study previously reported (*2*) the authors employed a type of distillation apparatus that lends itself well to the investigation of several of the means suggested for preventing oxidation in the distillation flask under closely comparable conditions. Such an investigation has been made upon sulfurous acid solutions, and the results are shown in Table I. Except in the two cases noted, the solutions were made by passing sulfur dioxide gas from a cylinder into ordinary dis-

TABLE I. DETERMINATION OF SULFUROUS ACID

EXPERIMENT	METHOD	SO_2 ADDED	TOTAL ACID AS SO_2	RECOVERED IN DISTILLATE[a]		SO_4 IN DISTILLING FLASK AS SO_2		TOTAL S ACCOUNTED FOR AS SO_2[b]
				Volumetric method	Gravimetric method	Original	Found	
		Gram	*Gram*	%	%	*Gram*	*Gram*	%
1	$HCl + NaHCO_3$[c]	0.0346	0.0424	76.9 ± 2.0	......	0.0078	0.0158	100.0 ± 1.2
2	$HCl + NaHCO_3$	0.0369	0.0368	95.7 ± 0.0	......	0.0001	0.00005	96.0 ± 0.0
3	$HCl + NaHCO_3$[d]	0.0362	0.0444	88.4 ± 0.5	......	0.0082	0.0086	91.2 ± 7.8
4	$HCl + NaHCO_3$. Vent closed	0.0369	0.0368	94.9 ± 0.0	......	0.0001	0.00035	96.1 ± 0.0
5	$HCl + NaHCO_3$. No vent	0.0369	0.0368	80.7 ± 3.9	......	0.0001	0.0064	98.3 ± 0.9
6	$HCl + NaHCO_3$. Air stream	0.0367	0.0404	93.2 ± 0.8	......	0.0037	0.0039	94.5 ± 1.1
7	$HCl + NaHCO_3$. CO_2 stream	0.0367	0.0404	94.8 ± 1.7	......	0.0037	0.0029	93.1 ± 1.4
8	HCl but no $NaHCO_3$	0.0369	0.0368	96.8 ± 0.7	......	0.0001	0.0000	97.0 ± 0.7
9	$H_3PO_4 + NaHCO_3$. Distilled into H_2O_2	0.0391	0.0411	......	70.8 ± 3.9	0.0020	0.0120	96.6 ± 4.7
10	$HCl + NaHCO_3$. Distilled into H_2O_2	0.0400	0.0414	73.0 ± 0.8	71.0 ± 0.8	0.0014	0.0122	98.1 ± 0.8[e] 100.0 ± 1.2[f]
11	Monier-Williams	0.0367	0.0404	85.9 ± 0.1	99.2 ± 0.3	0.0037	0.0002	78.3 ± 0.3[f] 90.5 ± 0.5[e]
12	Monier-Williams. No preliminary heating	0.0367	0.0404	88.7 ± 0.3	98.6 ± 0.2	0.0037	0.0001	80.8 ± 0.1[f] 89.8 ± 0.1[e]
13	Monier-Williams. No preliminary heating; no guard trap	0.0400	0.0414	88.0 ± 0.2	93.5 ± 1.4	0.0014	0.0000	85.0 ± 0.2[f] 90.3 ± 1.3[e]

[a] Referred to third column.
[b] Referred to fourth column.
[c] Sulfurous acid solution in tap water.
[d] Sulfurous acid solution in recently boiled distilled water.
[e] Based on gravimetric determination of SO_2 in distillate.
[f] Based on volumetric determination of SO_2 in distillate.

tilled water. Thiosulfate guard traps were used in experiments 6 and 7.

Included in the table are also observations on certain modifications of the method suggested by Monier-Williams (*1*). The modifications include omission of the preliminary heating of the acidified water (experiment 12), the elimination of the guard trap (experiment 13), and the direct rather than reflux distillation of the sulfurous acid into cold hydrogen peroxide without use of the carbon dioxide stream (experiments 9 and 10).

In all cases where the filtered residue after distillation gave a perceptible precipitate with barium chloride, the amount was determined gravimetrically.

The concentration of sulfurous acid in the initial solutions used was determined by titration into iodine checked against 0.1 *N* sodium thiosulfate. The total acid was determined by 0.1 *N* alkali titration after oxidation of the sulfurous acid by neutral hydrogen peroxide, and was calculated as sulfur dioxide. The difference between this value and that obtained by titration into iodine was considered as the amount originally present as sulfate. In calculating the per cent recovery of sulfurous acid in the distillate, the basis for calculation was the value obtained for the original solution by iodine titration. In calculating the per cent recovery of total sulfur—that is, the sum of the recoveries in distillate and distilled residue—the basis was the alkalimetric titration of the oxidized original solution.

DISCUSSION

When the Monier-Williams method (experiment 11) and modifications of it were used, the recovery in the distillate by the gravimetric method was higher than that by the volumetric (alkali titration). That this does not necessarily occur when hydrogen peroxide is used as the oxidant is shown by experiment 10 in which both volumetric and gravimetric determinations were made with the regular apparatus, not using a reflux condenser. This also seems to indicate that no appreciable amount of hydrochloric acid was distilled over when no reflux condenser was used.

From the averages of the probable errors of the means, given in Table I, it appears that the accuracy of the volumetric determinations of sulfurous acid in the distillates by volumetric methods was slightly less than 1 per cent; the accuracy of gravimetric determinations was approximately 1.3 per cent; and the accuracy for the total recovery was 1.5 per cent by volumetric and 1.6 per cent by gravimetric methods. The results therefore appear dependable to the nearest milligram of sulfur dioxide. Considering the highest values obtained for the distillate, whether volumetric or gravimetric, low recoveries of sulfurous acid in the distillate were generally accompanied by increased yields of sulfate in the distilled residue.

So far the results indicate that when low values were obtained in the distillate, oxidation in the distilling flask was appreciable (experiments 1, 5, 9, and 10). However, it is not clear why such oxidation and low sulfurous acid recovery in the distillate did not take place in other experiments. For example, oxidation apparently occurred in experiment 10, but not in experiment 2. These experiments differ only in that the oxidants used were different, and there is no reason to suppose that this would influence oxidation in the distilling flask.

No advantage appears to result from the use of recently boiled distilled water either for making up the sulfurous acid solutions or in the distillation flask (experiments 2, 3, 11, and 12). The use of tap water in making up the sulfurous acid solution resulted in a lower yield (experiments 1 and 2).

No advantage resulted from using a carbon dioxide stream during distillation (experiments 2 and 7), and the use of an air stream in the distillation flask did not accelerate oxidation (experiments 2 and 6). This is further indicated by a comparison of experiments 2, 4, and 5. Removal of the vent tube (experiment 5) should hasten the elimination of air from the flask as compared with using a vent tube closed off at the top (experiment 4) or using a vent tube open at top and bottom (experiment 2), but this did not increase the yield of sulfurous acid. No explanation is offered for the greater apparent oxidation that occurred when the vent tube was removed altogether (experiment 5).

The use of sodium bicarbonate did not increase the yield from sulfurous acid solutions.

SUMMARY

None of the various means that have been suggested for preventing flask oxidation and increasing the yield in the determination of sulfurous acid proved to solve the problem in the authors' experiments.

Gravimetric determinations by the Monier-Williams method gave the highest yields, and it appeared that the preliminary heating could be omitted without serious loss of accuracy.

Among volumetric methods, that of Nichols and Reed, but with the omission of sodium bicarbonate, gave the highest results.

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"That which is brief, if it be good, is good twice over."

Mold Growth Test for Minute Amounts of Arsenic

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The unusual property of certain mold growths in liberating arsenic in the form of gas having a characteristic garlic-like odor was clearly demonstrated in a series of experiments reported by Gosio in 1892 (*3*), and has been studied by many other investigators. A recent contribution by Thom and Raper (*7*) shows the particular molds that have this property and also gives references to the literature on the subject. Tanner (*5*) gives the method developed by Schneider (*4*) for using these molds in testing for the presence of arsenic. Challenger et al. (*1*) examined the gas evolved and found it to be trimethyl arsine. They give data as to the gas itself and certain of its compounds.

The present work gives some convenient ways for growing the mold, suggests methods for carrying out the test for arsenic in food products, records the results obtained with known amounts of arsenic in different kinds of foods, shows that many classes of arsenic compounds respond to the test, and points out certain limitations.

The authors believe that this mold test for arsenic has a value that is not generally appreciated by those interested in food technology. It provides a presumptive test materially more sensitive than existing chemical tests. It should have marked qualitative value in supplementing chemical quantitative tests where large numbers of samples of unknown arsenic content are to be tested. The production of mold growth and method of treatment are procedures that could be reduced to practical simplicity in routine examination.

In this work only one kind of mold was used—namely, *Scopulariopsis brevicaulis (Sacc.) Bainier*. This appears in the older literature as *Penicillum brevicaule Sacc.* It is described in detail by Thom (*6*) and the particular strain used is listed in his collection as No. 480.2. The authors are indebted to Doctor Thom for the original spores of this mold and for many helpful suggestions about the work here reported.

The mold grows freely on many kinds of food materials, as well as in the usual culture solutions. Tomato broth, pea broth, shrimp meat, potted meat, and apple pomace were observed to support vigorous growths. In order to simplify and standardize the tests a synthetic medium, Czapek's solution with agar, was used. This medium is easily prepared from usual laboratory reagents that are free from arsenic. Because many bacteria do not grow well in this medium the harmful effects of this type of contamination are minimized.

Czapek's Solution Agar

Water	1000 cc.
	Grams
Sodium nitrate	3
Potassium monohydrogen phosphate	1.0
Magnesium sulfate	0.5
Potassium chloride	0.5
Sucrose	30.0
Agar agar	15.0

If arsenic is present in the media on which this mold is grown, the gaseous arsenic compound which may be detected by its characteristic garlic-like odor is given off. But a more satisfactory way to conduct the test, originally established by Gosio (*3*), involves the cultivation of a vigorous growth of the mold on the surface of a solid or semisolid arsenic-free medium in separate containers and subsequent addition of the sample to the surface of the mat of mold mycelium. Less than 0.001 mg. of arsenic will give a definite odor in 2 hours under the conditions described.

Experimental

Short wide tubes and also Petri dishes were used to give a large surface of agar media on which to grow the mold. A thin layer of melted media was poured into the sterile Petri dishes and allowed to solidify. The melted medium in the sterile tubes was cooled with the tubes inclined to give slants with the maximum surface. A few drops of a suspension of the mold spores in sterile water were spread over the surface of the solid media in the dishes and in the tubes. Tests showed that the mold grows best at about 30° C. Incubation of the inoculated media at 30° C. produced a vigorous growth of mycelium in 48 to 72 hours.

Experiments showed that the first noticeable growth of mold is able to generate the test gas, but more complete growth gives the test more quickly and with a smaller amount of arsenic. A thick mat of white mycelium gives best results. After spore formation has become general, as shown by the brownish color over most of the surface of the mold, the reaction is less definite. The generation of the test gas by the action of the mold on the sample takes place at least as well at room temperature as in the incubator at 37° C.

The sample may be in the form of a dry powder or a liquid. The test gas seems to be evolved as a product of respiration of the growing mycelium in contact with the sample. The arsenic in the sample is apparently dissolved by moisture on the surface of the mycelium and the test gas seems to be given off from the surface of the mold. In order to make possible the greatest amount of contact of the sample with the mold, the dry sample should be ground coarsely and sprinkled evenly over the surface of the mold. If the sample is in liquid form not more than 1 cc. should be used. It was at first thought that a liquid sample would be better because of more complete contact with the mold, but the first experiments showed that a small amount of arsenic finely divided with inert material such as sand gave as good a test as the same amount of arsenic in liquid form.

Since the test depends on the development of arsenic vapor sufficiently concentrated to detect by the odor, the amount of gas space confined above the mold during the test is important. The relation of the area of actively growing mold to the volume of gas in the test apparatus will influence the concentration of the test gas developed from the arsenic present. Thus Petri dishes gave a better test than stoppered tubes because the relation of mold area to air space was greater. Moreover, by gently tilting the cover of the Petri dish at one side the gas may be readily detected.

It was possible to obtain a definitely positive test in 2 hours with only 0.5 microgram of arsenic trioxide present, either dried on 1 gram of sand or dissolved in 1 cc. of water. This is equivalent to 1 part in 2 million or 0.00005 per cent. The actual weight of arsenic in the gas mixture that gives a distinct odor must be exceedingly small, because only a small portion of the dry sample can come into actual contact with the mold and the gas continues to be given off for several hours. Using 100 micrograms of arsenic trioxide on sand a definite odor was obtained in 20 minutes.

POLITECHNIKI

Different kinds of food products were tested with and without added arsenic. Products which could be dried were coarsely ground and used directly on the mold. Large amounts of fat in meat products delayed for several hours the formation of sufficient gas to give the test. This delay was avoided by preliminary extraction with ether and alcohol followed by drying and grinding of the sample. Fine powders such as flour formed a cake which interfered with the contact with the mold. This was overcome by adding a little calcium carbonate, ashing, neutralizing with hydrochloric acid and using either the solution or the residue after evaporation to dryness. This ashing procedure is also advantageous with samples that have a strong odor that might confuse the test. In all these tests 1 microgram of arsenic trioxide in 1 gram of sample was easily detected.

As has been reported elsewhere (*7*), the nature of the arsenic compound that may be present does not seem to affect the test. Five kinds of arsenic compounds were tested to indicate its general applicability. With each compound, an amount of sample equivalent to 1 microgram of arsenic trioxide gave a definite test in 2 hours.

1. Arsenous oxide, an insoluble white arsenic powder.
2. Sodium arsenite, a simple soluble compound.
3. Paris green, a complex metallic compound.
4. Sodium cacodylate, a very stable arsenic radical.
5. Neosalvarsan, a highly complex organic compound.

The presence of fruit acid in reasonable amounts does not prevent the test. One per cent citric acid either dry-mixed with the sample or in solution with the sample did not interfere. One per cent sodium carbonate in solution with the sample prevented the test with small amounts of arsenic. Larger amounts of arsenic gave a delayed test. One per cent sodium carbonate dry, mixed with the powdered sample, made the test less satisfactory. Small amounts of ammonium hydroxide, enough to give a perceptible odor, did not obscure the test.

The presence of inorganic mercury compounds completely prevents the test. The gas that is formed combines easily with mercury to form stable compounds (*1*, *4*). Mercury through its toxicity may also paralyze the respiratory mechanism and thus prevent production of the test gas. Antimony compounds to not interfere. One hundred micrograms of antimony chloride gave no test. Selenium and tellurium compounds give gases similar to those of arsenic, but these elements are very rare (*7*).

Attempts were made to gain an insight into the mechanism by which the test gas is formed. Enzymes were produced by the method described by Dox (*2*) and were tested with arsenic-containing substrates. Results were uniformly negative, and even though no claim for exhaustive treatment is made this fact is regarded as significant in indicating that the gas production is intimately associated with the active mold growth. Also supporting this viewpoint are the following observations:

When plates showing vigorous growth were thoroughly cooled by subjecting to ice box temperature for 30 minutes, 20 micrograms of arsenic trioxide failed to give a positive test in 2 hours' continued exposure to that temperature.

When normal growth was inhibited by covering the mold mat with distilled water 100 micrograms of arsenic trioxide applied with sand failed to present a positive test in 30 minutes, 1 hour, 5 hours, and 30 hours, whereas the control dish without water gave a strong test in 20 minutes.

Quicker reactions were observed when the test substance was applied to actively growing mold rather than one in which sporulation had progressed to an advanced degree.

RECOMMENDED PROCEDURE

The following is suggested as a workable procedure that will apply to a wide classification of food products:

1. Prepare and sterilize Czapek's solution agar. This may be prepared in large quantities and held in stock.

2. Sterilize Petri dishes and, using precaution against contamination, introduce thin layers of Czapek's medium after previously liquefying by heat.

3. Allow the medium to harden in the Petri dishes. Inoculate with a spore suspension in water by dropping 3 or 4 drops on the surface of the medium and, by tilting the plates, cover the surface as completely as possible. The spore suspension is prepared by flooding the surface of an old slant culture with 5 cc. of sterile water and scraping the spores into the water by means of a sterile platinum needle or pipet. Slants are prepared by the usual bacteriological method, using Czapek's agar. They may be made in large quantities and the inoculated slants held in stock.

4. Incubate the plates 48 to 72 hours at 30° C. or at lower temperatures, until an obviously active growth covers the inoculated portion of the plate.

5. Prepare the test substance by one of the following methods:

SOLID MATERIALS. Wherever practicable dry, if necessary, and grind to a coarse powder.

If the product is distinctly oily, extract with two or three portions of ether or chloroform by stirring and decantation. Dry if necessary, and grind to a coarse powder.

If the product is a very fine powder such as flour, add an excess of sodium or calcium carbonate, char completely, acidify with dilute hydrochloric acid, filter, and test the filtrate as directed below.

If the product has a strong odor, char and extract as described above.

LIQUID MATERIALS. Adjust the acidity with dilute acid or alkali until the solution is barely acid to litmus. Concentrate by evaporation if desirable.

6. Apply the sample to the mold growth:

Using the prepared solid sample material, sprinkle about 1 gram fairly evenly over the mold surface.

Using the prepared liquid sample, transfer about 1 cc. to the surface of the mold growth. The liquid stays in large drops which may be better distributed by first sprinkling on a few grains of clean sand. Shake the dish to spread the liquid somewhat, but it is not desirable to cover the entire surface of the mold growth.

7. Allow to remain at room temperature in a room free from pronounced odors. Test for the characteristic odor in 0.5, 1, 2, and 5 hours. If small amounts (0.000001 gram) of arsenic are present, the odor should be apparent in 2 to 5 hours. A quicker reaction will indicate the presence of larger amounts. Consider the test negative after 16 to 20 hours without the characteristic reaction.

SUMMARY

Analysts are sometimes called on to test a small sample for possible traces of arsenic. Even the Gutzeit test is not satisfactory with only 1 or 2 micrograms of arsenic present. This mold test may be used with 1 gram or less of sample and detects easily one part per million of arsenic.

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An Accurate Semimicro-Kjeldahl Method

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Descriptions of the determination of nitrogen by the Kjeldahl method and its modifications usually include no estimate of the accuracy of the results. In the exceptionally careful work of Andersen and Jensen (*1*), results accurate to 0.1 or 0.2 per cent were obtained after long periods of digestion, 4 to 8 hours. Although much faster micromethods have been described, Peters and Van Slyke (*12*) advise the use of macromethods if the error is to be kept under 1 per cent. Northrop (*8*) has used a semi-micromethod with an accuracy of 0.2 per cent. The authors have modified his method by the use of mercury and selenium together as catalysts, having confirmed the finding of Osborn and Krasnitz (*9*) and of Taylor (*14*) that the combined catalysts work faster than either alone.

Method

Five-cc. samples of solution, containing 5 to 6 mg. of nitrogen, were pipetted into 100-cc. Pyrex Kjeldahl flasks having a constriction about halfway up the neck (*8*). After the addition of 2 cc. of concentrated sulfuric acid, 1 gram of potassium sulfate, 70 mg. of mercuric oxide, and 2 drops of selenium oxychloride, together with a few pieces of broken alundum to minimize bumping, the digestion was carried out over microburners, the flasks being protected from superheating by asbestos board having a 2-cm. hole under each flask. The time required to drive off the water was about 20 minutes, the mixtures became clear in 6 to 8 minutes more, and digestion was continued for 20 minutes after clearing. After adding 35 cc. of water and 5 cc. of a solution composed of 500 grams of sodium hydroxide, 500 cc. of water, and 80 grams of anhydrous sodium thiosulfate, the ammonia was distilled through 2 traps fused together in series (*8*) and a Pyrex condenser into 25 cc. of 0.02 *N* hydrochloric acid. Distillation was continued until violent bumping occurred, the time required being about 20 minutes and the volume of the distillate being about 25 cc. The excess acid was titrated with 0.02 *N* sodium hydroxide, using methyl red as indicator. Blank determinations were carried out with 5 cc. of water, digested and distilled in exactly the same way.

Results

Analyses were run in quadruplicate, the titrations usually agreeing within 0.1 cc. of a 0.02 *N* solution, the average deviation from the mean of individual titrations in a set of 4 being 0.02 to 0.03 cc. Blank titrations varied from 0.05 to 0.15 cc. with different lots of distilled water, the average deviation of any set of 4 being 0.01 to 0.02 cc. Since the ammonia amounted to about 20 cc. of a 0.02 *N* solution, a liberal estimate of the mean error, considering only the agreement of duplicates, would be 0.2 per cent.

The weight of pure nitrogenous substance in each 5-cc. sample analyzed was known to within 0.1 per cent, as samples of 0.6 to 1.4 grams were weighed, dissolved, and diluted to 100 cc. The concentrations given are based on dry weight determinations of 1-gram samples which were dried *in vacuo* to constant weight in 1 to 2 days at 75° C. in an Abderhalden drier containing anhydrous magnesium perchlorate (Anhydrone) in the bulb.

The materials analyzed were tyrosine, glycine, edestin, casein, and egg albumin. The tyrosine was prepared from casein and purified by three recrystallizations from water, as previously described (*4*). The glycine solution was prepared by Owen (*3, 11*), and its concentration is based on his dry weight determinations. Edestin was prepared from hemp seed according to Osborne, recrystallized, and washed free from salt, as described elsewhere (*5*). The casein was Casein II, described in a previous paper (*6*). The egg albumin was prepared by a method developed by Cannan (*2*) involving crystallization from sodium sulfate solutions. It was twice recrystallized, and freed from salt by dialysis until a 7 per cent solution had a specific conductivity of 1.1×10^{-4}. Its concentration was determined by evaporating 10-gram samples of solution at 50° C. and drying at 75° C. as described. Another 10-gram sample of this solution was diluted to 100 cc., and 5-cc. samples of the dilute solution were analyzed.

Table I. Determination of Nitrogen in Amino Acids and Proteins

Substance	Substance in Sample	Nitrogen Found		Accepted Value	Source of Accepted Value
	Mg.	*Mg.*	%	%	
Tyrosine	70.57	5.45	7.72	7.735	Formula
Glycine	36.65	6.84	18.66	18.67	Formula
Edestin	28.02	5.22	18.63	18.69	Osborne (*10*)
Casein	34.45	5.34	15.50	15.49	Authors' macro
Egg albumin	35.09	5.47	15.59	15.64	Sörensen (*13*)

In the case of the two amino acids, the results check the theoretical within 2 parts in 1000. In the case of edestin and egg albumin, the results are 3 parts in 1000 lower than figures selected as the most reliable in the literature. For casein the values in the literature vary from 15.4 to 15.8 per cent. Since Linderström-Lang (*7*) has shown casein to be a mixture, such variations in different preparations are to be expected. Accordingly, the authors have compared their result with one obtained with the same casein solution, using a macromethod and a digestion period of more than 4 hours.

Acknowledgment

The authors are indebted to J. H. Northrop for advice in connection with earlier forms of this method, to R. K. Cannan for directions for crystallizing egg albumin, to Philip Dow for preparing the egg albumin, and to B. B. Owen for the glycine solution.

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Direct Titration of Sulfate

Tetrahydroxyquinone as an Internal Indicator

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ALMOST none of the methods suggested for the rapid determination of the sulfate content of a solution make possible direct titration without recourse to the use of outside indicators, a back-titration, or a filtration. The tetrahydroxyquinone method described in the present paper makes it possible to titrate the sulfate present in a sample directly with a standard barium chloride solution. The end point is indicated by the appearance of the red barium salt of tetrahydroxyquinone.

The present study was made possible through the financial support of the Joint Research Committee on Boiler Feed-water Studies, and, naturally, a large share of emphasis in the development of the method has been placed on making it applicable to the analysis of boiler waters. The concentration ranges considered and the effect of various impurities which were studied are those which might be expected in boiler water analysis. The actual application should, however, by no means be limited to any one particular field, and with proper preliminary investigation the method may be widely useful.

Review of the Literature

The gravimetric method for the determination of sulfate is very accurate and, except where occlusion and adsorption errors are high, is free from serious interference. It has the disadvantage of being time-consuming and of requiring the use of a balance, which is not always available for routine analysis. For these reasons methods which were essentially gravimetric were not considered in the present investigation.

Several methods which might be classified as colorimetric have been suggested for the determination of sulfate (*41, 59, 69, 99, 116–118*). Most of them, while perhaps satisfactory in laboratory work, are too complicated for routine analysis.

The methods suggested in the literature as suitable for the rapid determination of sulfate may be roughly divided into three classes: first, filtration methods; second, those determinations in which a titration is used, with internal or external indicators; and third, turbidimetric methods.

Filtration Methods. The benzidine method is probably the best known example of a filtration method. It has been the subject of extensive investigation (*16, 20, 49, 84, 109*) and the concentrations of impurities (*16, 17, 20, 37, 56, 91, 105, 109*), concentrations of reagents (*17*), temperature and method of titration (*31, 37, 46, 57, 90, 95, 105*), and the method of filtration and washing (*31, 95, 119*) have all been carefully studied.

Carbonate salts are also often used (*9, 11, 23, 34, 53, 83, 108*). For example, to a solution containing sulfate a standard barium chloride solution may be added, followed by sodium carbonate; after filtering off the barium carbonate and sulfate precipitated, the carbonate in either the filtrate or precipitate may be determined by a titration and from this the sulfate can be calculated. Chromate (*1, 12, 13, 15, 29, 39, 50, 51, 61, 63, 68, 72, 75, 81, 92, 94, 97, 100, 102, 111*), phosphate (*74*), lead (*36, 85*), and oxalate salts (*93*) are often used in a somewhat similar manner.

In another method, which does not involve a filtration but which depends on a partial separation of the solution and solid, the solution is centrifuged and the volume of the precipitate measured (*3, 4, 44, 71*). Where a centrifuge is available this method is sometimes satisfactory for the routine determination of sulfate.

All these procedures demand a filtration, which necessarily makes the method rather long. Direct titration methods would have considerable advantage in regard to the speed with which a determination could be made.

Titration Methods. Several methods which have been worked out for the titration of sulfate depend on the use of lead salts (*40, 58, 78, 82, 85*). In general, however, the lead sulfate which is precipitated is too soluble to make these methods readily applicable in dilute solutions.

Three methods are available for the determination of sulfate in which outside indicators are used to determine the end point. The indicators used are starch–potassium iodide paper (*18*), congo red and ammonium dichromate (*110*), and benzidine paper (*30*). Other methods use chromate salts for the titrating solution and various indicators (*38, 96, 113, 114*). For routine analysis the use of outside indicators is too slow and subjects the method to inaccuracies.

Several titration methods use internal indicators. One series depends on the hydrolysis of a salt of a strong base and a weak acid to indicate the end point—for example, a method which adds excess barium chloride and titrates the excess barium with sodium carbonate in the presence of phenolphthalein. When all the barium has been precipitated as barium carbonate, the addition of a slight excess of sodium carbonate will cause the phenolphthalein to turn pink (*19, 22, 101*). A number of salts, such as sodium carbonate, potassium chromate (*7, 14, 45, 57, 104*), potassium stearate (*5*), or potassium palmitate (*6, 60, 120*), have been used in this titration.

In many cases titration methods which depend on hydrolysis reactions are satisfactory. They are, however, subject to interference from the presence of phosphate and carbonate, and to some extent from other buffer salts, such as silicates and aluminates.

Some titration methods have been evolved which depend on the use of adsorption indicators (*8, 112*).

Another internal indicator method titrates with potassium chromate to the end point of silver chromate (*70*), but is, of course, subject to interference by chloride. Other titration methods depend on conductivity measurements (*32, 35, 55, 64, 66, 77, 80*), thermometric measurements (*25, 33*), refractometer measurements (*10*), and various other means of determining the end point, but are not in the main readily applicable to routine analysis.

An internal indicator method which seems to be convenient and rapid has been worked out recently in Germany (*65, 89, 103*). This adds excess standard barium chloride and titrates back with standard sodium sulfate in the presence of a rhodizonate salt. It will be considered further in the discussion of the tetrahydroxyquinone method.

Turbidimetric Methods. Several rather different methods have been suggested as being applicable to the turbidimetric determination of sulfate. One compares the turbidity of the unknown solution with a known solution (*2, 21, 24, 26–28, 62, 67, 73*). A second measures the time required for a solution to become turbid after the precipitating agent has been added (*115*). The third, which is most used at the present time, measures the depth of turbid liquid required to obscure a light filament (*43, 47, 87, 88*).

Much study has been devoted to the method based on the measurement of the depth of liquid required to obscure the light filament. Various ways of adding the barium chloride used in the precipitation have been tried (*47, 54, 76, 79, 106*), and the effect of various salts, the effect of temperature, method, and time of addition of acid and various other reagents, and the acid concentration of the sample during precipitation (*48, 54, 76, 79, 86, 87, 106*) have all been extensively investigated.

The accuracy of the turbidimetric methods has been the subject of much discussion (*48, 54, 86*). In general investigators are not in good agreement as to accuracy.

The turbidimetric method for the determination of sulfate has found wide application and in many instances is entirely

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satisfactory. Its chief disadvantages are: As ordinarily carried out the method requires the construction of a calibration curve; some special equipment aside from the regular analytical equipment is necessary; the range of concentrations over which the method may be used is quite short; the method is considerably influenced by other salts in the solution; and its accuracy in some instances is subject to considerable doubt.

It is evident that the benzidine method, the hydrolysis methods, and the turbidimetric methods should prove of considerable value in the determination of sulfate. In the present investigation the benzidine method and the turbidimetric methods were extensively studied, but the results will not be discussed here. Because of the particular solutions in which the authors were interested the hydrolysis methods did not seem satisfactory and were not considered in detail.

The rhodizonic acid method (*89*, *103*) seemed to promise a very satisfactory method for the rapid determination of sulfate and offered considerable improvement in many respects over the three methods mentioned. For this reason it was investigated further and this investigation will be considered briefly below.

Investigation of Tetrahydroxyquinone Method

In 1929 Strebinger and Zombory (*103*) suggested the use of rhodizonic acid in the titration of sulfate. The determination was carried out by the addition of an excess of standard barium chloride to the sample, followed by the addition of a small amount of the sodium salt of rhodizonic acid. The excess barium was titrated back with a standard sodium sulfate solution. The addition of the barium chloride caused the precipitation of the sulfate and also of the barium salt of rhodizonic acid. This salt has a bright red color which is readily distinguished in the solution. On back-titration with sodium sulfate the barium salt of rhodizonic acid is destroyed because of the precipitation of barium sulfate, and the end point is denoted by the disappearance of the red color. If the titration is being carried out in a neutral solution, the rhodizonate salt goes back into solution to form the sodium salt and the end point is a change from red to yellow. If the titration is being carried out in an acid solution, the rhodizonate salt is destroyed and the end point is a change from red to colorless. The barium salt of rhodizonic acid is quite stable in a dilute acid solution.

In the present study the use of rhodizonic acid was investigated. In solutions about 0.1 or 0.2 *N* with respect to sulfate the method was found satisfactory, although the results obtained were not as accurate as those obtained by Strebinger and Zombory. The method was not found satisfactory on more dilute solutions. It was also impossible to use rhodizonic acid as indicator in the direct titration of sulfate with barium chloride. Some of the rhodizonic acid used in this investigation was secured from Germany and some was prepared in the laboratory.

Tetrahydroxyquinone is used in a similar manner to rhodizonic acid and gives the same end-point reactions. It is, however, more satisfactory in dilute solutions and can be used in the direct titration.

Results of Back-Titration. In making rhodizonic acid it was necessary as one of the preliminary steps to prepare some tetrahydroxyquinone. Its use as a qualitative indicator for barium has been noted (*42*), and a few preliminary experiments indicated that it might be used in a quantitative determination.

The tetrahydroxyquinone was made by treating glyoxal sodium bisulfite, prepared by treatment of acetaldehyde with nitric acid and sodium bisulfite (*107*), with a solution of sodium carbonate (*52*). Solutions of tetrahydroxyquinone in water are not sufficiently stable to be added to the sample in this form. It is also inconvenient to make up fresh solutions of the indicator every time it is desired to use it. It has been found very satisfactory to grind up a small amount of the indicator with a large amount of potassium chloride and add a few tenths of a gram of this mixture to the sample to be analyzed. In this form the indicator is stable for a year or longer. This method of adding the tetrahydroxyquinone to the sample was used throughout the present investigation.

A few preliminary results for the back-titration involving the titration of solutions of barium chloride with potassium sulfate are shown in Table I. The results, as seen, are satisfactory. In this titration it was found desirable to have alcohol present in the sample, since this hastened the precipitation of the barium sulfate.

Table I. Titration of Barium Chloride with Potassium Sulfate

Sample	$BaCl_2$ Solution	$BaCl_2$ Corrected to 0.05 *N*	K_2SO_4 0.05 *N*
	Cc.	*Cc.*	*Cc.*
1	1.00	1.98	2.03
2	1.00	1.98	2.05
3	5.00	9.90	9.95
4	5.00	9.90	9.90
5	10.00	19.80	19.75
6	10.00	19.80	19.70

50-cc. samples with 15 cc. of alcohol added.
Solutions approximately 0.03 *N* with respect to hydrochloric acid.
$BaCl_2$ solution 0.1 *N*. Correction factor = 0.990.

The effect of acid concentration, temperature, and various other ions on this back-titration was studied. The solution to be titrated should be kept below 0.05 *N* with respect to hydrochloric acid. The temperature should also be below 30° C. Hydroxide, chloride, carbonate, silicate, calcium, magnesium, and aluminum do not interfere unless they are present in high concentrations. If the sample is made sufficiently acid during the addition of the barium chloride and then this acidity is neutralized before the back-titration with sodium sulfate, fairly high concentrations of phosphate may be present without causing interference. Iron present in the sample causes interference and must be removed.

Results of Direct Titration. In the direct titration the sample to be analyzed is neutralized and then titrated directly with a standard barium chloride solution to the appearance of the red color of the precipitate of the barium salt of tetrahydroxyquinone. During the present investigation an approximately 0.025 *N* barium chloride solution was used in all the titrations. A fairly high concentration of alcohol in the sample was also found very desirable during the titration.

Table II. Analysis of Sodium Sulfate Solutions by Direct Titration Method

Sample	$BaCl_2$ Used	SO_4 Present	SO_4 Found
	Cc.	*Mg.*	*Mg.*
2	4.2	5.00	5.02
3	6.2	7.50	7.48
4	8.2	10.00	9.92
1	10.1	12.50	12.2
5	14.4	17.50	17.5
6	16.2	20.00	19.7
7	19.8	25.00	24.2

$BaCl_2$ solution 0.025 *N*. Correction factor = 1.020.
25-cc. samples with 25 cc. of alcohol added.
Blank = 0.1 cc.

In Table II are shown the results of a few preliminary titrations by the direct method on solutions containing only sodium sulfate. The results are satisfactory. It will be noticed that for samples containing more than 20 mg. of sulfate in the 25 cc. of solution titrated there is some tendency toward low results. This was confirmed by further investigation, and in order to avoid this error it seems best to keep the concentration of sulfate below 20 mg., using not more than 16 or 17 cc. of the 0.025 *N* barium chloride solution in a titration. The 0.1-cc. blank indicated in this table is the amount of barium chloride required to give a visible precipitate with the indicator when no sulfate is present.

The effect of various ions on the direct titration is shown in Table III. Carbonate, aluminum, silicate, and magnesium have little effect. Carbonate and aluminum in concentrations higher than those shown in the table tend to make the end point slightly less sharp.

TABLE III. EFFECT OF VARIOUS IONS ON DIRECT TITRATION

SAMPLE	ADDED ION		$BaCl_2$ USED	SO_4 PRESENT	SO_4 FOUND
		Mg.	*Cc.*	*Mg.*	*Mg.*
12	CO_3	4.0	2.10	2.50	2.45
13	CO_3	4.0	6.3	7.50	7.60
14	CO_3	4.0	12.3	15.00	14.9
8	CO_3	8.0	4.2	5.00	5.02
9	CO_3	8.0	10.4	12.50	12.6
10	CO_3	8.0	16.6	20.00	20.2
11	CO_3	8.0	20.2	25.00	24.6
20	Al	2.5	2.30	2.50	2.70
21	Al	2.5	6.2	7.50	7.47
22	Al	2.5	12.2	15.00	14.8
23	Al	5.0	2.30	2.50	2.70
24	Al	5.0	6.5	7.50	7.83
25	Al	5.0	12.2	15.00	14.8
28	SiO_3	5.1	2.20	2.50	2.57
29	SiO_3	5.1	6.3	7.50	7.60
30	SiO_3	15.3	2.20	2.50	2.57
31	SiO_3	15.3	6.2	7.50	7.47
32	SiO_3	25.5	2.15	2.50	2.51
33	SiO_3	25.5	6.2	7.50	7.47
34	SiO_3	25.5	12.3	15.00	14.9
39	Mg	2	2.30	2.50	2.70
40	Mg	4	6.1	7.50	7.35
41	Mg	10	12.2	15.00	14.8
35	Ca	5.0	2.10	2.50	2.45
37	Ca	0.25	6.1	7.50	7.35
38	Ca	0.50	6.4	7.50	7.70
15	PO_4	0.9	2.30	2.50	2.45
16	PO_4	0.9	6.5	7.50	7.60
17	PO_4	1.7	2.80	2.50	2.70
18	PO_4	1.7	7.0	7.50	7.83
19	PO_4	1.7	12.9	15.00	15.1

$BaCl_2$ solution 0.025 *N*. Correction factor = 1.020.
25-cc. samples with 25 cc. of alcohol.
Blank, 0–0.6 mg. PO_4 = 0.1 cc.
0.6–1.2 mg. PO_4 = 0.3 cc.
1.2–1.8 mg. PO_4 = 0.6 cc.

Table IV shows the results of the direct titration on solutions containing several ions. These samples were all made up with sodium salts of the various ions shown.

TABLE IV. DIRECT TITRATION OF SAMPLES CONTAINING HYDROXIDE, CHLORIDE, CARBONATE, AND PHOSPHATE

SAMPLE	IONS PRESENT				$BaCl_2$ USED	SO_4 PRESENT	SO_4 FOUND
	OH	Cl	CO_3	PO_4			
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Cc.*	*Mg.*	*Mg.*
42	2.6	2.5	1.0	..	2.10	2.50	2.45
43	2.6	2.5	1.0	..	6.1	7.50	7.35
44	2.6	2.5	1.0	0.42	2.10	2.50	2.45
45	2.6	2.5	1.0	0.42	6.1	7.50	7.35
46	2.6	2.5	1.0	0.42	18.2	22.50	22.2
47	5.2	5.0	1.0	1.25	2.50	2.50	2.50
48	5.2	5.0	1.0	1.25	6.4	7.50	7.47
49	5.2	5.0	1.0	1.25	12.6	15.00	15.10

$BaCl_2$ solution 0.025 *N*. Correction factor = 1.020.
25-cc. samples with 25 cc. of alcohol.
Blank, 0–0.6 mg. PO_4 = 0.1 cc.
0.6–1.2 mg. PO_4 = 0.3 cc.

Table V shows the results for several samples analyzed by both titration and gravimetric methods. These samples were taken from a boiler and contained the concentrations of hydroxide and carbonate shown. They also contained small amounts of calcium, silicate, and various other impurities, as well as moderate concentrations of chloride.

CONCLUSIONS

Detailed directions are given below for carrying out a determination of sulfate by direct titration using tetrahydroxyquinone as the indicator.

REAGENTS NEEDED. (1) A 0.025 *N* barium chloride solution, standardized gravimetrically. (2) A mixture of potassium chloride and tetrahydroxyquinone, prepared by grinding the disodium salt of tetrahydroxyquinone with dried potassium chloride in a 1 to 400 ratio.

PROCEDURE. A 25-cc. sample, containing between 2 and 20 mg. of sulfate, in a 150-cc. Erlenmeyer flask, is carefully neutralized until it is just acid to phenolphthalein. The hydrochloric acid used to acidify the sample should not be stronger than 0.030 *N*, and must be added carefully from a buret. The sample should be below 30° C.

Add 25 cc. of ethyl alcohol or 25 cc. of alcohol denatured by formula 30.

Add 0.20 to 0.22 gram of the tetrahydroxyquinone–potassium chloride mixture. It is best to use a small cup to measure out the mixture. Swirl the flask until this is dissolved. This will give the solution a fairly deep yellow color.

Run in the 0.025 *N* barium chloride at a steady dropping rate with constant swirling of the flask, until a brown color begins to form. This is not the end point but indicates its approach. Add the barium chloride from here on, 2 or 3 drops at a time, with steady swirling until a red color appears; this is the end point. The red color appears throughout the body of the solution and not as spots of color. If the sample contains between 2 and 20 mg. of sulfate this titration will require less than 17 cc. of the barium chloride solution.

After deducting the 0.1-cc. blank, each cubic centimeter of the 0.025 *N* barium chloride solution is equivalent to 1.2 mg. of sulfate.

If more than 0.6 mg. of phosphate is present, the blank should be increased. For concentrations from 0.6 to 1.2 mg. of phosphate the blank should be 0.3 cc.; for concentrations from 1.2 to 1.8 mg. of phosphate the blank should be 0.6 cc.

TABLE V. COMPARISON OF RESULTS OF ANALYSIS OF SAMPLES GRAVIMETRICALLY AND BY TITRATION

SAMPLE[a]	OTHER IONS PRESENT[b]		RESULTS OF ANALYSIS[c]	
	OH	CO_3	Gravimetric SO_4	Titration SO_4
	Mg.	*Mg.*	*Mg.*	*Mg.*
1	1.1	0.16	2.60	2.48
2	2.0	0.23	9.82	9.70
3	1.7	0.22	8.75	8.72
4	2.0	0.35	10.60	10.80
5	5.2	0.16	19.40	19.20
6	6.5	0.38	23.13	23.10
7	6.7	0.38	30.13	30.90
8	3.0	0.38	15.35	15.45
9	1.5	0.20	7.35	7.25
10	1.7	0.29	8.78	8.85
11	2.0	0.13	6.45	6.40
12	2.7	0.25	7.25	7.50
13	2.3	0.22	9.08	8.98
14	2.5	0.26	9.55	9.80

[a] Samples taken from drum of an operating boiler.

[b] Chloride and small amounts of calcium, silicate, etc., present but not determined.

[c] Analyses shown, both gravimetric and titration, were carried out by S. J. Meisenberg, University of Michigan.

Analysis on aliquots diluted to 25 cc. which required less than 17 cc. of 0.025 *N* $BaCl_2$ solution. 25 cc. of alcohol added to samples.

In this direct titration the amount of various other ions which may be tolerated without causing error is 7.5 mg. of carbonate, 5 mg. of aluminum, 25 mg. of silicate, and 15 or more milligrams of magnesium. Calcium has no effect so long as the addition of the alcohol does not cause the precipitation of calcium sulfate. This precipitation must be prevented. Hydroxide and chloride are without effect. Iron above 0.1 mg. interferes and must be removed.

It is highly desirable to titrate a few samples of known sulfate concentration before using the method on unknowns. This is especially true in the present titration because the end point is somewhat different from those usually encountered and the best way to learn to recognize it is to titrate a few samples of known concentration.

The method is accurate within ±0.2 mg. of sulfate.

The use of the tetrahydroxyquinone method on solutions having a higher sulfate concentration than those indicated in the present discussion has not been investigated. It is possible that the method would be considerably more accurate in more concentrated solutions, and there are indications that the use of alcohol might be eliminated or the amount necessary in the sample during the titration considerably reduced. This should offer a fertile field for further investigation.

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Distillation of Hydrocyanic Acid from Sulfuric Acid Solutions

Quantitative Determination

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Pagel and Carlson (*9*) recently published a method for the accurate determination of hydrocyanic acid in the presence of various salts (including chlorides) showing that the quantitative distillation of hydrocyanic acid from dilute sulfuric acid solution takes place within 15 minutes under specified conditions. Richards and Singer (*10*) claimed that many hours' boiling (8 to 10) is necessary to remove all the hydrocyanic acid from solutions containing appreciable amounts of chlorides, the retardation being ascribed to the formation of a complex between the chloride ion and hydrocyanic acid. Richards and Singer found that a much shorter time (less than 2 hours) suffices to remove hydrocyanic acid from solution in the absence of more than a trace of chloride ion.

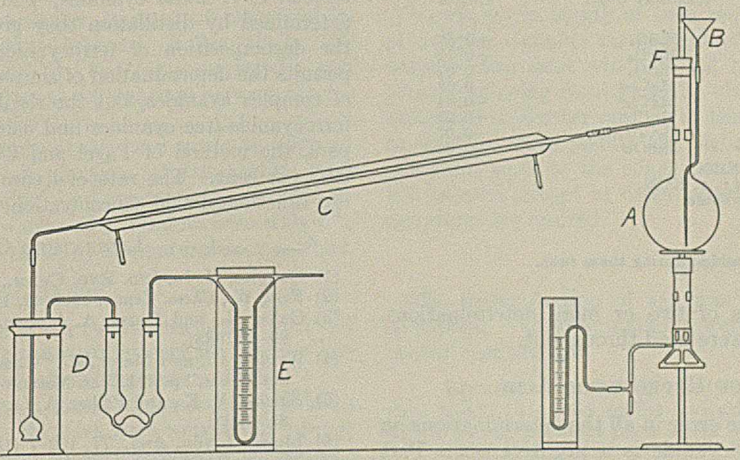

Figure 1. Diagram of Apparatus

A, 500-ml. Pyrex distilling flask with sealed-in capillary
B, long-stemmed funnel through which acid is added
C, special Pyrex condenser
D, absorption apparatus
E, flowmeter
F, tinfoil-covered rubber stopper

Method and Apparatus

When an attempt was made to determine hydrocyanic acid quantitatively by the method of Pagel and Carlson (*9*) certain difficulties were encountered which were traced to adsorption of hydrocyanic acid in the rubber stopper of the distilling flask and to the presence of ferrocyanide in the cyanides used. The optimum conditions reported in their paper were maintained. The excess sulfuric acid was calculated on the basis of the amount of cyanide used and was 0.35 *N* (*8*). Stock solutions of approximately 0.1 *N* alkali cyanides were used. The cyanide content was determined according to Liebig's method (*6*), with potassium iodide as the indicator. Titers of the stock solution were determined just before use. An enhanced Tyndall effect was obtained by using a focusing arc light (*1*).

To insure the same conditions in all experiments the flow of gas to the burner was regulated by a manometer and a flowmeter was used to regulate the flow of air through the capillary. The same pipet and buret were used throughout. Fifty milliliters of stock solution were used in all experiments. The solution in the distilling flask was heated to boiling as quickly as possible. Time of distillation was 15 minutes unless otherwise noted. Rate of distillation was 75 ml. per 15 minutes. Fifteen milliliters of 6 *N* sulfuric acid were used unless otherwise stated.

Pagel and Carlson's apparatus was modified as shown in Figure 1.

Adsorption of Hydrocyanic Acid by Stoppers

A quantitative comparison was made between determinations in which the stopper was covered with tinfoil and in which it was not, and the results are shown in Table I. The data are averages of two or more determinations. With tinfoil-covered stoppers the individual determinations agreed within 0.03 ml.

Table I. Absorption of Hydrocyanic Acid by Stoppers

Experiment	Cyanide[a] Used	Distillation	Kind of Stopper	Error
		Min.		%
1	NaCN	15	Rubber	−0.14
2	NaCN	30	Rubber	−0.12
3	NaCN	15	Rubber covered with tinfoil	−0.02
4	NaCN	15	Cork	−0.28

[a] Sodium cyanide free from ferrocyanide, prepared by distilling hydrocyanic acid into sodium hydroxide.

In two runs, when the stoppers were not protected by tinfoil, distillation was continued after the initial 15 minutes. Cuts were taken at the end of 30 and 45 minutes, and were redistilled once according to the procedure of Morris, Callaghan, and Dunlap (*7*). The distillate was tested for hydrocyanic acid by the Prussian blue method of Viehoever and Jones (*13*). All cuts gave the Prussian blue test, showing that adsorbed hydrocyanic acid was given up by the rubber stoppers.

Interference of Ferrocyanide

According to Roe (*11*) simple cyanides cannot be determined by distillation in the presence of complex cyanides. In carrying out these determinations many of the commercial brands of c. p. potassium cyanide were tested for ferrocyanide by the method of Krauch (*4*). Ferrocyanide was present in all cases tested; in but two cases was the presence admitted on the label. According to Sharwood (*12*) the presence of ferrocyanide causes high results when Liebig's method is used. This was confirmed by adding potassium ferrocyanide to sodium cyanide and titrating in the usual manner.

Ferrocyanide gave high results in all the cases where it was present.

Feld (*2*) reports that the simple cyanides may be determined in the presence of complex cyanides by distilling the mixture with magnesium chloride. The magnesium chloride yields sufficient hydrochloric acid to displace the hydrocyanic acid from the simple cyanides, but not from the complex cyanides. Tartaric acid is frequently recommended in cyanide distillations, especially in forensic examinations. The results obtained with these various reagents upon different cyanides are reported in Table II.

TABLE II. DISTILLATION WITH VARIOUS REAGENTS

EXPERIMENT	CYANIDE USED	REAGENT USED	ERROR
			%
1	KCN[a]	H_2SO_4	+0.69
2	KCN[b]	H_2SO_4	+0.72
3	NaCN[c]	H_2SO_4	−0.02
4	NaCN[c]	$MgCl_2$[d]	−0.08
5	NaCN[c]	$MgCl_2$[e]	−0.04
6	KCN[a]	$MgCl_2$[e]	−0.22
7	NaCN[c]	$H_2C_4H_4O_6$[f]	−0.07
8	NaCN[c]	H_2SO_4[g]	−0.04

[a] Well-known brand of c. p. KCN.
[b] Second well-known brand of c. p. KCN.
[c] Ferrocyanide-free sodium cyanide.
[d] 60 ml. of 3 *N* $MgCl_2$.
[e] 15 ml. of 3 *N* $MgCl_2$.
[f] 15 ml. of 6 *N* tartaric acid.
[g] 1 to 5 grams of NaCl were added during these runs.

The data are averages of two or more determinations. Tinfoil-covered stoppers were used throughout.

HYDROLYSIS OF HYDROCYANIC ACID

It will be noted that the error in all the determinations on ferrocyanide-free sodium cyanide is a negative one. Part of this loss is due to hydrolysis of hydrocyanic acid to ammonium formate. In a few cases the amount of hydrolysis during distillation was determined by a modification of the method of Gales and Pensa (*3*). After distilling off the hydrocyanic acid for a stated time (15 minutes) sodium hydroxide solution was added to the distilling flask and the ammonia was distilled off and determined in the distillate by nesslerization. A blank determination was made on the reagents and this value subtracted from the total amount of ammonia found. It is impossible, of course, to determine the amount of ammonia present in the cyanide solution directly by nesslerization; so a freshly prepared solution of sodium cyanide was used. In one case the amount of hydrolysis under the usual conditions was determined. The average error of four determinations was −0.06 per cent. An average of 0.04 mg. of nitrogen was found in the distillate after the addition of the sodium hydroxide. Making correction for this hydrolysis, the final error of the determination was +0.008 per cent. In another series (error −0.02 per cent) after correction for hydrolysis the final error was +0.04 per cent.

Since Krieble and Peiker (*5*) have shown that the rate of hydrolysis is dependent upon the acid concentration, it is advantageous to keep the concentration of the acid low.

RECOMMENDED PROCEDURE

In order to avoid loss of hydrocyanic acid by adsorption, rubber stoppers should be covered with tinfoil, or ground-glass joints should be used. By modifying the condenser as shown in Figure 1 a good joint can be made with heavy rubber tubing, which exposes very little rubber to the distillate. In order to avoid excessive hydrolysis, the concentration of acid should be kept low; the excess acid should be kept within 0.35 *N*. Either sulfuric or tartaric acid may be used to liberate the hydrocyanic acid. Fifteen minutes' distillation, when the total volume is 250 ml., is sufficient to remove all the hydrocyanic acid from solution when the rate of distillation is 300 ml. per hour. A slight vacuum should be maintained on the distilling flask at all times.

SUMMARY

No evidence was found that the distillation of hydrocyanic acid from sulfuric acid solutions was retarded by the presence of the chloride ion; this supports the findings of Pagel and Carlson rather than those of Richards and Singer. It was found that the removal of hydrocyanic acid was rapid and complete when stoppers were protected with tinfoil. Unprotected rubber stoppers and corks were found to adsorb hydrocyanic acid and very slowly give it up again. Ferrocyanide has been found to be a common impurity in commercial c. p. alkali cyanides; and when such cyanides are determined by distillation they give high results, owing to the decomposition of ferrocyanide. The method of Feld permits the determination of simple cyanides in the presence of complex cyanides, but the results are rather low. With ferrocyanide-free cyanides and using protected rubber stoppers, the method of Pagel and Carlson is accurate within 0.05 per cent. The rate of hydrolysis of hydrocyanic acid is a function of acid concentration.

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A Convenient Weighing Buret

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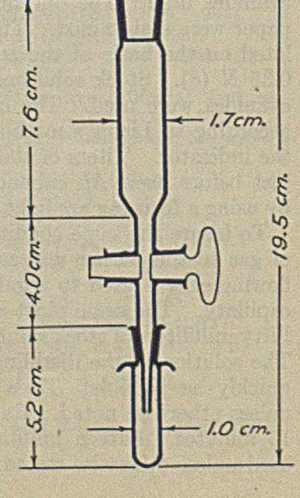
Iowa

The accompanying illustration represents the cross section of a weighing buret that has been found to be of good design and convenient to use. Such a buret, having a graduated barrel, may be made from an old buret.



RECEIVED August 25, 1933.

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Technic in Chemical Analyses of Casein

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In a former paper (*11*) a comparison of approved methods of analyzing casein showed considerable variation in results and indicated the necessity of further study with the hope of evolving standard methods of analysis. Browne (*5*), Shaw (*9*), and Sutermeister (*10*), who have reported on the physical and chemical analysis of casein, state that further study is necessary because of discrepancies occurring in results of various analysts. Zoller (*12*) in 1920 reported on the borax solubility test for commercial casein and suggested a modified test to differentiate between caseins made at high and low temperatures.

In the present paper studies have been made on methods of determining moisture, ash, nitrogen, fat, free acidity, total acidity, pH values, solubility, and conductivity. The samples used in this work were selected at random from sixty-five commercial lots of casein made by the natural-sour method.

Moisture

In Tables I and II are given summaries of the effect of different temperatures and amounts of vacuum used in drying samples from various commercial plants in Idaho.

An attempt was first made to obtain constant weights on samples dried at 102° C. Samples were weighed at periods of 5, 8, 24, and 30 hours and steadily increasing percentages of loss were obtained. A temperature of 90° C. was then tried in an attempt to find a lower temperature at which excessive losses did not occur. Losses continued to take place, although in lesser amounts than at 102° C., and were attributed largely to caramelization, because the samples gradually turned darker as they were heated longer. Whether the excess loss is due entirely or partially to caramelization or to changes in molecular structure was not determined. The temperature was then lowered to 80° C. and in order to hasten loss of moisture the samples were placed in a vacuum of 11 inches. No caramelization took place and constant weights were obtained in 24 hours. This method of 80° C. with 11 inches of vacuum was used as standard in determining moistures.

It was felt that this method required too much time to be practical for use in commercial laboratories, and that a shorter period of time with higher temperature, or with higher temperature and increased vacuum, might be used. Table II gives results of moistures determined at 100° C., 90° C. with 11 inches of vacuum, 100° C. with 22 inches of vacuum, and 135° C. with 22 inches of vacuum. Determinations were made at intervals of 0.5, 1, 2, 3, 4, and 5 hours.

Variations in length of time required to obtain moistures of different samples made it practically impossible to set a definite time limit which would be applicable in all cases. Closely agreeing results can be obtained at higher temperatures and in shorter periods of time, but the uncertainty as to whether these results are higher or lower than the true moistures leads to the conclusion that such methods should not be used except in cases where only approximate determinations are desired.

Ash

The determination of ash was very difficult because of spattering. Various methods were used in an attempt to control this problem.

1. Samples were charred slowly on a hot plate for 5 hours, then placed in a cold muffle and gradually heated to 650° C., which usually required from 2.5 to 3 hours. The samples were held at this temperature from 5 to 6 hours or until a white ash was secured.
2. Samples were charred on a hot plate 5 hours, 5 cc. of concentrated nitric acid were added, and heated in the muffle as above.
3. Samples were charred on a hot plate 5 hours, varying amounts of calcium acetate were added (5 and 3 cc. of a 10 per cent solution), then heated in the muffle as above. Blank determinations gave the amount of calcium oxide left on burning.
4. Same as (3) except that calcium acetate was added before charring.
5. Five and 3 cc. of calcium acetate were added, and samples were placed directly in the cold muffle without charring and heated as in (1).

Two-gram samples of casein were used in all ash determinations. The results are given in Table III. The best checks and highest ash content were obtained when 5 cc. of calcium acetate were added to the sample and placed in the cold muffle without previous charring. It is necessary to bring all the casein in contact with the calcium acetate solu-

Table I. Comparison of Methods of Determining Moisture Content of Casein

Sample	102° C.				90° C.				80° C. + 11-Inch Vacuum			
	5 hrs.	8 hrs.	24 hrs.	30 hrs.	5 hrs.	8 hrs.	24 hrs.	30 hrs.	5 hrs.	8 hrs.	24 hrs.	30 hrs.
	%	%	%	%	%	%	%	%	%	%	%	%
1	5.25	5.18	5.26	5.57	4.78	4.79	5.25	5.65	4.13	4.28	4.39	4.38
2	5.42	5.54	5.49	5.89	4.61	4.68	5.27	5.46	4.17	4.27	4.84	4.59
3	5.35	5.48	5.50	5.58	4.59	4.68	5.25	5.17	3.95	3.99	4.48	4.34
4	7.60	7.72	7.78	7.82	7.08	7.02	7.55	7.73	6.46	6.68	7.00	7.03
5	5.46	5.47	5.48	5.64	4.97	4.98	5.30	5.34	4.04	4.63	4.70	4.67
6	5.52	5.50	5.68	5.87	5.43	5.44	5.54	5.54	4.75	4.95	4.99	5.05
7	4.50	5.29	5.34	5.55	4.57	4.76	4.83	4.87	3.89	4.34	4.36	4.29
8	4.74	5.01	5.20	5.18	4.62	4.98	5.10	5.09	3.31	3.78	3.86	4.11

Table II. Comparison of Methods of Determining Moisture Content of Casein

Sample	100° C.						90° C. with 11-Inch Vacuum						100° C. with 22-Inch Vacuum					135° C. with 22-Inch Vacuum					
	0.5 hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	0.5 hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	0.5 hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	3.46	4.30	4.33	4.82	5.03	5.03	2.83	3.55	4.64	4.85	4.95	5.10	5.03	5.41	5.47	5.50	5.51	5.40	5.79	6.05	6.25	6.36	6.61
2	3.67	5.12	5.45	6.01	6.28	6.34	2.92	3.69	4.72	5.00	5.18	5.34	5.21	5.58	5.88	5.96	5.96	5.54	6.11	6.50	6.74	6.88	7.03
3	3.48	4.36	4.93	5.12	5.33	5.48	3.05	3.93	4.80	5.01	5.16	5.31	5.36	5.60	5.76	5.80	5.82	5.80	6.21	6.50	6.73	6.90	7.02
4	3.95	5.27	5.38	6.03	6.16	6.20	3.52	4.71	5.49	5.83	5.82	5.98	6.05	6.34	6.40	6.46	6.47	6.44	6.64	6.98	7.13	7.16	7.13
5	3.18	4.34	5.21	5.33	5.54	5.69	3.52	4.00	5.05	5.33	5.41	5.62	5.54	5.93	5.99	6.03	6.03	5.60	6.08	6.41	6.51	6.55	6.66
6	3.56	4.34	5.20	5.57	5.72	5.81	3.35	3.38	5.17	5.37	5.47	5.59	5.48	5.92	6.01	6.05	6.05	5.41	6.07	6.39	6.60	6.64	6.73
7	2.65	3.84	4.80	5.05	5.35	5.47	2.92	3.67	4.65	4.98	5.07	5.25	4.96	5.52	5.61	5.65	5.69	5.40	5.95	6.22	6.37	6.41	6.58
8	2.56	3.49	4.37	4.87	5.15	5.22	2.56	3.25	4.32	4.57	4.76	4.93	4.42	5.05	5.26	5.33	5.33	4.98	5.76	5.98	6.12	6.18	6.33

tion and allow it to stand for about 20 minutes before placing in the muffle. This permits the casein to become thoroughly moistened and apparently aids in the prevention of spattering. Three cubic centimeters of calcium acetate solution did not seem to be a sufficient amount to moisten the entire sample and prevent spattering.

When the sample was charred on the hot plate without the addition of calcium acetate, some spattering occurred. When calcium acetate was added before charring, the sample apparently dried out on the hot plate and there was some spattering in the muffle. When nitric acid was added, spattering always took place, regardless of whether it was added before or after charring or placed directly in the muffle. Spattering can never be prevented when the temperature in the muffle is raised too fast. Best results were obtained when 2.5 to 3 hours were allowed to raise the temperature to 650° C.

TABLE III. COMPARISON OF METHODS OF DETERMINING ASH CONTENT OF CASEIN

(5.5 hours in muffle at 650° C.)

			CALCIUM ACETATE USED					
			Added after charring		Added before charring		No charring	
SAMPLE	CHARRED	CHARRED 5 CC. HNO_3 ADDED	3 cc.	5 cc.	3 cc.	5 cc.	3 cc.	5 cc.
	%	%	%	%	%	%	%	%
1	2.75	3.25	3.31	3.29	3.40	3.31	3.29	3.79
2	3.20	3.21	3.09	3.20	3.37	3.11	3.00	3.37
3	2.71	4.71	3.16	3.39	3.50	3.73	2.71	4.17
4	3.00	3.79	3.40	3.51	3.26	3.32	2.94	3.94
5	2.73	2.66	3.11	2.98	3.10	3.37	3.36	3.45
6	3.52	3.61	3.32	3.44	3.31	3.42	2.88	3.47
7	1.92	3.38	3.05	2.97	3.36	3.44	2.97	3.50
8	2.99	2.67	3.19	3.19	3.38	3.18	1.93	3.55

NITROGEN

In Table IV are presented the results on total nitrogen determined by the Gunning method and Kjeldahl mercury method (*2*), with the exception that the samples were digested longer than the 2 hours suggested. The samples were digested over ordinary gas burners using gasoline gas, on which a pyrometer registered a heat of approximately 850° C. It is possible that higher heats might have brought about complete digestion in a shorter period of time. Sutermeister (*10*) states there is present in casein from 1.2 to 3.43 per cent of humin nitrogen largely derived from tryptophane, which is rather difficultly hydrolyzed even in strong acids. It is therefore questionable whether a 2-hour digestion will render all the nitrogen available. In the authors' experiments at least 4 hours with the Gunning method and 6 hours with the Kjeldahl mercury method were required to bring about complete digestion. The Kjeldahl mercury method seemed somewhat slower than the Gunning method in bringing about complete digestion and the final results even after 8 hours were slightly lower, although the difference was so small as to be negligible.

TABLE IV. TOTAL NITROGEN CALCULATED ON MOISTURE-FREE BASIS

SAMPLE	GUNNING METHOD				KJELDAHL MERCURY METHOD			
	1 hr.	4 hrs.	6 hrs.	8 hrs.	1 hr.	4 hrs.	6 hrs.	8 hrs.
	%	%	%	%	%	%	%	%
1	13.36	14.16	14.33	14.25	13.34	14.04	14.24	14.21
2	13.03	14.13	14.21	14.21	13.48	13.98	14.15	14.15
3	13.14	14.10	14.14	14.14	13.18	13.91	14.07	14.09
4	13.26	14.27	14.34	14.31	13.47	14.04	14.26	14.29
5	13.16	14.37	14.41	14.40	13.22	14.06	14.21	14.31
6	13.72	14.34	14.34	14.34	13.60	14.02	14.23	14.25
7	13.36	14.13	14.15	14.16	13.20	13.80	13.96	13.96
8	13.32	14.19	14.19	14.20	12.95	13.80	13.92	13.94

Table V presents data showing the calculation of nitrogen on the moisture-free basis and the moisture-, fat-, and ash-free basis as recommended in the usual method of procedure.

According to the United States Government specifications for water-resistant glues for use in airplanes as given by Bogue (*3*), casein must contain not less than 14.25 per cent nitrogen, calculated on the moisture-, fat-, and ash-free basis. The American Medical Association (*1*) states that "calcium casein should contain not less than 1 per cent calcium, 0.6 per cent phosphorus, and 14 per cent nitrogen on the moisture-free basis."

TABLE V. TOTAL NITROGEN BY GUNNING METHOD

(4 hours' digestion)

Sample	1	2	3	4	5	6	7	8	PURE CASEIN (HAMMARSTEN)
	%	%	%	%	%	%	%	%	%
Moisture-free basis	14.16	14.13	14.10	14.27	14.37	14.34	14.13	14.19	15.08
Moisture-, fat-, and ash-free basis	14.80	14.69	14.75	14.87	15.02	14.95	14.78	14.74	15.53

A number of impurities are present in casein, such as mineral salts, fat, albumen, lactose, and acids. Other research workers have felt that it is possible to estimate to a certain extent the undetermined impurities in casein by calculating nitrogen on the moisture-, ash-, and fat-free basis. However, since the determination of nitrogen in casein is meant to show not merely the undetermined impurities but rather the total amount of impurities present in the sample, the authors feel that the determination should be made on the moisture-free basis only.

Comparative determinations were made as to length of time required for digestion on gas and electric burners. Further work was also done, using selenium oxychloride as a catalyst, recently recommended by Lauro (*6*), Osborn and Krasnitz (*8*), Messman (*7*), and others. Various combinations of catalysts were also used, as shown in Table VI.

TABLE VI. TOTAL NITROGEN CALCULATED ON MOISTURE-FREE BASIS

(Sample F16)

ELECTRIC BURNERS					GAS BURNERS				
	Na_2SO_4 + $CuSO_4$	Na_2SO_4 + $CuSO_4$ + $SeOCl_2$	Na_2SO_4 + Hg + $SeOCl_2$	Na_2SO_4 + $CuSO_4$ + Hg + $SeOCl_2$		Na_2SO_4 + $CuSO_4$	Na_2SO_4 + $CuSO_4$ + $SeOCl_2$	Na_2SO_4 + Hg + $SeOCl_2$	Na_2SO_4 + $CuSO_4$ + Hg + $SeOCl_2$
Hrs.	%	%	%	%	*Hrs.*	%	%	%	%
0.5	...	14.16	14.20	14.23	1	...	14.16	14.37	14.37
1	14.13	14.37	14.25	14.44	2	14.30	14.33	14.41	14.35
1.5	14.22	14.40	14.45	14.37	3	...	14.35	14.43	14.35
2	14.37	14.37	14.41	14.25	4	14.38	14.37	14.46	14.37
4	14.38	14.40	...	...	6	14.39	14.39	...	...

With the higher heat of the electric burners a considerable saving in length of time was experienced, digestion being complete in 2 hours. With selenium oxychloride in addition to copper sulfate, mercury, or copper sulfate and mercury in combination, the time of digestion was shortened to 1 hour on the electric burners and 2 hours on the gas burners. With the three catalysts in combination, 1 hour apparently was sufficient to obtain all the nitrogen on the gas burners. When the samples were digested longer than 2 hours on the electric burners a loss occurred in the nitrogen due to evaporation of the sulfuric acid and increase of concentration of salts in the solution. These losses were prevented by additions of sulfuric acid as required. No losses of nitrogen occurred with the gas burners, regardless of the length of time of digestion.

FATS

Table VII gives the results of fat determinations by various methods. The ether extraction was made in the regular way (*2*), using a 2-gram sample of casein and extracting for 48 hours. The sample was ground to pass a 20-mesh sieve, giving various degrees of fineness from 100 mesh to 20 mesh. A 1-gram sample was used in the Roese-Gottlieb method: 10 cc. of water, 2 cc. of concentrated ammonia, and 10 cc. of 95 per cent alcohol were added, shaken until completely dissolved, and the fat extracted in the usual way with ether and petroleum ether. Results by this method were much higher than by other methods because of the fact that a white colloid-like substance passed through the filter paper along with the dissolved fat. This material precipitated out in the flask on partial evaporation of the ether. Attempts were made to filter it out at this stage, but the final results, while lower, were so inaccurate, owing to the small amount of fat and the uncertainty as to whether all the colloidal material had been filtered out, that the method was finally abandoned.

TABLE VII. INFLUENCE OF METHOD OF ANALYSIS ON PER CENT FAT

SAMPLE	ETHER EXTRACTION	ROESE-GOTTLIEB	BABCOCK
1	0.37	1.16	0.36
2	0.27	0.97	0.36
3	0.22	0.68	0.27
4	0.13	1.03	0.14
5	0.34	1.64	0.28
6	0.29	1.79	0.32
7	0.32	1.89	0.32
8	0.18	1.52	0.16

TABLE VIII. EFFECT OF SIZE OF CASEIN PARTICLES ON FAT EXTRACTION

(Adams ether extraction 48 hours)

SAMPLE	100 MESH	65 MESH	40 MESH	20 MESH
	%	%	%	%
11	0.31	0.28	0.14	0.15
12	0.26	0.26	0.23	0.16
13	0.28	0.22	0.12	0.12
14	0.50	0.29	0.21	0.20
15	0.37	0.14	0.05	0.05

The Babcock method used, given by Sutermeister (*10*), approximates very closely the official ether extraction method, and is probably the best practical method to use in commercial plants. Attempts were made to dissolve the casein in various other solvents than those given by Sutermeister, such as sodium borate, sodium phosphate, and ammonium and sodium hydroxides. These solvents dissolved the casein very rapidly, but when sulfuric acid was added the reaction was so violent that it was almost impossible to prevent some loss of the sample from the bottle. The best results were obtained by the use of 1 gram of casein, 10 cc. of water, 4 cc. of butyl alcohol, and 2 cc. of concentrated ammonium hydroxide. The casein dissolved readily and did not cause very violent reaction when 15 cc. of concentrated sulfuric acid were added.

The Mojonnier method was also tried, but the same difficulties were found as in the Roese-Gottlieb method.

In Table VIII is shown the effect of the size of casein particles upon fat solubility by the ether extraction method. The results are self-evident. Apparently some fat is held within the larger particles of casein so that it cannot be extracted. No attempt was made to grind the casein finer than 100 mesh, and it is possible that a small amount of fat remained in the casein, but it was felt that this degree of fineness is sufficient to obtain practically all the fat. In fat determination on casein, therefore, the authors believe that the ether extraction method is the most accurate of any tried, providing the sample is ground to 100 mesh and extracted for at least 48 hours.

COMPARISON OF FREE ACIDITY, TOTAL ACIDITY, pH VALUE, CONDUCTIVITY, SOLUBILITY, AND ASH CONTENT

Table IX gives the results on free acidity, total acidity, pH value, conductivity, and ash on eight commercial samples of casein and a pure casein (Merck, purified according to Hammarsten).

Free acidity was determined by adding 100 cc. of water to 10 grams of casein, allowing it to stand for five hours, filtering and titrating 50 cc. of the filtrate with 0.1 *N* sodium hydroxide. Total acidity was obtained by dissolving 1 gram of casein in 25 cc. of 0.1 *N* sodium hydroxide, adding 50 cc. of water, and titrating back with 0.1 *N* sulfuric acid, using phenolphthalein as an indicator. pH values were determined by both the hydrogen electrode and quinhydrone methods, using a 5 per cent suspension of casein. In determining conductivity, a 5 per cent suspension of casein was used in specially prepared conductivity water and allowed to stand for 17 hours, or overnight, before running.

Ash was determined by the calcium acetate method discussed previously. Solubility was determined in minutes required completely to dissolve a given amount of casein in 300 cc. of a 2.5 per cent solution of sodium borate at 65° C.

In the determination of pH values the stirring hydrogen-electrode method developed by Bollen (*4*) was used. Comparisons were made with the quinhydrone method in order to determine whether this simpler method could be used. No practical differences were obtained and it is felt that for all practical purposes the quinhydrone method may be used for determination of pH values on casein.

In Table X is given a comparison of the effects of time, strength of solution, and size of particles on pH values. The casein was allowed to stand for at least 1 hour in solution in order that it might become thoroughly saturated. Since no differences were obtained regardless of fineness of particles, length of time in solution after 1 hour, or amounts of casein in solution, it was decided to use the 5 per cent suspension because of the greater ease of handling.

TABLE X. EFFECT OF STRENGTH OF SOLUTION AND SIZE OF CASEIN PARTICLES ON pH VALUE

	EFFECT OF AMOUNT OF CASEIN ON pH VALUE						EFFECT OF SIZE OF PARTICLES OF CASEIN ON pH VALUE			
	5 %		10 %		20 %	50 %	20 mesh	40 mesh	65 mesh	100 mesh
Hours										
1	3.80	3.82	3.83	3.88	..	..	3.95	3.90	3.92	3.92
18	3.80	3.80	3.85	3.85	3.85	3.93	3.88	3.88	3.88	3.92

In Table XI is shown the effect of these same factors upon conductivity. Apparently at least 17 hours or overnight standing in solution is necessary to reach a constant. Fineness of particles also has considerable effect, the salts seeming to go into solution much more rapidly when the casein is ground to smaller mesh. However, there is no difference in conductivity if the sample is allowed to stand overnight. Slightly higher results were obtained when a 5 per cent suspension was used, probably because of a more complete solution of the salts present. The 5 per cent suspension was decided upon as the more convenient to use.

TABLE IX. COMPARISON OF FREE ACIDITY, TOTAL ACIDITY, pH VALUE, CONDUCTIVITY, AND ASH OF NINE SAMPLES OF CASEIN

SAMPLE	FREE ACIDITY	TOTAL ACIDITY	HYDROGEN ELECTRODE pH	QUINHYDRONE pH	CONDUCTIVITY	RESISTANCE	SOLUBILITY 10 GRAMS CASEIN	ASH CONTENT
	Cc.	*Cc.*				*Ohms*	*Min.*	%
1	12.70	14.72	3.90	3.99	1.41×10^{-3}	709.0	8.5	3.79
2	12.85	14.75	3.90	3.91	1.40×10^{-3}	714.0	6.0	3.37
3	12.10	14.62	3.97	4.04	1.62×10^{-3}	617.0	7.5	4.06
4	11.65	14.50	3.91	4.12	1.40×10^{-3}	714.0	6.0	3.69
5	7.15	14.10	4.21	4.21	1.01×10^{-3}	990.0	5.5	3.63
6	7.85	13.90	4.27	4.28	1.21×10^{-3}	825.0	5.5	3.56
7	9.55	13.60	4.11	4.10	1.19×10^{-3}	840.0	6.5	3.85
8	10.95	14.01	3.81	3.85	0.975×10^{-3}	1025.0	6.0	3.47
Pure casein (Hammarsten)	1.60	9.75	5.64	5.64	0.148×10^{-3}	6754.0	1.0	2.44

Table XI. Effect of Strength of Solution and Size of Casein Particles on Conductivity

Casein in Solution	Conductivity				
	Immediately	4 hours	6 hours	17 hours	45 hours
%					
5	0.72×10^{-3}	1.20×10^{-3}	1.54×10^{-3}	1.43×10^{-3}	1.40×10^{-3}
10	1.88×10^{-3}	2.55×10^{-3}	2.77×10^{-3}	2.68×10^{-3}	2.67×10^{-3}
20	2.31×10^{-3}	4.10×10^{-3}	4.51×10^{-3}	4.97×10^{-3}	4.95×10^{-3}
Particle Size	10 Per Cent Solution				
20 mesh	1.88×10^{-3}	....	....	2.73×10^{-3}	....
40 mesh	2.35×10^{-3}	....	....	2.73×10^{-3}	....
65 mesh	2.53×10^{-3}	....	....	2.75×10^{-3}	....
100 mesh	2.62×10^{-3}	....	....	2.76×10^{-3}	....

Considerable difficulty was experienced in an attempt to arrive at a solubility factor for the various caseins. The regular procedure of using 50 grams of casein in 300 cc. of 2.5 per cent sodium borate solution heated to 65° C. was followed. It was found impossible to determine the end point accurately, because of the milky whiteness of the solution, which obscured the last particles of casein to such an extent that one could not see whether they were in solution or not. The method was modified after various trials with different indicators by the addition of 1 cc. of a 1 per cent solution of corallin in alcohol. This gave a red color to the casein solution which permitted easy visibility of the particles not in solution. It was found by this method that casein ground to pass a 20-mesh sieve dissolved rather readily in fairly definite lengths of time, but that a few larger lumps were always left which would not dissolve even in an hour's time. The method was then modified, using the same strength of sodium borate solution and the same temperature, but dissolving only 10 grams of casein. Complete solution was obtained by this method.

The results are given in Table IX. Since the value of the borax test lies in its ability to give direct evidence as to the value of a casein for glue-making, paper-sizing, etc., further work must be done upon this phase of the problem before any definite conclusions may be drawn.

From the results given in Table IX, it seems evident that some relation exists between acidity, pH values, conductivity, and solubility. Where acidity is low and conductivity shows a high resistance there is always a tendency toward a low ash content and a rapid solubility. When the commercial samples are compared with the analyses of pure casein (purified according to Hammarsten), this fact becomes self-evident. Pure casein gives a much lower free acidity and a considerably higher resistance in ohms, while the ash content is lower and the solubility much more rapid. The pH value also indicates that there is much less acidity in the sample of pure casein than in the commercial caseins.

The method of treatment of the commercial sample in its preparation will obviously have a considerable influence on all methods of analysis proposed, but in the authors' estimation the sensitivity of conductivity to variable factors gives it an importance above all other methods in determining the impurities present in the sample. pH values also aid in determining the acidity of the sample and should be studied along with the free acidity and total acidity determinations.

Methods of analysis for moisture, ash, nitrogen, fat, pH value, and conductivity as recommended in this paper have been used by five research workers in analyzing approximately three hundred samples of casein. Extremely satisfactory results have been obtained.

Summary

In order to determine moisture accurately it is necessary to use temperatures which will not cause caramelization of the sample. The best results were obtained when the samples were dried in vacuum at 80° C. for 24 hours, a sufficient time to produce constant weight.

Regardless of care in manipulation, it was found impossible to burn the samples for ash by ordinary methods and obtain accurate results. Spattering always occurred when nitric acid was added or when calcium acetate was used in too small amounts. Charring the sample previous to burning in the muffle aided only partially. The only method that gave accurate checks was the use of 5 cc. of calcium acetate solution, allowing it to stand in contact with the casein for 20 minutes, then placing it in the cold muffle and gradually bringing to a temperature of 650° C. The burning was continued at this temperature until a white ash was obtained.

In total nitrogen determinations it was found necessary to digest the sample at least 4 hours by the Gunning method and 6 hours by the Kjeldahl mercury method on gas burners before all the nitrogen was obtained. Electric burners shortened the length of time of digestion to 2 hours. When selenium oxychloride was added to the copper sulfate, mercury, or copper sulfate and mercury in combination, the length of time of digestion was shortened to 1 hour on the electric burners and 2 hours on the gas burners.

The modified Babcock test for fat gave results agreeing very closely with the official ether extraction method. The official method gave the best results, if the sample was ground to at least 100 mesh and extracted for 48 hours.

The quinhydrone method of determining pH values of casein can be used satisfactorily.

The determination of conductivity is proposed as an additional aid in evaluating caseins. Its extreme sensitivity to variable factors in the preparation of caseins makes its determination of value.

Further studies are being carried out on the solubility factor. Present methods are rather unsatisfactory when accurate analysis is desired.

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Scientists of the Bureau of Standards have developed a modified type of ink which, it is believed, will have no deteriorating effect on paper. Experts found, by inking papers and subjecting them to accelerated aging by the application of heat, that the ordinary type of writing ink caused rapid embrittlement of the papers. In some cases folding endurance was decreased by as much as 50 per cent. After many experiments, the ink found satisfactory in this connection is alkaline, ammonia replacing the acid of the usual type of ink. There was practically no embrittlement of papers inked with the newly developed preparation when they were subjected to the heat test.

Determination of Sulfuric Anhydride in Sulfonated Oils and Other Products

New Direct Gravimetric Method

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IN THE analysis of sulfonated (sulfated) oils for organically combined sulfuric anhydride by the present direct method (*1*) or the sulfuric acid titration method, the sample is boiled with sulfuric acid and the increase in acidity, which corresponds to the organically combined sulfur, is determined volumetrically in the presence of methyl orange indicator. The method is rapid and reliable, and has replaced to a considerable extent, in this country as well as abroad, the old gravimetric method consisting of two barium sulfate determinations. The method, however, fails in the presence of titratable salts, such as sodium acetate, that do not give a sharp end point with indicators. Moreover, the titration method as well as the old gravimetric method is not applicable to oils of the true sulfonic type which are not hydrolyzed by acids.

In connection with an investigation of sulfonated oils by a committee, of which the writer is chairman, appointed by the American Association of Textile Chemists and Colorists, a new direct gravimetric method has been developed by the writer—the ash-gravimetric method—which seems applicable to all types of sulfonated oils, including those containing troublesome titratable salts. The ash-gravimetric method consists essentially in isolating the sulfonated compound free from inorganic salts and determining the ash of the purified product. The method is direct in the sense that it requires only one determination and the inorganic sulfate present in the oil need not be determined separately.

Preliminary tests have indicated that the new method will determine the combined sulfur not only in sulfonated oils of the usual kind—i. e. ester type—but in special sulfonated products, such as sulfonated mineral oils, sulfonated saponifiable oils of the true sulfonic type, sulfonated aromatic hydrocarbons, and sulfonated fatty alcohols, esters, and other compounds which have recently appeared on the market (Nekal, Gardinol, Igepon etc.) as substitutes for soap and wetting-out agents. The only requirement in the successful application of the method is that the product may be completely extracted by solvents over a saturated solution of sodium chloride or sulfate.

It was found that the ash of the pure sulfonated product consists of sodium sulfate and represents just half of the organically combined sulfuric anhydride. The reaction during ignition is as follows, where R stands for the organic radical:

$$2\text{R-SO}_4\text{Na} \longrightarrow \text{Na}_2\text{SO}_4 + \text{SO}_3 + \text{etc.}$$

or

$$2\text{R-SO}_3\text{Na} \longrightarrow \text{Na}_2\text{SO}_4 + \text{SO}_3 + \text{etc.}$$

In the calculation it is assumed that the ash consists of sodium sulfate rather than potassium or other metal sulfate. This assumption applies to nearly all commercial oils, since the sulfonic (or sulfate) group is almost completely neutralized during the washing, which is usually done with a solution of either sodium chloride or sulfate.

PROCEDURE

The procedure is varied somewhat, depending upon whether or not the product contains ammonia, and whether or not when dissolved in ether it forms emulsions with saturated salt solutions.

A. REGULAR PROCEDURE. Weigh 10 grams of the sample into a 250-cc. pear-shaped separatory funnel containing 50 cc. of 25 per cent sodium chloride solution. Add 5 drops of a 0.1 per cent solution of methyl orange and 75 to 100 cc. of ether, and acidify with approximately normal sulfuric acid until the lower layer is distinctly pink (about 0.2 cc. excess). Add solid sodium chloride equal to one-third of the acid added, shake vigorously until the salt is practically dissolved, and allow the layers to separate.

Draw off the lower layer into another separatory funnel and wash the ether layer with 25 cc. of the salt solution. Combine the salt layers and extract twice with 20-cc. portions of ether. Combine the ether layers and, after carefully removing any water that may settle, shake well for 3 to 5 minutes with 10 cc. of 25 per cent sodium sulfate solution, at 50° C. Separate the lower layer as completely as possible, warming it in warm water or with steam to keep the salt from crystallizing. After the water layer is removed, however, crystallization of any salt that may be dissolved in the ether layer should be induced by cooling to about 15° C. and, if necessary, by scratching the wall of the funnel with a glass rod.

Filter into a dry 250-cc. beaker, washing the funnel and crystals, if any, with three 10-cc. portions of ether or until all the fatty matter has been transferred. Cool the filtered ether solution in ice water for 15 minutes, warm to 25° to 30° C., filter again into a dry 300-cc. flask, and wash the beaker and filter paper with three 10-cc. portions of chilled ether. The filtered solution when again chilled to 0° C. and warmed to 25° to 30° C. should remain perfectly clear. A flocculent precipitate during chilling that does not clear upon warming indicates insufficient solvent to keep the fat in solution at that temperature, in which case more solvent should be added.

Distill off the ether until the volume has been reduced to about 20 cc. and transfer to a tared 50-cc. crucible (high form), which is allowed to float in a 100-cc. beaker filled with warm water. Rinse the flask with two 10-cc. and two 5-cc. portions of ether, respectively, or until all the oil has been transferred to the crucible, each addition being made only after the ether of the previous portion has practically evaporated. Care should be taken during the evaporation to prevent loss of oil by creeping; this may be avoided and the evaporation hastened by constant stirring with a glass rod, which is ultimately wiped clean with ashless filter paper that is added to the crucible. After the ether is evaporated, burn the oil gently and ignite to constant weight. To complete the oxidation of any remaining carbon or traces of sulfide that may be formed, moisten the ash with a few drops of 30 per cent hydrogen peroxide and again carefully ignite to constant weight.

B. PROCEDURE IN PRESENCE OF AMMONIA. Dissolve 10 grams of the sample in 80 cc. of water in a 300-cc. beaker, add 10 cc. of 0.5 *N* sodium hydroxide, and boil the solution gently until wet litmus paper no longer indicates ammonia. Cool and transfer into a 300-cc. pear-shaped separatory funnel and add about 33 grams of solid sodium chloride, or enough to make finally a 25 per cent salt solution. Add 5 drops of a 0.1 per cent solution of methyl orange and proceed with the neutralization and extraction as directed in A.

C. PROCEDURE IN CASE EMULSIONS FORM. Dissolve the sample in 50 cc. of water and transfer carefully to a separatory funnel. Add 100 cc. of ether and enough solid sodium chloride to saturate the water layer and leave some solid salt in excess. Shake well, add methyl orange indicator, and acidify as directed under regular procedure. If emulsions form, add 2 cc. of alcohol at a time until the emulsion breaks, mixing gently but not shaking after each addition of the alcohol. Proceed then following procedure A, except that whenever emulsions are formed, break them with alcohol as outlined.

DISCUSSION

According to Nishizawa and Winokuti (*2*), sulfonated oil is least soluble as its monosodium compound—i. e., free from soap—and in that form it is entirely insoluble in, or may be completely extracted from, saturated solutions of either sodium chloride or sodium sulfate. Hence in the procedure enough acid is added to the sample before extracting just to decompose the soap. A very slight excess of acid is permissible. Sodium chloride rather than sulfate is used for the first few washes because it gives a much sharper color change with methyl orange and because the salt does not tend to crystallize. The purpose of the final wash with sodium sulfate is to dehydrate the ether extract as much as possible.

The addition of caustic soda to samples of sulfonated oil containing ammonia is required only where the combined SO_3H group is partly or wholly neutralized by the ammonia. In that case unless converted into the sodium salt there would be a loss of combined sulfate due to the volatilization of the ammonium salt upon being ignited. Ammonium soaps, however, do not interfere with the regular procedure.

In the presence of sodium acetate, the acidification as outlined probably decomposes the acetate incompletely into acetic acid, which is partly extracted by the ether. This does not interfere with the method, since during ignition the acetic acid is entirely volatilized. The ether layer probably becomes contaminated also with some of the undecomposed sodium acetate which, however, is removed together with other foreign inorganic salts by the Glauber's salt wash and during the chilling process.

ANALYSIS OF SAMPLES

To test the possibilities of the new method in the case of the ordinary commercial sulfonated oils and similar products containing sodium acetate, the committee was requested to analyze two samples of sulfonated oils, samples B and B-1, by both the sulfuric acid titration method and the new ash-gravimetric method. The results are given in Table I. Sample B was a highly concentrated sulfonated (sulfated) castor oil and sample B-1 was a mixture of equal parts of sample B and a 5 per cent solution of anhydrous sodium acetate. In the case of sample B-1 the committee reported unanimously that accurate end points were impossible; hence, no data are listed under the sulfuric acid titration method.

TABLE I. DETERMINATION OF COMBINED SULFURIC ANHYDRIDE IN SULFONATED OILS BY NEW AND OLD METHODS

	SAMPLE B					SAMPLE B-1		
	ASH-GRAVIMETRIC METHOD			SULFURIC ACID TITRATION METHOD		ASH-GRAVIMETRIC METHOD		
ANALYST	I	II	AV.	AV.	ANALYST	I	II	AV.
	%	%	%	%		%	%	%
1	5.37	5.37	5.37	5.24	1	2.51	2.58	2.55
2	..	..	..	5.39	3	2.48	2.52	2.50
3	5.05	4.98	5.02	5.18	4	2.52	2.50	2.51
5	..	..	..	5.26	5	2.51	2.57	2.54
6	5.04	5.10	5.07	5.10	6	2.65	2.54	2.60
7	5.26	5.18	5.22	5.16	7	2.63	2.64	2.64
8	5.22	5.17	5.20	5.17	8	2.67	2.61	2.64
9	5.20	5.24	5.22	5.25	9	2.50	2.54	2.52
10	5.27	5.29	5.28	5.19	10	2.46	2.57	2.51
Mean			5.20	5.22				2.56[a]
Greatest difference			0.35	0.29				0.14
Average deviation			0.09	0.06				0.05

[a] By calculation, 2.60.

It will be noticed that the mean for sample B by the new and old methods was 5.20 and 5.22 per cent, respectively; also that for sample B-1 the mean by the new method was 2.56 per cent compared with 2.60 per cent by calculation. It will also be observed that the different analysts obtained good agreement in the results by the new method; thus the greatest differences were 0.35 and 0.14 per cent, and the average deviations were 0.09 and 0.05 per cent, respectively, for samples B and B-1.

COMBINED SULFURIC ANHYDRIDE IN COMMERCIAL SULFONATED COMPOUNDS

Sulfonated products of different types were analyzed in the writer's laboratory by the new method and the results are listed in Table II. Where the method could be used, results by the sulfuric acid titration method are also given. Where it was not possible to compare the two methods, the combined salt water washes by the new method were further extracted with ether or ether-alcohol, but in all cases the residues in the extracts were found to be negligible. Furthermore, the ash invariably gave a negative test for chloride, indicating the probability that the ether extracts were free from Glauber's salt. Because of troublesome emulsions with samples 4, 5, 6, and 7, the combined sulfuric anhydride in these products was determined by procedure C.

TABLE II. DETERMINATION OF ORGANICALLY COMBINED SULFURIC ANHYDRIDE IN SULFONATED COMPOUNDS

SAMPLE	DESCRIPTION	ASH-GRAVIMETRIC METHOD	SULFURIC ACID TITRATION METHOD
		%	%
1	Sulfated castor oil	5.23	5.19
2	Sulfated castor oil[a]	2.58[b]	...
3	Sulfated olive oil[c]	3.90	3.82
4	Sulfonated oil[d]	3.00	0.00
5	Sulfated fatty alcohol	16.18	15.80
6	Sulfonated fatty ester[e]	6.25	0.00
7	Sulfonated aromatic hydrocarbon[f]	10.70	0.00
8	Sulfonated mineral oil	14.21	0.00
9	Sulfonated mineral oil[g]	4.88[h]	0.00

[a] Equal parts of sample 1 and 5 per cent solution of sodium acetate.
[b] By calculation 2.60.
[c] Neutralized with ammonia.
[d] Saponifiable, true sulfonic acid type.
[e] Fatty acid combined with sulfo-alkylamine.
[f] Isobutyl naphthalene sodium sulfonate.
[g] One part of sample 8 and two parts of 25% solution of Na_2SO_4.
[h] By calculation 4.74.

SUMMARY

A new gravimetric method, called the "ash-gravimetric" method, is outlined for the determination of organically combined sulfuric anhydride in sulfonated oils. The method is direct and seems to be applicable to all types of sulfonated oils, including: the sulfate or ester type, with or without titrable salts; sulfonated saponifiable oils (true sulfonic type); sulfonated mineral oils; sulfonated aromatic hydrocarbons; and sulfonated or sulfated fatty alcohols and esters —the last two being soap substitutes recently brought on the market. In many of these cases the present sulfuric acid titration method is not applicable. In the new method only one sample is required for analysis, compared with two by the other methods. The manipulations are comparatively simple, check results are easily obtained, and the concordance among different analysts is very satisfactory.

ACKNOWLEDGMENT

The writer wishes to express his appreciation to M. B. Hart of this laboratory for assistance with the analytical work, and to L. A. Olney, chairman of the Research Committee of the American Association of Textile Chemists and Colorists, under whose guidance the subcommittee on sulfonated oils is working.

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Inhibiting Effect of Certain Substances upon Oxidation of Sulfurous Acid

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THE literature regarding the determination of sulfurous acid contains many indications that incomplete recovery may be due to oxidation of sulfite or bisulfite to sulfate. Many of these have been summarized by Monier-Williams (*3*). Among the substances mentioned early as hastening the oxidation are included oxalic acid, carbon dioxide, ozone, and copper. Among substances reported as retarding the oxidation are mannitol, benzaldehyde, ethyl alcohol, glycerol, benzylic alcohol, sucrose, invert sugar, asparagine, aspartic and glutamic acids, potassium lactate, and stannous and stannic chlorides. Recently Kolthoff (*2*) has published observations on a number of the above substances and also on manganous and ferrous ions, glucose, lactose, and boric acid in the oxidation of 0.05 *M* sodium sulfite and sodium bisulfite solutions standing at room temperature.

Waterman (*5*) observed that excess alkali increased the oxidation of sodium sulfite. Observation that sodium sulfite oxidized more rapidly than sulfurous acid solutions led Nichols and Reed (*4*) to choose the latter as a reference substance in distillation experiments.

Experiments with Sulfurous Acid Solutions

It was thought desirable to extend to sulfurous acid solutions a study of some of the substances used with sulfite and bisulfite solutions by Kolthoff. This study[1] was carried out as follows:

The sulfurous solutions were prepared by passing sulfur dioxide gas from a cylinder into distilled water and diluting to the desired strength. For each substance studied, 50 cc. of the diluted solution were made up in a 500-cc. volumetric flask. After thorough mixing, this was divided equally by means of a 250-cc. volumetric flask and each portion poured gently into a 500-cc. Erlenmeyer flask containing one of the substances in the amount indicated in Table I. Where necessary the flasks were rotated gently to cause the inhibitor to go into solution as far as possible. The flasks were closed with paraffined cork stoppers and kept in a dark cupboard at room temperature between observations.

Table I. Decomposition of 0.0573 *M* Sulfurous Acid at Room Temperature

Substance Added to 250 cc. of Solution	Diminution of Titer of Sulfurous Acid Solution 8 days	16 days	23 days
	%	%	%
5.0 g. sucrose	3	12	16
5.0 g. mannitol	2	12[a]	18[a]
5.0 g. lactose	6	14	18
5.0 cc. glycerol	3	13	18
0.05 g. stannous chloride	12	20	23[a]
0.5 g. stannic chloride	10	20	27[a]
10.0 cc. ethyl alcohol	9[a]	22[b]	32[b]
20.0 mg. Cu ion (cupric tartrate)	15	28	37
0.5 g. $SnCl_4$ and 0.5 g. H_3PO_4	15	27[a]	39
3.0 g. boric acid	16	31	41
0.5 g. molybdic acid	17	33	44
0.5 g. boric acid	22	40[b]	47[b]
No addition	17	42	52[b]
10.0 mg. ferrous ion (sulfate) and 1.0 g. H_3PO_4	40	79	[c]
50.0 mg. ferrous ion (sulfate)	75	[c]	[c]

[a] Duplicate determinations differed from mean by more than 2 per cent.
[b] Duplicate determinations differed from mean by more than 5 per cent.
[c] Remaining solution insufficient for titration.

The initial concentration of sulfurous acid was 0.0573 *N*. The per cent loss in concentration of sulfurous acid as shown by titration into 0.1 *N* iodine after 8, 16, and 23 days is shown in Table I, the substances added being listed in order of their effectiveness in preventing oxidation at the time of the last observations.

Several of the inhibitors that appeared to be effective at room temperature were next used in the distillation of sulfurous acid into iodine, using the method and apparatus described by Nichols and Reed (*4*).

The sulfurous acid solutions were prepared as before by bubbling sulfur dioxide from a cylinder through distilled water and diluting to the desired strength. Of the diluted solutions 10 cc. were introduced into an 800-cc. Kjeldahl flask which was immediately connected, through a condenser and adapter, to a 500-cc. Erlenmeyer flask standing in an ice-water bath and containing 50 cc. of approximately 0.1 *N* iodine solution. Through a vent tube with a narrow tip dipping below the solution in the Kjeldahl flask were then added in succession 10 cc. of 10 per cent sodium bicarbonate and 10 cc. of concentrated hydrochloric acid. Following these additions, 150 cc. were distilled over into the receiving flask, and the residual iodine was titrated with 0.1 *N* sodium thiosulfate. Blank determinations were made in a similar manner in all cases, omitting only the sulfurous acid solution, and the corrections were applied before calculating the per cent recovery.

The results are given in Table II, showing in each case the calculated probable error of the mean percentage recovery.

Table II. Effect of Inhibitors on Percentage of Sulfurous Acid Distilled from Sulfurous Acid Solutions

Inhibitor Added Kind	Amount	Blank Correction as SO_2	SO_2 Recovered
	Grams	*Gram*	%
None	....	−0.0006	92.7 ± 0.8
Dextrose	6	+0.0003	103.8 ± 1.0
Sucrose	6	−0.0006	97.9 ± 0.2
Tartaric acid	6	−0.0004	98.3 ± 1.1
	Cc.		
Glycerol	10	+0.0002	89.5 ± 1.8
Benzyl alcohol	2	−0.0004	94.9 ± 3.9
Ethyl alcohol	10	−0.0099	82.2 ± 3.2
Mannite	6 grams	−0.0001	104.0 ± 2.2

Experiments with Dried Fruit

The inhibitors used with sulfurous acid solutions were employed in the determination of sulfurous acid in several samples of dried fruit, using the method described above. The results corrected for blanks and with the probable errors of the means are shown in Table III, with the exception that mannite was tried with only one sample of fruit (apricots). In this case the corrected value was 490 p. p. m. ± 3 without the inhibitor, and 493 p. p. m. ± 2 with the addition of 6 grams of mannitol.

Jeu and Alyea (*1*) have reported that hydroquinone and other phenols exert a powerful retarding effect upon the oxidation of sulfite under the conditions of their experiments; hence several of these were tried in the distillation of sulfurous acid from dried fruits. Metallic zinc (dust) and tin (mossy) were also tried, as was the addition of a layer of refined mineral oil (Nujol). The equivalent ratio of sulfur dioxide to phenol in the experiments with apricot sample 2 was 25; with pears it was 18; with apricot sample 1 it was 0.9 and 4.5 (pyrogallol). The results are given in Table IV, in which as in preceding tables the probable errors of the means are also shown.

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[1] Begun by C. M. Wiedmann in this laboratory.

TABLE III. EFFECT OF INHIBITORS ON AMOUNT OF SULFUROUS ACID DISTILLED FROM FRUIT

INHIBITOR ADDED		SULFUR DIOXIDE					
		APPLES		APRICOTS		PEACHES	
Kind	Amount	Found	Increase	Found	Increase	Found	Increase
	Grams	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
None	..	809 ± 2	...	1877 ± 23	...	1891 ± 12	...
Dextrose	6	839 ± 12	30	1914 ± 0	37	1812 ± 19	− 79
Sucrose	6	830 ± 6	21	.....	...	1867 ± 17	− 24
Tartaric acid	6	801 ± 20	− 8	1902 ± 12	25	1728 ± 32	−163
	Cc.						
Glycerol	10	852 ± 16	43	1899 ± 3	22	1884 ± 6	− 7
Benzyl alcohol	10	683 ± 8	−171	1607 ± 68	−270	.....	...
Ethyl alcohol	10	539 ± 0	−270	1699 ± 2	−178	1549 ± 76	−342

TABLE IV. EFFECT OF INHIBITORS ON AMOUNT OF SULFUROUS ACID DISTILLED FROM FRUIT

INHIBITOR ADDED		SULFUR DIOXIDE					
		APRICOTS 1		APRICOTS 2		PEARS	
Kind	Amount	Found	Increase	Found	Increase	Found	Increase
	Gram	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
None	.....	436 ± 20	..	2646 ± 2	...	1786 ± 52	...
Catechol	0.0055	....	..	2559 ± 3	− 87	.....	...
Resorcinol	0.0055	....	..	2537 ± 8	−109	.....	...
Hydroquinone	0.0055	....	..	2602 ± 3	− 44	.....	...
Hydroquinone	0.0275	455 ± 0	19	.....	...	.....	...
Pyrogallol	0.0042	419 ± 3	−17	2654 ± 48	8	1725 ± 0	61
Pyrogallol	0.0210	465 ± 4	29	.....	...	.....	...
Phloroglucinol[a]	0.0054	....	..	2664 ± 15	18	.....	...
Zinc, metallic	0.2	425 ± 11	−11	1845 ± 6	−801	.....	...
Tin, metallic	0.36	440 ± 5	4	.....	...	1822 ± 25	36
	Cc.						
Mineral oil	50	....	..	.....	...	1720 ± 31	− 66
Ethyl alcohol	10	....	..	.....	...	1584 ± 27	−202

[a] Including water of crystallization.

DISCUSSION

In the experiments with the sulfurous acid standing at room temperature the inhibiting or accelerating effects of the different added substances were in a general way similar to those reported by Kolthoff for sodium sulfite and bisulfite. Only ferrous ion had a definite accelerating effect. All the other added substances appeared to have more or less inhibiting effect, although in several cases the differences are probably too small to be of significance. Sucrose, mannitol, lactose, and glycerol had effects of undoubted significance, reducing the oxidation by two-thirds or more. While stannous and stannic chlorides and ethyl alcohol were less effective, even these substances reduced the oxidation by half or more.

In the distillation experiments with sulfurous acid solutions mannitol, dextrose, tartaric acid, and sucrose increased the recovery by an apparently significant amount. Benzyl alcohol was of doubtful effect and the determinations made with this inhibitor were noticeably erratic. Glycerol was also of doubtful value, while ethyl alcohol decreased the yield by a significant amount, although here again the determinations were somewhat erratic. The blank correction for most of the inhibitors used was small, usually amounting to about that for the reagents without inhibitors which is assumed to be due to loss of iodine by volatilization. The small positive corrections for dextrose and glycerol are probably errors. The blank correction for ethyl alcohol, however, is 15 or more times as large as for the other inhibitors, and has the effect of reducing the yield from over 100 to slightly over 80 per cent.

In the distillation of sulfurous acid from dried fruits, the data of Nichols and Reed (*4*) seem to support the conclusion that too high results are unlikely. Hence it is assumed that the highest values obtained by distillation into iodine approach most closely the true values.

Examination of the figures in Tables III and IV indicates that in the distillation of sulfurous acid from dried fruit none of the inhibitors used consistently increased the yield by a significant amount. Benzyl and ethyl alcohols again gave erratic results, and the yields were consistently and significantly lower.

The use of a layer of mineral oil was intended to keep the boiling liquid out of contact with the atmosphere in the distillation flask. This failed of its purpose, for severe bumping occurred and the layer was not entire during boiling; the oil separated in several large globules or agglomerations.

Quite commonly during distillation the side walls of the adapter in the receiving flask became coated with a somewhat waxy, yellowish, granular deposit at the surface of the liquid. When apricot sample 2 was being studied with zinc dust this deposit was unusually prominent. In this case the yield of sulfurous acid was remarkably low. The deposit was soluble in carbon bisulfide and was suspected of being sulfur, but was not identified. The occurrence of a deposit of similar appearance in subsequent blank determinations made it appear doubtful if it were free sulfur. When metallic tin was used the deposit was not unusually large. In this connection it is interesting to note that Zerban and Naquin (*6*) reported deposits of free sulfur in tin condensers during the distillation of sulfurous acid.

SUMMARY

Inhibiting effects of various substances noted by Kolthoff in the oxidation of sodium sulfite and bisulfite solutions at room temperature have been found to occur in sulfurous acid solutions. The authors' experiments indicate that none of the substances suggested as sulfite oxidation inhibitors and tried by them are effective in increasing the yield of sulfurous acid distilled from dried fruits.

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THE DISCOVERY that vitamin D is produced by the action of ultra-violet rays on organic substances started experiments to produce or multiply the vitamin in foods. Two German research workers claim to have discovered that prolonged treatment with ultra-violet rays produces poisonous substances.

Determination of Silicon in Sea Water

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THE presence of compounds containing silicon dissolved in natural waters was apparently first noted by Bergman (*3*) in 1770 and the first quantitative data were reported by Bunsen (*4*) in 1847. Three years later, Forchhammer (*7*) noted the presence of silicates in sea water collected near Copenhagen. In 1891 Murray and Irvine (*11*) summarized the quantitative data of other investigators on the silicon content of sea water, elaborated considerably on previous work, and attempted to show the role of the compounds containing silicon in the sea. This pioneer work may now be criticized because of the admitted lack of suitable analytical refinement and the failure to prevent contamination of the water samples. In 1905 Raben (*12*) made a detailed study of the determination of silicon in sea water using a gravimetric method which has since been improved by Wells (*18*). This procedure is undoubtedly the most reliable of the gravimetric methods, but the main objections to it are the large supply of water necessary for a determination, the length of time required, and the ease with which a sample may be contaminated.

The first application of a colorimetric method for silicates was that by Jolles and Neurath (*8*). These investigators used as their reagents concentrated nitric acid and a 16 per cent solution of potassium molybdate. The yellow color, developed by the formation of the silicomolybdate complex, was shown to reach maximum intensity when heated for a short interval. Solutions of water glass of known silicon content, accorded the same treatment as the samples, were used as standards. Later workers (*10, 13, 14*) eliminated heating and substituted the use of other mineral acids. In 1914 Winkler (*19*) introduced the use of potassium chromate solutions as artificial color standards and thus avoided any contamination of water-glass standards by glass vessels. Dienert and Wandenbulke (*6*) modified Winkler's procedure by the introduction of standards prepared from picric acid solutions. Atkins (*2*) showed that the colorimetric method was applicable to sea water, while the preparation of the picric acid standards for such determinations has been made the subject of investigation by King and Lucas (*9*).

COLORIMETRIC DETERMINATION OF SILICON

The chemistry of the method, as shown by Asch (*1*), depends upon the formation of a yellow heteropoly acid, having the probable formula of $H_8Si(Mo_2O_7)_6$ when an acidified solution of a soluble silicate is treated with ammonium molybdate. The method is accurate and is particularly advantageous because of the small amount of sample required and the ease and rapidity of manipulation. The procedure and preparation of the reagents required are as follows:

AMMONIUM MOLYBDATE REAGENT. Ten grams of ammonium molybdate are dissolved in 90 grams of distilled water. The heptamolybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, is the usual compound employed for this reagent and should be examined from time to time to insure freedom from silicates.

PREPARATION OF PURE PICRIC ACID. Forty grams of picric acid are dissolved in 100 ml. of benzene on a water bath. The resulting solution is filtered with suction through a Büchner funnel, leaving behind by decantation as much water as possible. The benzene is then partially evaporated, under reduced pressure, until water again appears in dark globules. These globules are decanted off and the excess benzene evaporated completely at reduced pressure, until the picric acid is dry and free from benzene. The drying under reduced pressure is performed on a water bath. Small quantities of picric acid are placed in clean, dry test tubes, and the tubes are sealed and stored until ready for use.

PREPARATION OF PICRIC ACID STANDARDS. A solution is prepared by dissolving 314.2 mg. of the vacuum-dried, recrystallized picric acid in distilled water and making up to a volume of exactly 1 liter. This solution has a color equivalent of 10 mg.-atoms of silicon per kilogram for sea water of chlorinities from 14.5 to 19.5 per mille. Fifty milliliters of the solution are diluted to a volume of 1 liter and portions of it are taken and diluted in volumetric flasks to 250 ml. Four milliliters of the picric acid solution, when diluted to 250 ml., are equivalent to 0.008 mg.-atoms of silicon per kg. when a 50-ml. Nessler tube is filled to the graduation. Solutions with different portions of picric acid are thus prepared and transferred to glass-stoppered bottles. When standards are desired, a series of 50-ml. Nessler tubes are filled to the mark with these solutions. Each increase of 2 ml. of the picric acid on dilution to 250 ml. gives an increase of 0.004 mg.-atoms of silicon per kg. A series of such standards is most convenient for field work and is stable over a considerable period of time.

If it is desired to report as milligram-atoms of silicon per liter, the original picric acid solution should contain 307.5 mg. of picric acid per liter instead of 314.2 mg.

METHOD. To 50 ml. of freshly sampled sea water, secured directly from the sampling apparatus as it arrives aboard ship, 2 ml. of the ammonium molybdate reagent are added and 4 drops of 18 *N* sulfuric acid. After 5 minutes, the resulting color is compared either with a picric acid standard in a colorimeter or with a series of standard solutions in Nessler tubes.

FURTHER EXPERIMENTAL INVESTIGATIONS

A study of four possible factors that might influence the colorimetric determination of silicon in sea water was made and the observations noted are summarized below.

POSSIBLE DIFFERENCES IN BEHAVIOR OF META- AND ORTHOSILICATES. To ascertain whether an inherent error in the determination may be encountered when different ions containing silicon are present, two standard solutions, one of sodium metasilicate and the other of sodium orthosilicate, were prepared. Weighed amounts of pure silica were fused with sodium carbonate and sodium hydroxide, respectively. The fused masses were dissolved in water, neutralized, and each diluted to a volume of 1 liter. Immediate analysis of these solutions colorimetrically gave the following:

	SILICA	
	True value *Mg.-at./l.*	Value obtained *Mg.-at./l.*
Orthosilicate	0.083	0.082
Metasilicate	0.083	0.082

These data were explained by the fact that one atom of silicon occurs in the ortho ion as well as in the meta ion and thus the same coördination of the silicon atoms with the molybdate radicals takes place and develops the same color intensity.

EFFECT OF TEMPERATURE ON SILICOMOLYBDATE COLOR. A series of samples containing the same amount of silicon was run at various temperatures from 7° to 25° C., but change in color intensity could not be detected with either the samples or the standard picric acid solutions.

EFFECT OF FUNGUS GROWTHS IN PICRIC ACID STANDARDS. A fungus growth was noticed in several picric acid standard solutions and the colonies started were permitted to continue. Three months later, on dilution of the standard and comparison with freshly prepared solutions, no diminution in color intensity was discernible.

EFFECT OF LONG STANDING ON PICRIC ACID STANDARDS. Picric acid solutions to be used for the preparation of standards were made in March, 1930. They were allowed to stand 17 months, part of the time subjected to the action of sunlight. In August, 1931, these samples were diluted in the usual manner and compared with freshly prepared solutions. No change whatsoever was observable. One year later (August, 1932), standards were again made from these solutions and compared with those freshly prepared and no change was noted. This fact appears to contradict the observations reported by Atkins (*2*), who noted a change in 3 months, but the authors have likewise observed that continual exposure of the diluted solution to the dust of the air, etc., may cause a fading in color within the period mentioned by Atkins. However, these diluted solutions may be kept for a considerable period in stoppered tubes, the stoppers being removed only when comparisons are to be made.

USE OF COLORIMETRIC METHOD

As the result of a detailed study of the method used in the laboratory and aboard ship, the following notes summarize certain observations and precautions necessary in the application of the method:

1. A greenish tinge is sometimes obtained with water having more than 0.07 mg.-atoms of silicon per kg., especially if Nessler tubes are employed. This interference may usually be eliminated by the use of the colorimeter or by the reduction of the size of the sample to 25 ml.
2. With waters of low silicon values, 100-ml. samples should be utilized. A sensitivity is obtained with Nessler tube series of 2 parts of silicon to 100,000,000 parts of water.
3. An excess of sulfuric acid causes a diminution in the color intensity, but no effect is noted with slight excesses of the molybdate solution. The yellow color of the heteropoly acid reaches its maximum intensity within 5 minutes after the addition of the reagents and remains constant for nearly 3 hours. However, the samples should be compared with the standards as soon as possible to avoid any increase in silicates caused by the dissolving action of the sea water on the glass container.
4. A maximum probable error of 5 per cent occurs when Nessler tubes are employed and this may be reduced by the employment of the colorimeter.
5. Dissolved compounds containing iron or phosphorus in sufficient quantities to affect the determination are not encountered in sea water (*1, 15*).
6. Organisms and finely divided inorganic material, if present in sufficient quantities, may be removed by filtration or centrifuging.
7. Contamination from glass bottles containing the sea water samples is very marked, as shown by Atkins (*2*) and Thompson and Johnson (*17*). Thus water that has been exposed to glass for some length of time should not be analyzed for silicon. If containers other than glass are employed, they soon corrode and the sediment settling to the bottom may absorb silicates. Thus for reliable results analyses should be performed only on freshly sampled sea water.
8. The C. P. picric acid contains varying quantities of water, and such material should never be used for the preparation of standards without recrystallization and drying.
9. Picric acid standards should never be prepared with sea water, as the dissolved salts have a very pronounced "salt effect."
10. Should it be deemed advisable to dilute samples with distilled water, an examination of the latter for silicon should first be made.
11. To insure concordant results on long trips, it is advantageous to prepare two standard stock solutions from two different batches of pure picric acid. The comparison standards are made from one of these solutions and these are checked occasionally against the second standard.
12. Various means of reporting the quantity of dissolved silicates in sea water occur in the literature. The authors feel that the most logical form of reporting the results is that recommended by a committee of chemists representing the different marine and oceanographic institutions on the Pacific Coast of Canada and the United States. The committee recommended that the constituents of sea water be reported as milligram-atoms of the element determined per kilogram of water. A milligram-atom is defined as the result obtained when the number of milligrams of the determined element per kilogram of sea water is divided by the atomic weight of the element (*5*).
13. The silicon content varies considerably in sea water ranging from less than 0.01 mg.-atom of silicon per kg. in surface waters where there is marked plankton growth to as high as 0.3 mg.-atom in the bottom ocean waters. Generally speaking, the silicon content increases with depth, and coastal waters as well as those of estuaries will show a seasonal fluctuation.

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Note on Shaffer and Hartmann Combined Carbonate-Citrate Method for Determination of Glucose

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IN MANY respects one of the most rapid and convenient methods for the determination of dextrose after the hydrolysis of starch by a malt solution is that of Shaffer and Hartmann[1] in which the "combined carbonate-citrate solution" is used. This is a single stable alkaline copper solution to which is added sufficient potassium iodide and potassium iodate to yield a 0.1 *N* iodine solution when acidified. With this combined reagent it is necessary only to add the dextrose solution, boil, cool, acidify, and titrate the excess iodine liberated.

In checking this method with a washed starch and also against dextrose (No. 41, Bureau of Standards), the amount recovered for the latter, calculated from the copper : glucose ratios of Shaffer and Hartmann, averaged 2.3 mg. more than that started with. In other words, in the authors' hands and under their conditions, with the standardization of uniform heating by an electric hot plate[2] in bringing the solution to a boil, there was somewhat more reduction from a given amount of glucose than that reported by Shaffer and Hartmann.

A preliminary examination of the data showed that there

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[1] Shaffer, P. A., and Hartmann, A. F., *J. Biol. Chem.*, **45**, 365 (1921).

[2] I. D. Jones has found that the rate of heating by the slightly fluctuating electric current may be readily controlled by the use of an ammeter and rheostat.

was a linear relation between the amounts of dextrose present and the amount of copper reduced. In order to derive an expression of this relation which would be more applicable under the authors' conditions than the published ratios, a straight line was fitted by the method of least squares to the results of 46 determinations (omitted).

This linear estimating equation was found to be:

Mg. of glucose = 0.458 (mg. of copper reduced) − 1.546, with a standard error of 0.74 mg. of glucose, over the range between 35 and 125 mg. of glucose.

These data indicate that the combined carbonate-citrate method gives results closely paralleling those published by the authors, but because of the number of factors which affect the reduction each analyst should carefully standardize his technic and for the more accurate work should derive an expression of the relation between the amount of dextrose present and the amount of copper reduced (or set of copper: glucose ratios) which is applicable under the conditions prevailing in his laboratory.

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Continuous Liquid Extractor

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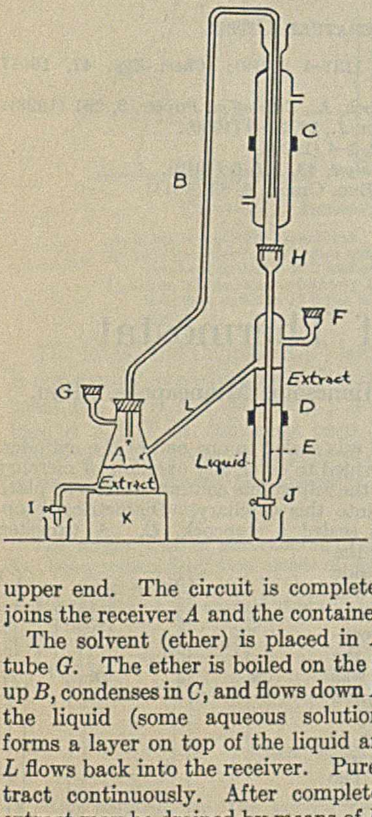
College of the City of New York, Convent Ave. and 140th St., New York, N. Y.

A CONTINUOUS liquid extractor for solvents having a lower specific gravity than the liquid to be extracted is shown in the figure.

The receiving flask *A*, containing the solvent, can be made from a 250-cc. Erlenmeyer flask. The container *D* consists of a large test tube constricted at both ends, the size of the tube varying with the quantity of liquid to be extracted. The side tubes *G* and *F* for filling the receiver and container, as well as *H*, are made by constricting the mouth of a 15 × 1.8 cm. test tube. The glass stopcocks *I* and *J* are used to drain the apparatus. If a glass-blower is available, *H* may be made with a mercury seal connecting the condenser and the container, thus doing away with a stopper. The tube *E* is joined to *D* at the upper end by an inner seal and extends down almost to the bottom of the tube; or, to do away with this inner seal, *E* can be joined to *D* by a stopper at the upper end. The circuit is completed by the tube *L* which joins the receiver *A* and the container *D*.



The solvent (ether) is placed in *A* by means of the side tube *G*. The ether is boiled on the steam bath *K*, vaporizes up *B*, condenses in *C*, and flows down *E*, bubbling up to extract the liquid (some aqueous solution). The ether extract forms a layer on top of the liquid and when it reaches tube *L* flows back into the receiver. Pure ether boils again to extract continuously. After complete extraction, the ether extract may be drained by means of *I* and the liquid removed from *D* by means of *J*.

The apparatus is absolutely stationary and never has to be moved or adjusted. It may be taken apart but can be filled and drained without disassembling very easily. A series of three or four of these extractors may be set up on a steam bath in a small hood. Both receiver and container may be varied in size, depending upon the quantities to be used. The container *D*, however, should be kept narrow, so as to have as much surface of the liquid as possible exposed to the ether bubbles. Complete extraction of a compound difficultly soluble in ether is accomplished in 8 to 10 hours.

Received July 31, 1933.

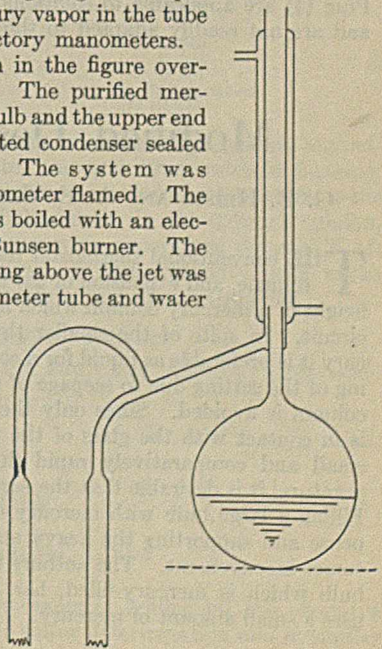
Apparatus for Filling Large Closed-End Manometers

Angus E. Cameron

School of Chemistry, University of Minnesota, Minneapolis, Minn.

THE ordinary method of filling a closed-end manometer and boiling out gases from the mercury during evacuation is attended with considerable danger of breakage when the manometer is of large bore and sufficient length to enable one to read pressures over a range of one atmosphere. Distillation of mercury into the manometer through a side tube seemed to permit trapping of gas or vapor below the wall of mercury vapor in the tube and result in unsatisfactory manometers.

The apparatus shown in the figure overcomes both difficulties. The purified mercury was placed in the bulb and the upper end of the short water-jacketed condenser sealed to a high-vacuum line. The system was evacuated and the manometer flamed. The mercury in the bulb was boiled with an electric heater or with a Bunsen burner. The mercury vapor condensing above the jet was delivered into the manometer tube and water vapor and gas passed up through the condenser. Once set in operation the system required no attention until sufficient mercury had accumulated in the manometer and then the closed end was sealed off at the strictured portion. Evacuation with a good oil pump should be sufficient to give a well evacuated manometer, since the device used to introduce the mercury is essentially a diffusion pump.

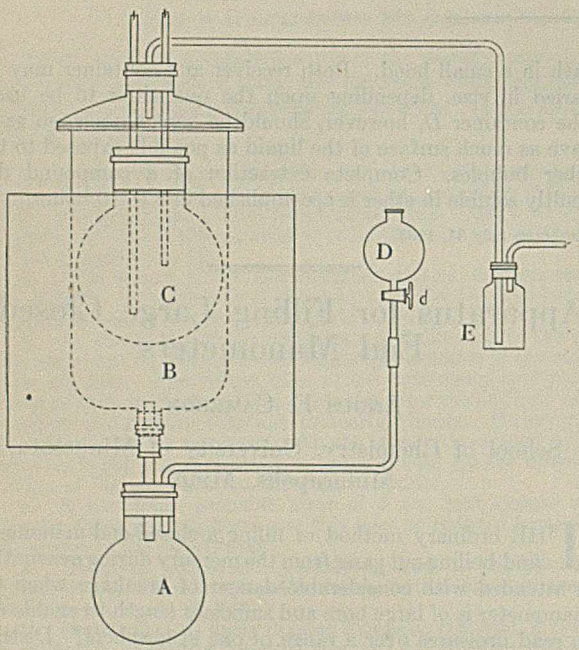


Received August 25, 1933.

Recovery of Iodine from Metallic Iodides by Oxidation with Technical Nitric Acid

Rush Fox McCleary and Ed. F. Degering, Chemical Laboratory, Purdue University, Lafayette, Ind.

IN THE preparation of zinc ethyl in this laboratory, it seemed advisable to devise a simple procedure for the recovery of iodine from the zinc iodide residues. The various methods for iodine recovery suggested by Torossian (*6*), Stephenson (*5*), Arndt (*1*), Kleinstück and Koch (*2*), and Puig (*4*) are applicable to solutions or finely divided solids, and are not readily adapted to the recovery of iodine from a zinc iodide cake. The procedure proposed by Lachman (*3*) involves the hazard of breaking the flask while crushing the hard cake of zinc iodide and unreacted zinc, and the procedure is a little involved. The apparatus shown in the figure eliminates this hazard, and also has the advantage of a simple procedure which gives a good initial yield of crude iodine.



Flask *A* contains the hard residue from the zinc ethyl distillation. *B* is an ordinary bell jar fitted with a ground-glass lid, and is surrounded by an ice bath. The system may be kept slightly evacuated through the water trap *E* by partially closing stopcock *d*. Crude concentrated nitric acid in slight excess of the calculated amount is introduced into flask *A*, in small portions, through funnel *D*. Stopcock *d* is left partly open and air is slowly and continuously drawn through the water trap *E*. This entrains the iodine vapors efficiently into the bell jar. Iodine which collects on the walls of flask *A* is easily removed by heating gently with a direct flame. Flask *C* is kept cool by means of circulating tap water.

In a recovery of zinc iodide residues which were calculated to contain 315.8 grams of iodine, 308.7 grams of crude iodine were recovered in the initial sublimation. This initial sublimate showed a purity of 90.83 per cent when titrated with standardized thiosulfate solution. By resublimation in the same apparatus, additional purification may be effected.

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(4) Puig, I., *Quím. e ind.*, 2, 1–4 (1925).
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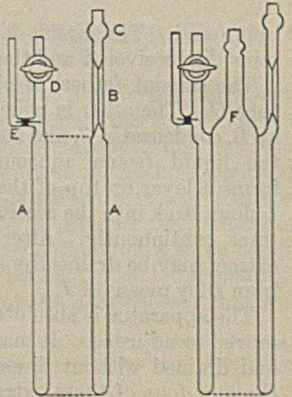
Received July 21, 1933.

Modified Design for Mercury Bulb of Thermostat

G. B. Heisig and A. E. Cameron, School of Chemistry, University of Minnesota, Minneapolis, Minn.

THE conventional thermostat regulator bulb is filled with toluene, and expansion of the toluene causes a change in height of a mercury column which makes or breaks the relay circuit. In spite of the smaller thermal expansion of mercury it is preferable as liquid for a control bulb because creeping of the setting due to seepage of toluene past the mercury column is avoided. Since only the layer of mercury which is in contact with the glass of the bulb can be effective for small and comparatively rapid fluctuations in bath temperature, it is desirable that the surface of the bulb be large. Filling a large bulb with mercury entails a considerable expense and supporting the heavy and rather fragile bulb becomes inconvenient. The authors have designed and used a bulb which is mercury-filled, has a large surface, and yet uses a small amount of mercury.

Two pieces of Pyrex tubing, as thin-walled as was consistent with mechanical strength, of diameters 3.5 and 2.5 cm., respectively, were placed one inside the other and sealed together at the ends to form a double-walled cylinder, a longitudinal section of which is shown at *A* in the accompanying sketch. A capillary tube, *B*, of 0.8-mm. bore was sealed to one end of the cylinder. A small bulb, *C*, was provided to catch any overflow of mercury from the capillary. For the adjustable contact an iron or platinum wire was inserted into this capillary. Diametrically opposite the capillary was sealed a stopcock, *D*. A tungsten wire was sealed through the stopcock arm from a side tube, *E*. The side tube was filled with mercury and a wire dipped into it to make contact to the mercury in the control bulb. The bulb was filled by evacuating it and running clean, dry mercury in through the capillary or through the stopcock, as was most convenient. The quantity of mercury in the bulb could be varied by opening the stopcock and allowing mercury to run into the bulb from the tube above the stopcock or by sucking mercury out of the bulb into this reservoir.



The control was immersed in the thermostat up to the stopcock key in such a location that water from the stirrer was circulated through the inside and around the outside of the cylinder. Using this control bulb and a radio tube relay device, the temperature of a 25-liter thermostat was maintained at 25° ± 0.002° C. A modification of the original design was suggested to one of the authors by Doctor Kingslake of the Institute of Applied Optics at the University of Rochester (New York). The inner tube of the cylinder was extended and drawn down as indicated at *F* to permit a hose to be attached to it. Water could then be drawn through the center of the bulb for use in maintaining a constant temperature in an apparatus which could not be immersed in a thermostat.

Received August 25, 1933.

Improved Lamp for Determination of Sulfur in Light Petroleum Products

E. R. Gillis, Casper Laboratory, Standard Oil Co., Casper, Wyo.

IT IS GENERALLY realized that the flame of the standard A. S. T. M. lamp is not readily controlled. This causes considerable loss of time, annoyance, and some inaccuracy in determining sulfurs by method D90-30T. Substitute lamps such as the Vapor Cresolene lamp (made by the Vapo-Cresolene Co., 62 Cortlandt St., New York, N. Y.) allow of ready flame control but have serious faults; the metal burner becomes very hot and causes undue evaporation of volatile oils such as light gasoline. This causes falsely low sulfur determinations and also makes it almost impossible to check results on such light petroleum products.

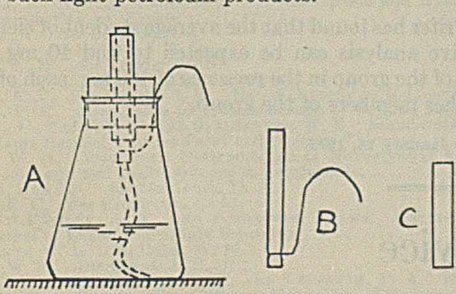


Figure 1. Improved Lamp

A, lamp completely assembled
B, adjusted sleeve with wire control. Approximate tubing size 0.125 × 2 inches (0.3 × 5 cm.)
C, outer tubing, approximately 1.5 inches (3.75 cm.) long and sufficiently large to slip over adjusting sleeve

The Edgar and Calingaert (*1*) lamp is very satisfactory but is not readily available in all laboratories and is not, properly speaking, an A. S. T. M. lamp. A slight modification of the regular A. S. T. M. lamp has been devised in this laboratory which is easily made by anyone and allows ready regulation of flame size without the necessity of taking the lamp from under the chimney.

The single piece of glass tubing of the regular A. S. T. M. lamp has been replaced by two pieces of different size, one within the other. The smaller piece is the same inside diameter as the old single piece and is recessed slightly near the bottom to allow a piece of fine wire about 7.5 cm. (3 inches) long and 0.5 mm. (0.020 inch) in diameter to be twisted around it. The larger piece is of sufficient size just to allow the smaller to slip freely within the larger. The larger, or outside piece of glass tubing, is held tightly in the cork. The smaller piece extends through and projects out of the larger at the bottom about 1.25 cm. (0.5 inch). To regulate the flame, the smaller piece which holds the wick is raised or lowered inside the larger by the wire which extends up through a groove in the cork. This groove is small enough to hold the wire by friction, which in turn holds the glass sleeve at any set position. Any vapors from light gasoline that pass up between the inner and outer tubing are burned in the flame along with gasoline fed through the wick. In other words, the vent for this lamp is the small annular space between the two pieces of glass tubing. The flame of course remains at the top of the larger piece at all times.

The author has run several samples of winter-grade gasoline and others even more volatile, using this new lamp, and finds that it gives very good results and requires much less attention than does the regular A. S. T. M. lamp. Some comparative results on the improved type of lamp and on the standard A. S. T. M. lamp are given below. Four runs were made with each type of lamp, using a cracked winter-grade gasoline of high sulfur content.

Improved Lamp Sulfur	A. S. T. M. Lamp Sulfur
%	%
0.249	0.240
0.255	0.209
0.252	0.237
0.247	Too badly smoked to titrate

None of the lamps of the improved type needed any adjusting or attention after the first 10 minutes of burning, while the A. S. T. M. lamps required full attention from the start until the finish of the burn. In the author's opinion, this new lamp is in many ways superior to the A. S. T. M. lamp for running gasolines of high volatility, and works equally well on heavy gasolines and illuminating oils.

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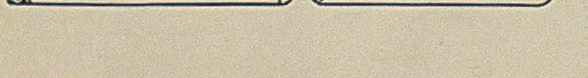
(1) Edgar and Calingaert, Ind. Eng. Chem., Anal. Ed., 2, 104 (1930).

Received August 5, 1933.

Stirring Rod with Fritted Glass Disk

John E. S. Han, 155/3 Route Stanislas Chevalier, Shanghai, China

FOR general use, the author has designed a stirring rod with a disk of fritted glass fused onto an end. The rod was made by the Jena Glass Works of Schott und Gen. and found to be highly serviceable in boiling off the excessive bromine during Eschka's sulfur determination and in similar operations. The rod is, however, not recommended for quantitative work where precipitation is involved, as precipitate is liable to lodge in the fritted glass.



Received September 26, 1933.

Qualitative Analysis of the Hydrogen Sulfide Group without Ammonium Polysulfide

Ralph W. Hufferd, DePauw University, Greencastle, Ind.

THE common practice in qualitative analysis is to oxidize the elements of the tin division of the hydrogen sulfide group to their higher valence with ammonium polysulfide. Because of the instability and variation in concentration of the polysulfide solution, it is not uncommon for stannous sulfide to resist the treatment and remain with the copper division precipitate. There is the added difficulty of having large quantities of the copper division sulfides, especially copper sulfide, carried over into the tin division. Polysulfide also introduces the nuisance of having a large bulk of sulfur mixed with the reprecipitated sulfides of the tin division, often leaving the analyst in doubt as to whether or not there is any sulfide there.

These difficulties can be either avoided or reduced so considerably as to cause no trouble to inexperienced students by the simple expedient of oxidizing the elements with bromine before precipitating them as the sulfides, and then making the division separation with ammonium sulfide. The sulfide is prepared as needed by passing hydrogen sulfide into 6 *N* ammonium hydroxide. As a precaution against oxidation of hydrogen sulfide to sulfur during precipitation of the sulfides, nitrate ion is destroyed by repeated boiling with 12 *N* hydrochloric acid.

Evaporate the filtrate from Group I to about 5 cc. but not to dryness. Add 10 cc. of 12 *N* hydrochloric acid and again evaporate to small volume. Repeat addition of hydrochloric acid and evaporation once or twice. This procedure does not take much time, but by destroying nitrate ion prevents excessive oxidation of hydrogen sulfide during precipitation.

Add 5 cc. of water and, if necessary, heat to dissolve any solid. It is sometimes necessary to add 2 cc. of 6 *N* hydrochloric acid. Add an excess of saturated bromine water, and boil off excess bromine. About 2 minutes' boiling will usually suffice. Starch-iodide paper can be used if there is any question. In the writer's laboratory the entire preparation is carried out in the 250-cc. Erlenmeyer in which precipitation is to take place. Neutralize the solution with ammonia and 6 *N* hydrochloric acid. Adjust acidity and volume in the customary manner, and precipitate with hydrogen sulfide.

Transfer the well-washed precipitate on the filter to a small beaker and add 10 cc. of fresh ammonium sulfide solution, prepared by saturating 10 cc. of 6 *N* ammonium hydroxide with hydrogen sulfide. Heat the beaker in boiling water for 3 minutes, stirring the contents occasionally. Unless the filter paper seems clean, no attempt should be made to remove it, as it will not interfere with the analysis of the copper division precipitate. This treatment will remove 100 mg. each of the three members of the tin division as sulfides.

After filtering and washing, the precipitate is ready for analysis for copper division elements. Precipitate the tin division sulfides from the filtrate in the customary way.

The writer has found that the average student of elementary qualitative analysis can be expected to find 10 mg. of any member of the group in the presence of 100 mg. each of several or all other members of the group.

Received January 18, 1933.

Filtering Device

E. B. Kester, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

CONSIDERABLE time is lost in the laboratory purifying by recrystallization of small quantities of substances, particularly derivatives of organic compounds such as oximes, hydrazones, semi-carbazones, anilides, and the like. Not only must a Büchner or Hirsch funnel and suction flask be arranged and filter paper installed, but precipitates must be transferred back and forth from funnel to flask. Losses are incurred inevitably. Moreover, it frequently happens that a chemist is isolating a product which during the earlier stages of purification melts below room temperature, in which case he finds it difficult if not impossible (without recourse to more elaborate preparations) to carry out a filtration before his product fuses.

The filtering device illustrated eliminates the need of transfers of solids or solid-liquid mixtures. Numerous successive recrystallizations can be carried out in a surprisingly short time with little loss of product save that which brings the mother liquors up to saturation. Filtrations of crystals obtained by chilling in refrigerating media can be conducted in the media. Increased pressure is obtainable over that secured in suction filtrations.

A large Pyrex test tube, preferably of 75 to 80 cc. capacity, is selected, care being taken to obtain one in which the bore is fairly uniform. A plunger of Bakelite, hard rubber, or other inert substance is turned out on a lathe to such dimensions that the plunger has only sufficient clearance to enable it to slip easily up and down the tube. A number of longitudinal pinholes (about 0.7 mm. in diameter) are bored for escape of the liquid.

When a crystallization has been completed, the filtration is accomplished by merely forcing the plunger to the bottom of the tube. This operation should be started slowly to permit a cake to build up that will prevent escape of crystals up the sides and through the orifices, but may be accelerated when such cake has formed. At the end, the plunger may be pressed down with considerable force so that the product is free of excess liquid when the mother liquors are poured off and the plunger has been withdrawn. It can then be washed, triturated, or recrystallized and filtered again in the same container and in the same way as before. Drying is effected by evacuation of the tube or passing a current of air over the cake.

A soft rubber plunger similarly molded affixed to a glass rod is even more satisfactory from the standpoint of cleanness of filtration, but it can only be used in connection with mild solvents. Benzenoid hydrocarbons, for example, rot soft rubber so rapidly there is serious danger of contamination of product, to say nothing of ruination of the device itself.

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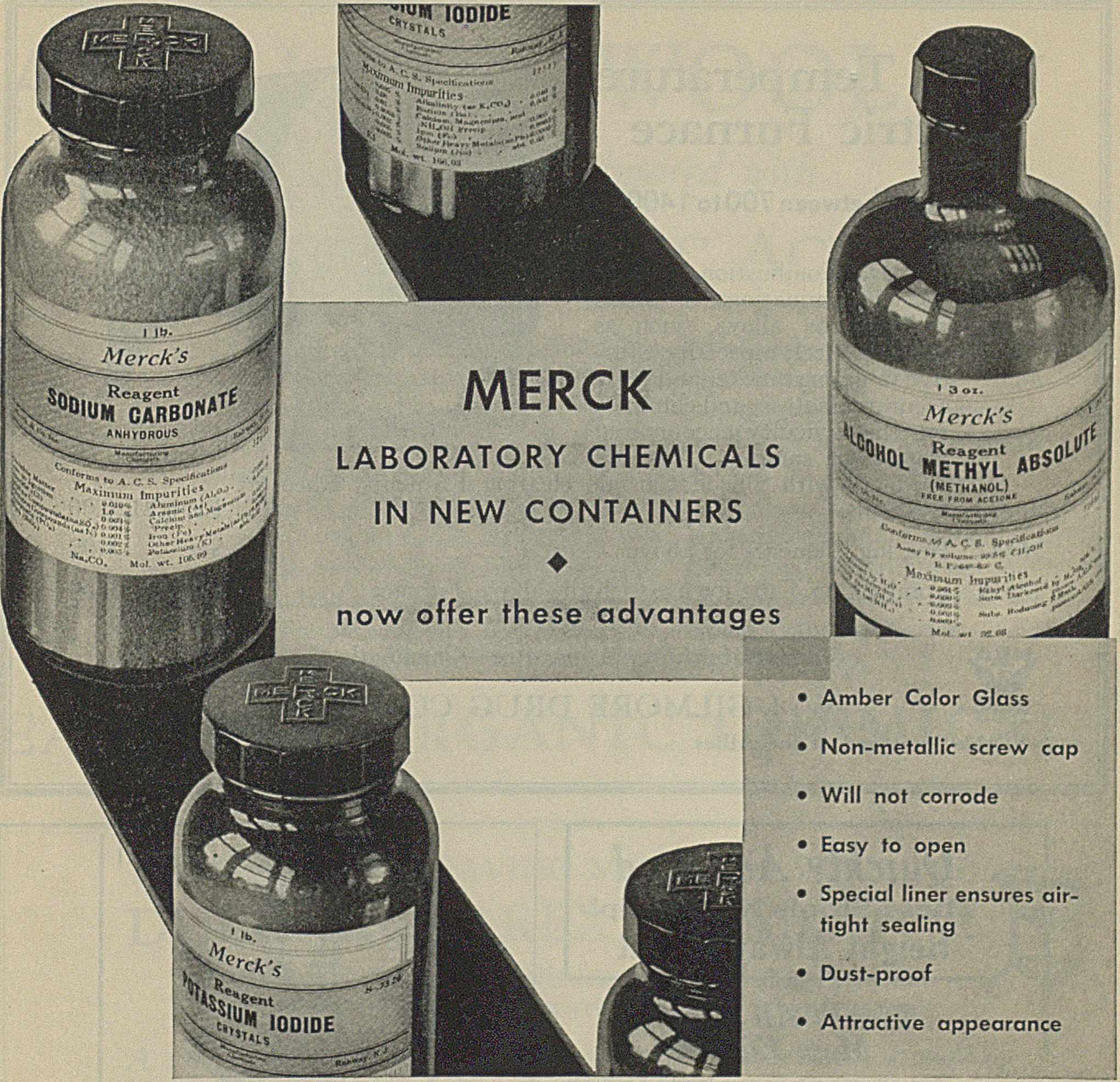

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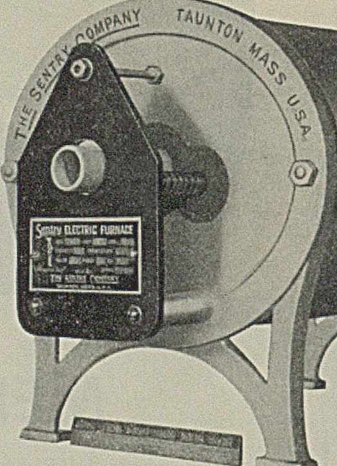

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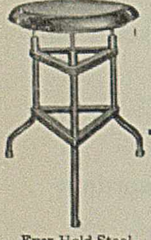

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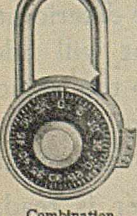

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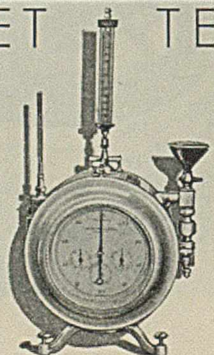

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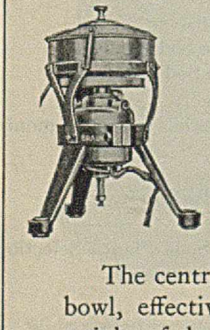

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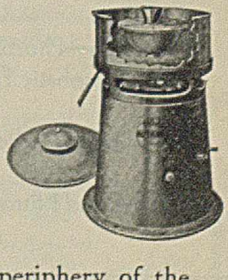

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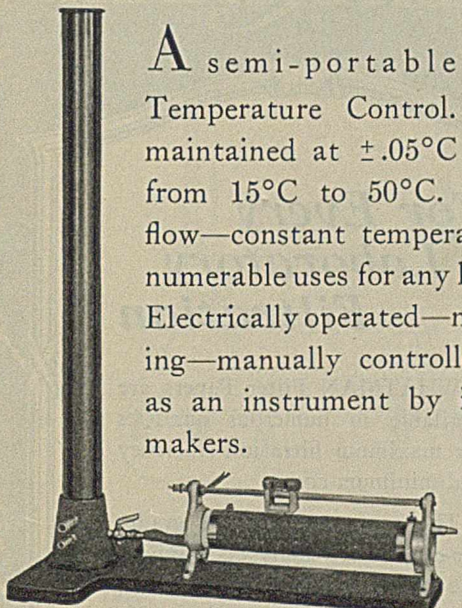

A semi-portable **$45.**

Temperature Control. Effluent maintained at ±.05°C at a range from 15°C to 50°C. Constant flow—constant temperature. Innumerable uses for any laboratory. Electrically operated—non-corroding—manually controlled. Built as an instrument by instrument makers.

BAUSCH & LOMB B&L GLASS IS USED IN B&L MICROSCOPES, TELESCOPES, BINOCULARS, SPECTACLE LENSES AND FRAMES, OPHTHALMIC APPARATUS, SCIENTIFIC INSTRUMENTS.

BAUSCH & LOMB OPTICAL CO., 603 ST. PAUL ST., ROCHESTER, N. Y., U. S. A.

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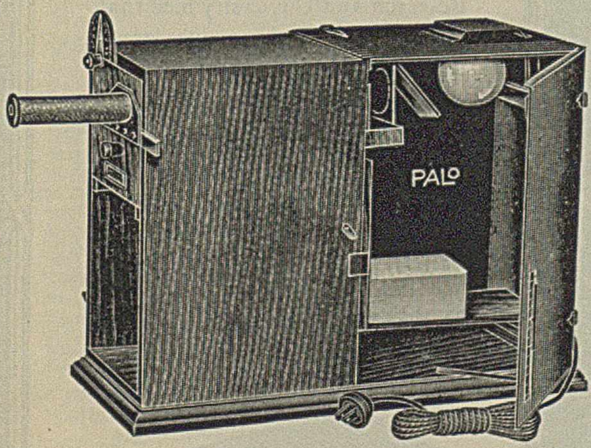
IVES TINT PHOTOMETER

FOR COLOR ANALYSIS



Widely used for matching and standardizing colors of both liquids and solids. It produces a numerical value which shows the relative amounts of the various colors in the samples tested.

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Apparatus for Industrial and Laboratory Use

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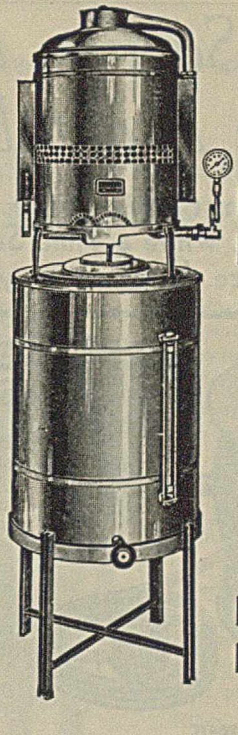

PRECISION WATER STILLS

Precision Water stills are meeting with increased favor because of their advanced design, economy of operation, and ease of cleaning. Substantially built of non-rusting metal, with entire condensation system block-tin lined, Precision Stills deliver their rated capacity continuously and automatically and produce a sterile, chemically pure water free from occluded gases. They are made in various types and sizes to operate on gas, steam, or electricity.

Illustration shows No. 7156 steam operated Still mounted on Precision Storage Tank. These tanks are of heavy copper, tinned inside, and provided with gauge glass and tinned faucet. Being neat, compact, and convenient the Precision Storage Tank is recommended as preferable to the usual glass container for distilled water.

7153—Precision Automatic Water Still, gas operated			
Capacity per hour, gal.		1	2
Price		65.00	100.00
7154—Precision Automatic Water Still, electrically operated			
Capacity per hour, gal.	1	1½	2
Price	78.00	98.50	122.00
7156—Precision Automatic Water Still, steam operated			
Capacity per hour, gal.		1 to 2	2 to 4
Price		78.00	110.00
7178—Precision Storage Tank, as illustrated, complete with stand			
Capacity, gal.	10	15	25
Price	25.00	30.00	42.50

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A Chemist's Time once used is gone, while a Time Saving Device lasts many years.

CENCO ELECTRIC FLASK HEATER

No. 9647C

Has all the advantages of a good Bunsen burner plus constancy and safety that can be obtained only with electrical heat. The conical heating unit gives a high temperature hot spot, which can be turned up or down like a gas burner.

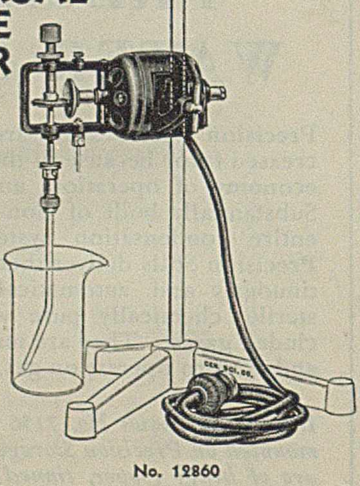
9647C. For 110 volts... $12.50

CENCO UNIVERSAL FRICTION-DRIVE MOTOR STIRRER

The relatively small size, the compact construction, the wide range of speed adjustment in either direction, the ease of clamping in any desired position, the interchangeable chucks for large and small diameter stirring rods, and the flexible shaft attachment for stirring in crowded positions, all contribute to produce a utility value in this stirrer far in excess of its actual cost.

12860. For 110 volts....... $30.00

(Flexible shaft not included)



No. 12860

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We have prepared a table showing, at a glance, grades recommended for the more common precipitates. Let us send it to you.

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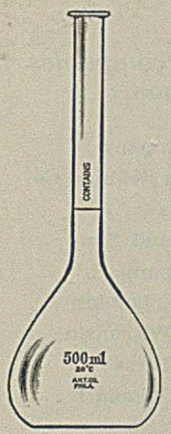
A. H. T. CO. SPECIFICATION

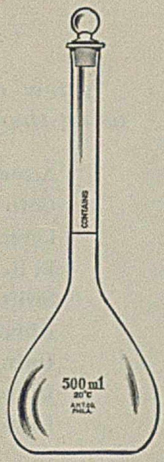
VOLUMETRIC FLASKS

OF RESISTANCE GLASS

STRAIN-FINDER TESTED



5460



5461

FLASKS, VOLUMETRIC, A. H. T. Co. Specification. Flasks so designated are made of an alkali-free resistance glass ***in accordance with specifications established by us in 1921.***

Graduation marks are ***thin, sharply defined white lines.*** The position of the graduation mark is carefully controlled and each flask is passed through a polariscopic strain-finder in our own establishment to detect internal strain.

The volume is adjusted for a temperature of 20° C and is guaranteed to be within the following tolerances:

Capacity less than and including:	Limit of error± (to contain):	Percentage error:
10 ml	0.06 ml	0.60%
25 ml	.06 ml	0.24%
50 ml	.10 ml	0.20%
100 ml	.16 ml	0.16%
200 ml	.20 ml	0.10%
250 ml	.22 ml	0.08%
500 ml	.30 ml	0.06%
1000 ml	.60 ml	0.06%
2000 ml	1.00 ml	0.05%

5460. Flasks, Volumetric, A. H. T. Co. Specification, as above described, of resistance glass; without stoppers.

To contain, ml	10	25	50	100	200
Each	.40	.42	.45	.50	.60
10% discount in carton cont'g.	24	24	24	24	24
20% discount in case cont'g.	96	96	96	96	72
Code Word	*Giqlr*	*Giqok*	*Giqsc*	*Giqwu*	*Giram*

To contain, ml	250	500	1000	2000
Each	.70	.85	1.15	2.00
10% discount in carton cont'g	24	12	12	....
20% discount in case cont'g	72	48	36	12
Code Word	*Girga*	*Girks*	*Girnl*	*Girqf*

5461. Ditto, but with ground glass stoppers.

To contain, ml	10	25	50	100	200
Each	.60	.65	.70	.80	.90
10% discount in carton cont'g.	24	24	24	24	24
20% discount in case cont'g.	96	96	96	96	72
Code Word	*Gismn*	*Gisqe*	*Gisty*	*Gisyo*	*Gitbi*

To contain, ml	250	300	500	1000	2000
Each	.95	1.10	1.20	1.50	2.50
10% discount in carton cont'g.	24	24	12	12	....
20% discount in case cont'g.	72	72	48	36	12
Code Word	*Gitfa*	*Gitkq*	*Gitoh*	*Gituv*	*Giuaj*

For complete assortment of Volumetric Flasks, including Certified, Student, Exax and Pyrex brands, etc., see pages 393-400, incl., of our new catalog.

Prices subject to change without notice.

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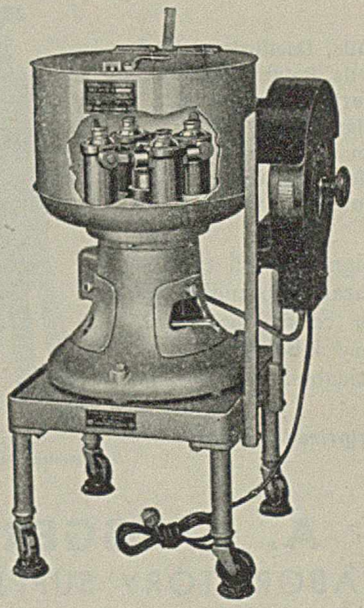

Many centrifuge users are demanding the 250 ml. containers to be operated at higher speed than is possible with the regular equipment. We are now able to offer for our Size 1 Type SB and Size 2 Centrifuges a pin type head and slotted metal cups properly reinforced for maximum motor speed of 3000 r.p.m.

The new head is of manganese bronze with stainless steel pins pressed into the arms. Cups are of manganese bronze. Forged duralumin cups may be had for liquids of specific gravity greater than 1.5.

REINFORCED

Size 1 Type SB Centrifuge with Stand

The reinforcement permits 50 per cent more speed with a resulting increase in the relative centrifugal force from about 900 × gravity to about 2100 × gravity. This affords a tremendous advantage in the modern laboratory and makes possible the throwing down of substances which are not satisfactorily separated at the lower speed.

The regular guard is replaced with an all welded heavy steel guard for added protection against careless operation at higher speeds.

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This useful laboratory combination is identical in construction with the well known International "Clinical Model" Centrifuge. The two models shown at right may be purchased as separate units or as a combination centrifuge at a substantially lower price. Send for Bulletins CC and CH.

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One Liter Capacity

The many uses for which it is adapted are:

Hydrogenation of Oils, Deodorization of Oils, Blowing of Oils, Polymerization of Oils, Sulphonation, Rendering, Renovating, Distillation Tests with Steam and Inert Gases under Pressure and Vacuum, Etc.

This device is designed to fill the demand for an apparatus to make the above tests under conditions which render the ordinary laboratory glass equipment impracticable.

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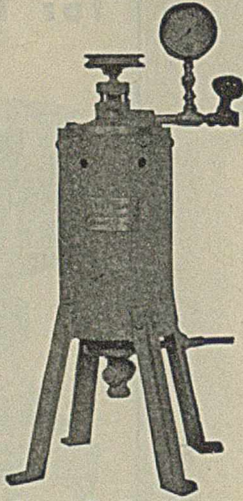

Patented October 28th, 1919

A few of the companies now using the equipment:

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Swift & Company
Kings College, London
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LABORATORY SUPPLIES AND CHEMICALS
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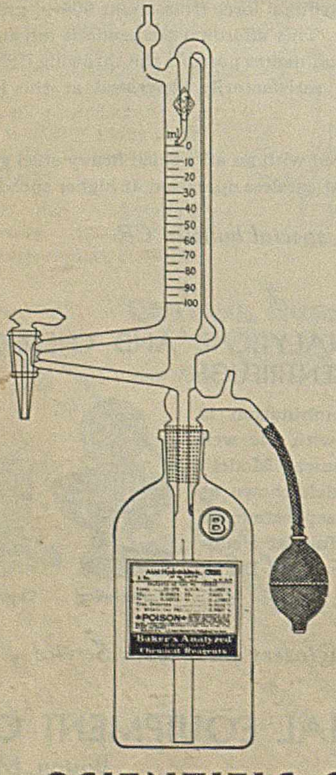
INTERCHANGEABLE GROUND GLASS JOINTS and STOPCOCKS



are still the most important *new* development in laboratory glassware.

They have been adapted to standard laboratory items, some of which are illustrated herewith, with great success.

It is a pleasure to order replacement parts, stoppers and stopcock plugs by size numbers, and be assured of a perfect fit.

We recommend the Acid burette as a time-saving, effort-saving and efficient piece of apparatus, for general laboratory use. This burette will fit any standard five pint acid bottle, and is constructed along lines similar to our All-Automatic burettes, with a zero point which sets in automatically.

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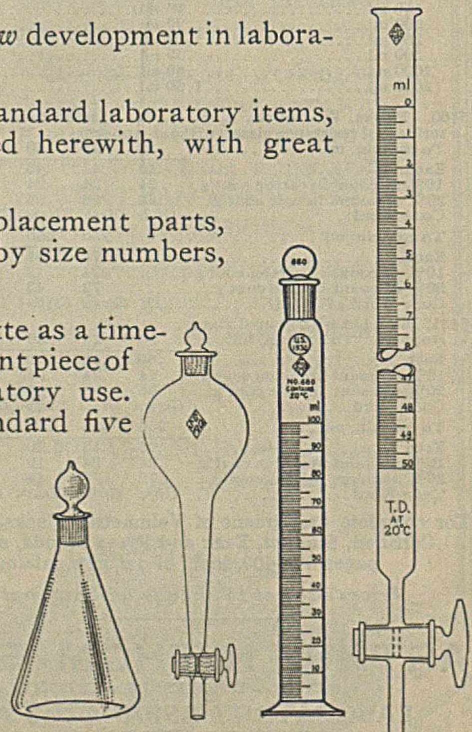

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