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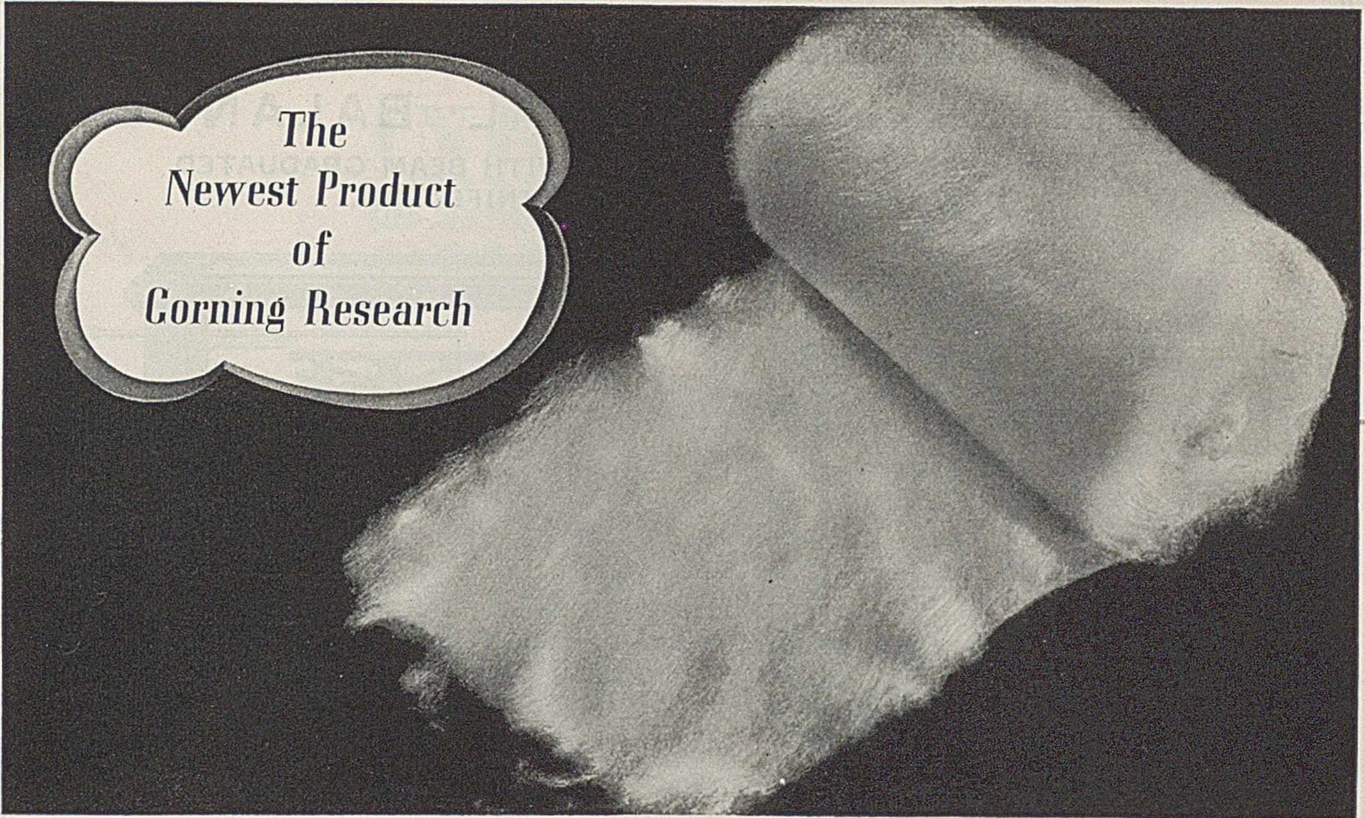

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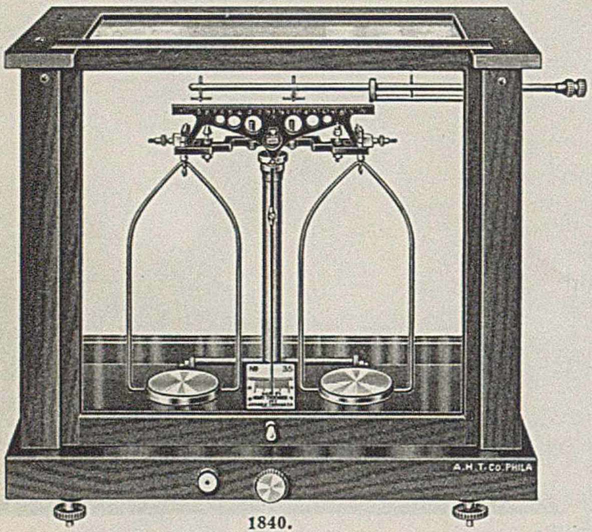
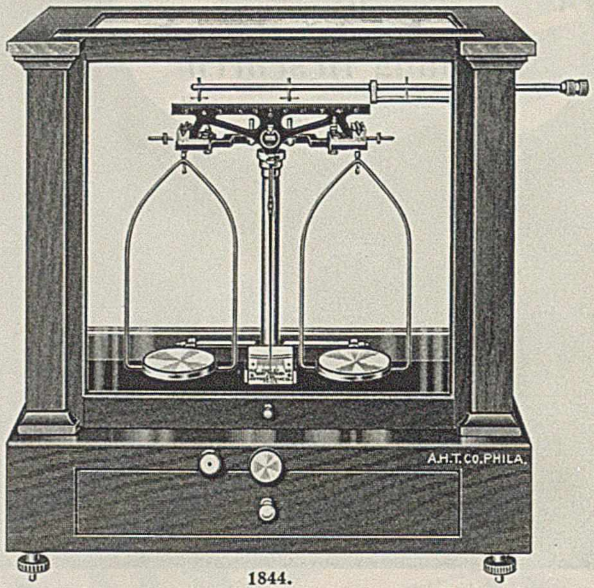


1840.



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ANALYTICAL EDITION

INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Improved Service to Analysts

THE Analytical Edition of Industrial and Engineering Chemistry has completed eight volumes and has developed its service to the point where its position in the field of chemical literature is unquestioned and is to be envied. Those who are served by this edition will be pleased with the action taken by the Board of Directors of the American Chemical Society, by which they will be enabled, beginning with this issue, to have their new analytical methods and procedures, including physical testing and new apparatus, in a monthly instead of a bimonthly edition.

Microchemistry will receive special recognition, the papers in that specialty being set aside as a separate section in each issue for which there are papers available, and this will be done without diminishing the number of pages available for papers in other fields of analysis.

We are fortunate in having the services of the Board of Advisory Editors set up in 1935 and shall rely extensively upon their guidance in the further developments of our Analytical Edition.

Note to Authors

IN THE preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental:
    - Outline of proposed method
    - Description of apparatus and reagents
    - Procedure
    - Data:
        - Interfering substances or conditions
        - Concentration range through which the method is applicable
        - Accuracy of the method
        - Precision of the method
3. Discussion and summary

The author should state at the outset what the original features of the paper are. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater detail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

Our "Suggestions to Authors" is available to those unfamiliar with the form of manuscript and illustrations preferred by Industrial and Engineering Chemistry.

Standard Methods for the Sampling and Analysis of Commercial Soaps and Soap Products, Revised

F. W. SMITHER, R. E. DIVINE, C. P. LONG, M. L. SHEELY, H. P. TREVITHICK, AND P. H. WALKER
Committee on Analysis of Soaps and Soap Products of the American Chemical Society

THE Committee on Analysis of Soaps and Soap Products of the AMERICAN CHEMICAL SOCIETY, appointed in 1935, has given careful consideration to criticisms of the methods published in 1922 (*6*), and to the coöperative studies carried out by the Soap Analysis Committee of the American Oil Chemists' Society (*14*), with the result that the following report was unanimously adopted October 31, 1935.

A. Sampling

The seller shall have the option of being represented at the time of sampling, and when he so requests shall be furnished with a duplicate sample.

I. CAKE SOAPS, FLAKE AND POWDERED SOAP PRODUCTS WHEN PACKED IN CANS OR CARTONS. One cake (can or carton) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds (22.7 kg.). In the case of smaller containers, a cake (can or carton) shall be taken at random from each lot of containers totaling not more than 5000 pounds (2270 kg.). The total sample shall in all cases consist of not less than three cakes (cans or cartons) taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 pounds (9 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds (9 kg.).

Wrap the individual cakes (cans or cartons) tightly in paraffined paper at once and seal by rubbing the edges with a heated iron. The inspector shall accurately weigh each wrapped cake (can or carton), record its weight and the date of weighing on the wrapper, place the wrapped cakes (cans or cartons) in an air-tight container, which should be nearly filled, and seal, mark, and send to the laboratory for test. Samples should be kept cool until tested.

II. FLAKE AND POWDERED SOAP PRODUCTS WHEN IN BULK. A grab sample of not less than 0.5 pound (227 grams) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 100 pounds (45 kg.). In case of smaller containers, a grab sample of not less than 0.5 pound (227 grams) shall be taken at random from each lot of containers totaling not more than 10,000 pounds (4540 kg.). The total samples shall in all cases consist of not less than three grab portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 pounds (9 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds (9 kg.). The inspector shall rapidly mix the sample, place in an air-tight container, which shall be filled, and seal, mark, accurately weigh, record its weight and date of weighing on the package, and send to the laboratory for test. Samples should be kept cool until tested.

III. LIQUID SOAP. A sample of not less than 0.5 pint (236.6 cc.) shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 10 gallons (almost 38 liters) each. In case of smaller containers, a sample of not less than 0.5 pint (236.6 cc.) shall be taken at random from each lot of containers totaling not more than 1000 gallons (37,853 liters). The total sample shall in all cases consist of not less than three portions of 0.5 pint (236.6 cc.) each taken at random from separate containers. Before drawing the sample from the container selected, the contents of the container shall be thoroughly agitated. The inspector shall thoroughly mix the samples drawn, place in clean, dry cans or bottles, which shall be completely filled and securely stoppered with clean corks or caps; seal, mark, and send to the laboratory for test.

IV. PASTE SOAP PRODUCTS. (1) *When packed in cans or cartons of 5 pounds (2.27 kg.) or less.* One can or carton shall be taken at random from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds (22.7 kg.). In case of smaller containers, a can or carton shall be taken at random from each lot of containers, totaling not more than 5000 pounds (2270 kg.). The total sample shall in all cases consist of not less than 3 cans or cartons taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 20 pounds (9 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 20 pounds (9 kg.). Wrap, seal, mark, and send to laboratory for test.

(2) *When packed in bulk.* Take a trial sample at random of not less than 0.5 pound (227 grams) from not less than 1 per cent of the vendors' shipping containers, provided such containers contain not less than 50 pounds (22.7 kg.). In case of smaller containers a trial sample shall be taken at random from each lot of containers totaling not more than 5000 pounds (2270 kg.). The total sample shall in all cases consist of not less than 3 half-pound (227-gram) portions taken at random from separate containers. With very large lots where the sample drawn as above will amount to more than 10 pounds (4.5 kg.), the percentage of packages sampled shall be reduced so that the amount drawn shall not exceed 10 pounds (4.5 kg.). The inspector shall promptly place the combined sample in a clean, dry, air- and water-tight container, which shall be filled, and seal, mark, and send to the laboratory for test.

B. Preparation of Samples

I. CAKE SOAP. In case of samples that can be easily disintegrated and mixed, run the entire sample through a suitable chopper. When the sample is large, each cake may be quartered and one-quarter of each cake run through the chopper. With samples that cannot be handled as above, select a cake of average weight, quarter it by cutting at right angles in the center, and shave equally from all freshly cut surfaces sufficient soap for analysis. Mix and weigh out all portions for analysis promptly. Preserve the remainder in an air-tight container in a cool place.

II. POWDERED AND CHIP SOAPS. Rapidly disintegrate and mix the sample; if desired, quarter down to about 1 pound (453.6 grams) and weigh out all portions for analysis at once. Unused portions of the sample for analysis shall be preserved in an air-tight container in a cool place.

III. LIQUID SOAP. No preparation of the sample, other than thorough mixing, is necessary unless it is received during very cold weather, when it should be allowed to stand at least 1 hour after it has warmed up to room temperature (20° to 30° C.) before it is noted whether it forms a satisfactory lather.

IV. Paste Soap Products. Mix thoroughly by kneading and quarter down to about 1 pound (453.6 grams). Weigh out all portions for analysis promptly and preserve remainder in an air-tight container in a cool place.

C. Methods of Analysis

When a determination shows nonconformity with the specifications, a duplicate shall be run.

I. Moisture. The oven method given below is generally applicable to all soaps. Experience has shown, however, that certain exceptions to this method must be made if accurate results are desired. These exceptions include: (a) For soaps containing appreciable amounts of sodium silicate the distillation method is preferred. (b) Soaps of linseed and other oxidizing oils absorb oxygen and if the oven method is used may gain in weight near the end of the test. Therefore, either an inert atmosphere or vacuum oven should be used. The distillation method is also applicable to these types of soaps.

(1) *Matter volatile at 105° C. (oven method).* Weigh 5 grams (±0.01 gram) of the sample in a porcelain or glass dish about 6 to 8 cm. in diameter and about 2 to 4 cm. deep, and dry to constant weight in an air oven at a temperature of 105° ± 2° C.

(2) *Distillation method* (*7*). For soaps containing from 5 to 25 per cent of moisture and volatile matter use a 20-gram (±0.04 gram) sample. For soaps containing more than 25 per cent moisture and volatile matter use a 10-gram (±0.02 gram) sample. The weighed sample is carefully transferred to a 500-cc. short-necked round-bottomed flask or an Erlenmeyer flask. Add approximately 10 grams of anhydrous, fused sodium acetate to prevent violent frothing, and then follow with 100 cc. of xylol which has previously been saturated with water by shaking the xylol with a small quantity of water and distilling. Use the xylol distillate for the determination. Attach the flask to a graduated 5- or 6-cc. distilling tube receiver, calibrated at 25° C., such as the Bidwell-Sterling or Stark and Dean apparatus, which is connected to a 48-cm. reflux condenser (19-inch Liebig condenser). Prior to starting the determination, fill the receiver with saturated xylol by pouring in through the reflux condenser.

So that the refluxing will be under better control, wrap the flask and the tube leading to the receiver with asbestos cloth. Apply heat to the flask by means of a gas burner or an electric heater and distill slowly. The rate at the start should be approximately 100 drops per minute. When the greater part of the water has apparently distilled over, increase the distillation rate to 200 drops per minute until no more water is collected. Purge the reflux condenser during the distillation with 5-cc. portions of xylol to wash down any moisture adhering to the walls of the condenser. The water in the receiver may be made to separate from the xylol by using a spiral copper wire. Move the wire up and down in the condenser occasionally, thus causing the water to settle to the bottom of the receiver. Reflux for at least two hours, after which the heat is turned off. Adjust the temperature of the distillate to 25° C. Read the volume of water and calculate the percentage of moisture in the soap, as follows:

$$\frac{\text{Volume in cc. at } 25^\circ \text{ C.} \times 0.997}{\text{Weight of sample}} \times 100 = \%\text{ moisture in soap}$$

II. Total Matter Insoluble in Alcohol. Free Alkali or Free Acid. (1) *Matter insoluble in alcohol.* Digest a 2- to 10-gram (±0.01 gram) sample with 200 cc. of freshly boiled ethyl alcohol (94 per cent or higher and neutral to phenolphthalein) in a covered vessel on a steam bath until the soap is dissolved. Filter through a counterpoised filter paper neutral to phenolphthalein, or a weighed Gooch crucible with suction, protecting the solution from carbon dioxide and other acid fumes during the operation. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap and reserve the filtrate and washings. Dry the filter paper or crucible with residue at 100° to 105° C. for 3 hours, cool, and weigh the total matter insoluble in alcohol. [The matter insoluble in alcohol will contain most of the alkaline salts, such as carbonates, borates, silicates, phosphates, and sulfates, as well as starch, and may be used for the approximate determination of these constituents. These salts are not entirely insoluble in alcohol, so for accurate determinations separate portions of the soap should be used. For determination of carbonates see C-XI; phosphates, C-XII; sulfates, C-XIII; silicates, C-X; borax, C-IX; starch, C-XIV (4).]

(2) *Free alkali or free acid.* Heat the reserved filtrate to incipient boiling and titrate with standard acid or alkali solution, using phenolphthalein as indicator, and calculate to sodium hydroxide (or potassium hydroxide) if alkaline, or to oleic acid, if acid.

(3) *Matter insoluble in water.* Proceed as in the determination of matter insoluble in alcohol. After filtering and thoroughly washing the residue, change receivers and extract it with water at 60° C., and wash the filter thoroughly. (When the matter insoluble in water is all inorganic, boiling water may be used for the extraction and washing.) Reserve the water solution. Dry the filter and residue at 100° to 105° C. for 3 hours, cool, and weigh matter insoluble in water. The nature of this matter may be determined by further examination.

(4) *Total alkalinity of matter insoluble in alcohol.* (*Alkaline salts.*) Titrate the water solution obtained in C-II (3) with standard acid, using methyl orange as indicator. Calculate the alkalinity to sodium oxide (Na_2O), and, if desired, to any other basis agreed upon by the parties interested.

III. Combined Alkali. Total Anhydrous Soap. Dissolve 5 to 10 grams (±0.01 gram) of the sample, depending upon the anhydrous soap content, in 100 cc. of water in a 250-cc. Erlenmeyer flask. When solution is complete, add dilute sulfuric acid in slight excess, insert a small funnel in the neck of the flask, and heat the flask at a temperature not exceeding 60° C. until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel, and shake the acid aqueous liquid with two 20-cc. portions of ethyl ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid and shake with 10-cc. portions of water until they are no longer acid to methyl orange. Unite the water portions used for washing and shake with 20 cc. of ether. Wash this ether until the wash water is neutral to methyl orange. Save the acid water for determination of chloride (C-IV).

Unite the ether solutions (if necessary, filter, washing the paper with ether) in a suitable weighed vessel, add 100 cc. of neutral alcohol free from carbon dioxide, add phenolphthalein, and titrate to exact neutrality with standard sodium hydroxide solution. Evaporate off the alcohol, dry to constant weight as in the determination of matter volatile at 105° C., and calculate the percentage of soda soap. This naturally includes any mineral oil and neutral fat, which, if determined separately, must be deducted from the result to obtain the true soap. Calculate the combined sodium oxide (Na_2O) and deduct from the weight of soda soap to give the acid anhydrides. If the original soap was potash soap, proper calculation must be made to reduce to potassium oxide (K_2O), or the titration made directly with standard potassium hydroxide solution. In case the soap shows an excess of free acid, proper corrections must be made in calculating the combined alkali in the original soap. (A blank test should be made on the sodium or potassium hydroxide solution for neutral salts and the proper corrections made if necessary.) With soaps containing a large amount of soluble silicates, and soap products containing a high percentage of finely divided material insoluble in water, the foregoing procedure cannot be applied as given. In such cases the filtrate obtained in the determination of total matter insoluble in alcohol can be used after neutralizing any free acid or alkali. Evaporate off the alcohol on a steam bath, take up in water, and proceed as above.

With soap products containing a high percentage of matter insoluble in alcohol where approximate results will suffice, such as may be the case with cleansers, soap powders, scouring compounds, pastes, etc., and where agreed upon by the parties interested, the alcoholic solution, obtained after filtering off and washing the matter insoluble in alcohol, may be evaporated directly in a weighed vessel, dried at 105° C. to constant weight, and the result reported as soap.

IV. CHLORIDE. Neutralize with chloride-free alkali the acid water obtained in paragraph C-III. Titrate with standard silver nitrate solution, using potassium chromate as indicator, and calculate the result to sodium chloride or potassium chloride as the character of the soap indicates.

In case the total anhydrous soap is not to be determined, it will be more convenient to use the following method (*4*): Dissolve 5 grams (±0.01 gram) of the sample in 300 cc. of water, boiling if necessary to effect solution. Add an excess of neutral, chloride-free magnesium nitrate solution [about 25 cc. of a 20 per cent $Mg(NO_3)_2 \cdot 6H_2O$ solution]. Without cooling or filtering, titrate with standard silver nitrate solution, using potassium chromate as indicator.

V. UNSAPONIFIED AND UNSAPONIFIABLE MATTER (*17*). (1) *Extraction cylinder.* The cylinder shall be a 250-cc. glass-stoppered cylinder about 35 mm. (1.375 inches) in diameter and about 30 cm. (12 inches) high.

(2) *Petroleum ether.* The solvent used should be of the pentane type, containing a minimum amount of isopentane, isohexane, and hexane, and meeting the following requirements:

Initial boiling point, not less than 35° C. nor over 40° C.
Dry-flask end point, not less than 50° C. nor over 60° C.
Distilling under 55° C., at least 95 per cent
Distilling under 40° C., not over 85 per cent
Specific gravity at 15.5° C. (60° F.), 0.630 to 0.675
Color, water white. Doctor test, sweet
Evaporation residue, not over 0.002 per cent by weight
Copper-strip corrosion test, noncorrosive
Unsaturated compounds, trace only permitted

(3) *Determination.* Weigh 5 grams (±0.2 gram) of the prepared sample into a 250-cc. Erlenmeyer flask or beaker which contains approximately 0.1 gram of bicarbonate of soda, and dissolve in 100 cc. of redistilled 50 per cent ethyl alcohol. Warm and shake to effect solution, keeping the temperature under 60° C., and filter off any undissolved residue on a Gooch crucible with an asbestos pad or in a funnel, using an asbestos pad deposited on a perforated porcelain disk. Wash three times with hot 50 per cent alcohol and then with 5 cc. of hot 95 per cent alcohol. Wash with a small amount of petroleum ether to remove any traces of unsaponified and unsaponifiable matter. Transfer the entire alcohol-water and ether filtrate to the extraction cylinder and make up to the 160-cc. mark with redistilled 50 per cent ethyl alcohol. Add 50 cc. of petroleum ether, shake vigorously for 1 minute, and allow to settle until both layers are clear. The volume of the upper layer should be about 40 cc. Draw off the petroleum ether layer as closely as possible, by means of a slender glass siphon, into a separatory funnel of 500-cc. capacity. Repeat the extraction at least six times using 50 cc. of petroleum ether each time. Wash the combined ether extracts first with a mixture of 15 cc. of 0.1 *N* sodium hydroxide solution and 15 cc. of 95 per cent alcohol, and then three times with 25-cc. portions of 10 per cent alcohol, shaking vigorously each time. Transfer the petroleum ether extract to a beaker and evaporate the petroleum ether on a steam bath by the aid of a current of air.

Test the residue for solubility by treating with 50 cc. of petroleum ether at room temperature. Filter and wash free from the insoluble residue, if any; evaporate and dry in the same manner on the steam bath, and finally in an air oven at 100° to 101° C. for 30 minutes. Weigh and return to the oven, reweighing at 15-minute intervals until constant weight is reached. Take up the residue in 50 cc. of warm ethyl alcohol, neutralized to phenolphthalein, titrate to the same color as original neutral alcohol with 0.04 *N* sodium hydroxide solution, and calculate to oleic acid. Deduct this figure from the gross weight previously found and report as "unsaponified and unsaponifiable matter." (Any blank from the petroleum ether must be deducted from the weight before calculating the unsaponified and unsaponifiable matter.)

(4) *Unsaponifiable matter.* Weigh 5 grams (±0.2 gram) of the prepared sample into a 200-cc. Erlenmeyer flask. Add 30 cc. of redistilled 95 per cent ethyl alcohol and 5 cc. of aqueous 50 per cent potassium hydroxide, and boil the mixture for 1 hour under a reflux condenser. Transfer to the extraction cylinder and wash to the 40-cc. mark with redistilled 95 per cent ethyl alcohol. Complete the transfer, first with warm and then with cold water, until the total volume is 80 cc. and finally with a small quantity of petroleum ether. Cool the cylinder and contents to room temperature and add 50 cc. of petroleum ether; and then proceed with the extraction as outlined above under "unsaponified and unsaponifiable matter," except that the alkaline wash may be omitted; weigh the residue and correct for fatty acids in the usual manner. Report the result as "unsaponifiable matter."

From the total unsaponified and unsaponifiable matter figured as found above, deduct the unsaponifiable figure and report as "unsaponified matter."

Thorough and vigorous shaking is necessary in order to secure accurate results. The two phases must be brought into the most intimate contact possible; otherwise low and disagreeing results may be obtained.

The above method will not remove all the unsaponifiable matter in soaps to which lanolin has been added. More extractions are required when substances of this nature are present.

VI. ROSIN-WOLFF'S METHOD, MODIFIED (*16*). PREPARATION OF FATTY AND ROSIN ACIDS. Dissolve 5 grams (±0.01 gram) of the sample in 100 to 200 cc. of hot distilled water in a 250-cc. beaker, add a slight excess of dilute sulfuric acid (1 to 1), heat on the steam bath until the fatty acids collect in a clear layer, cool to room temperature, and transfer to a separatory funnel, washing the beaker free from fatty and rosin acids with small portions of ethyl ether, adding the ether washings to the separatory funnel. Add about 50 cc. of ethyl ether to the separatory funnel and whirl to dissolve the fatty and rosin acids. After the solid acids have dissolved in the ether, let stand for at least 5 minutes.

Draw off the aqueous portion into another separatory funnel designated as No. 2, add about 30 cc. of ethyl ether to funnel No. 2, shake vigorously, allow to stand for at least 5 minutes, and then draw off the aqueous portion into another separatory funnel designated as No. 3. Transfer the ether extract to separatory funnel No. 1. Wash the aqueous liquid three more times, using for each washing about 30 cc. of ethyl ether, then discard the aqueous liquid and add the ether washings to funnel No. 1. Now add about 50 cc. of distilled water to the combined ether extracts in funnel No. 1, shake vigorously, and allow to stand for 5 minutes. Draw off the aqueous solution into another separatory funnel. Repeat this operation, combining the water washings until the ether is free from acid, using methyl orange as indicator. Add 50 cc. of ethyl ether to the water washings, shake the separatory funnel vigorously, and allow to stand for at least 5 minutes. Draw off and discard the aqueous solution and wash the ether layer with small portions of distilled water until free from acid, using methyl orange as indicator. Transfer the total ether extract to a 250-cc. Erlenmeyer flask, evaporate off the ether slowly on the side of a steam bath, dry 1 hour in an oven at 105° C., cool, and dissolve in 20 cc. of absolute alcohol.

(1) *First esterification.* Add 10 cc. of a solution of one volume of concentrated sulfuric acid (sp. gr. 1.84) in four volumes of absolute ethyl alcohol, bring to boil on the steam bath, and boil exactly 4 minutes under a reflux condenser. Remove from the steam bath, add to the liquid about five times its volume of 7 to 10 per cent solution of sodium chloride. Transfer to a separatory funnel,

washing the Erlenmeyer flask with small portions of ethyl ether, the ether washing being added to the aqueous solution in the separatory funnel. Add about 30 cc. of ethyl ether to the separatory funnel, shake vigorously, and allow to stand for at least 5 minutes. Draw off the aqueous solution into another separatory funnel (No. 2). Add about 30 cc. of ether to funnel No. 2, shake vigorously, allow to stand for at least 5 minutes, and then draw off the aqueous layer into another separatory funnel (No. 3). Repeat the extraction of the aqueous solution three more times. Then discard the aqueous liquid and add the combined ether solutions to separatory funnel No. 1. Add 50 cc. of sodium chloride solution (7 to 10 per cent) to the combined ether extracts, shake vigorously and allow to stand for at least 5 minutes. Draw off the aqueous solution into another separatory funnel.

Repeat this operation until the washings are neutral to methyl orange, all salt water washings being combined. Add 50 cc. of ether to the combined washings in the separatory funnel. Shake the funnel vigorously, allow to stand for at least 5 minutes, and then draw off and discard the aqueous salt solution. Add 50 cc. of sodium chloride solution and wash the ether layer until the aqueous salt solution is neutral to methyl orange. Dry the ether extract by the addition of about 3 grams of anhydrous sodium sulfate to the separatory funnel, filter into a 250-cc. Erlenmeyer flask, washing with ether, and evaporate off the ether slowly on the steam bath to dryness.

(2) *Second esterification.* Cool and dissolve the residue in 20 cc. of absolute ethyl alcohol and then proceed as above under "first esterification." Add 30 cc. of neutral alcohol (94 per cent or higher) and titrate rosin or rosin soap as desired, using phenolphthalein as indicator (1 cc. 0.5 *N* alkali = 0.173 gram of rosin or 0.188 gram of rosin soda soap). If the pure fatty acid soap is desired, subtract the rosin soap from the total anhydrous soap obtained under C-III.

The above method gives somewhat high results with low-rosin and approximately correct results with high-rosin soap. In all cases where the rosin content is found to be less than 5 per cent, the actual presence or absence of rosin should be checked qualitatively by the Liebermann-Storch test, which is as follows:

Transfer 1 to 2 cc. of the sample of fatty acids to a test tube, treat with 5 to 10 cc. of reagent grade acetic anhydride, and warm on a steam bath. After cooling, pour 1 to 2 cc. into a white porcelain dish and allow a drop or two of sulfuric acid (sp. gr. 1.53) to run down the side of the vessel. If rosin is present, a fugitive violet coloration changing to a brownish tinge is immediately produced at the margin of contact of the reagents. The test should be checked with a sample of fatty acids to which a small amount of rosin has been added.

[Sulfuric acid of 1.53 specific gravity is prepared by diluting 34.7 cc. of concentrated reagent grade sulfuric acid (sp. gr. 1.84) with 35.7 cc. of distilled water.]

VII. TITER TEST. (1) *Preparation of total fatty matter (fatty and rosin acids and unsaponified matter).* Dissolve about 50 grams of soap in 500 cc. of hot water, add 100 cc. of 30 per cent sulfuric acid, heat until the fatty matter collects in a clear layer, siphon off the aqueous acid layer, and wash the fatty matter free from sulfuric acid with hot water. Decant the fatty matter into a dry beaker, filter, using a hot-water funnel, or placing both funnel and receiving beaker in a water-jacketed oven, and dry for 20 minutes at the temperature of boiling water.

When other determinations are to be made on the total fatty matter, and volatile and readily oxidizable fatty acids are present, the following method should be used:

Dissolve about 50 grams of the soap in 300 cc. of hot water, transfer to a separatory funnel, add 150 cc. of approximately 2 *N* sulfuric acid, cool somewhat, add 120 cc. of ether, shake, draw off the acid layer, and wash the ether layer free from acid with a strong salt (NaCl) solution. Then draw off the aqueous layer as completely as possible, transfer the ether layer to a flask (it is not necessary to transfer quantitatively), add 20 to 30 grams of anhydrous sodium sulfate, stopper the flask, shake, and let stand at a temperature below 25° C. until the ethereal liquid becomes perfectly clear, showing that all water has been taken up by the sodium sulfate. Filter through a dry paper into another Erlenmeyer flask, and completely evaporate off the ether by passing through the flask a current of dry air and heating the flask to a temperature of about 50° C.

(2) *Determination* (*5*). (a) Thermometer. The thermometer shall be a standard titer thermometer graduated at zero and in tenth degrees from 10° to 65° C., and certified by the National Bureau of Standards.

(b) Procedure. Transfer the fatty acids prepared as under VII (1), when cooled somewhat, to a titer tube 25 by 100 mm. placed in a 273- to 275-cc. (16-ounce) saltmouth bottle of clear glass 70 by 150 mm., fitted with a cork that is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 r. p. m.) until the mercury remains stationary for 30 seconds. Allow the thermometer to hang quietly with the bulb in the center of the tube and report the highest point to which the mercury rises as the titer of the fatty acids. The titer should be made in a room at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

VIII. ACID NUMBER OF FATTY ACIDS. (1) *Preparation of fatty acids.* Follow procedure given under C-VII.

(2) *Determination.* In a 250-cc. Erlenmeyer flask dissolve 2 grams of the fatty acids, accurately weighed, in 20 to 30 cc. of neutral 95 per cent ethyl alcohol. Titrate with standard alkali, using phenolphthalein as indicator. Calculate the acid number (mg. of potassium hydroxide per gram of fatty acids).

IX. BORAX DETERMINATION (*12*). Weigh 10 grams (±0.02 gram) of the soap [or 5 grams (±0.01 gram) if more than 5 per cent of borax is present] into a platinum dish and add 2.15 grams of fusion mixture (consisting of 200 grams of sodium carbonate and 15 grams of silica in fine powder). To this mixture add 15 cc. of alcohol, mix with the aid of a glass rod and, after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until the combustible material is destroyed, cover the dish with a piece of platinum foil, and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to a 250-cc. round-bottomed flask. Acidify with 20 cc. of dilute hydrochloric acid (1 to 1), heat nearly to boiling, and add a moderate excess of dry precipitated calcium carbonate. Connect with a reflux condenser and boil vigorously for 10 minutes. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of liquid below 100 cc.

Return the filtrate to the flask, add a pinch of calcium carbonate, and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary temperature, add 50 cc. of neutral glycerol; and titrate the solution with 0.1 *N* sodium hydroxide, free from carbonate, using phenolphthalein as indicator. After the end point is reached, add 10 cc. more of glycerol and again titrate. Repeat this process until the addition of glycerol causes no further action on the end point. The number of cubic centimeters required multiplied by 0.00955 will give the equivalent of borax ($Na_2B_4O_7 \cdot 10H_2O$) present in the solution.

X. DETERMINATION OF SILICA PRESENT AS ALKALINE SILICATES. (1) When the material contains no mineral matter that is insoluble in water, ignite a sample of the soap containing not to exceed 0.2 gram of silica in a platinum dish at a low temperature. When charred, extract the soluble salts with water, return the paper and charred residue to the dish, and complete the ignition. Unite the residue in the dish and the water extract, carefully acidify with hydrochloric acid, finally adding the equivalent of from 5 to 10 cc. of strong hydrochloric acid in excess. The dish or casserole containing the solution should be covered with a watch glass while adding acid so as to avoid loss by spray.

(2) When the material contains mineral matter insoluble in water, or a determination of highest accuracy is not necessary, take a portion of the solution after titrating the matter insoluble in alcohol C-II (4) containing not more than 0.2 gram of silica and add 5 to 10 cc. of strong hydrochloric acid.

Evaporate the acidified solution (washing off and removing the cover glass if used) to dryness on a steam bath or hot plate at a temperature not exceeding 200° C. Cool, moisten with concentrated hydrochloric acid, and let stand 5 to 10 minutes, breaking up all lumps with a stirring rod. Add about 25 cc. of hot water. Heat a few minutes and filter through a small ashless paper. Wash thoroughly with hot water.

Evaporate the filtrate to dryness and repeat the above treatment, filtering on a second paper. Carefully ignite the two papers and contents in a weighed platinum crucible, first at a low temperature until the paper is consumed, then over the blast lamp. Cool in a desiccator, weigh, and repeat until constant weight is obtained. If extreme accuracy is desired, moisten the weighed contents of the crucible with water, add 10 cc. of hydrofluoric acid and 4 drops of strong sulfuric acid, evaporate to dryness over a low flame, ignite at the temperature of the blast lamp for about 2 minutes, cool in a desiccator, and weigh. The difference between this weight and the previous weight is the weight of the silica (SiO_2, *8*).

To calculate sodium silicate having the ratio $1Na_2O:3.25 SiO_2$, multiply the weight of SiO_2 by 1.308 (*15*).

XI. DETERMINATION OF CARBON DIOXIDE (CARBONATES). For most determinations the dry matter insoluble in alcohol as obtained in C-II (1) will be suitable for this determination. In some cases it might be desired to run the test directly on an original sample of the soap. This should always be done when the highest accuracy is required. Any reliable absorption method for determining carbon dioxide may be used (*1*).

The following is a method which has proved satisfactory:

A 250-cc. Erlenmeyer flask is placed on a gauze over a burner. The flask is equipped with a 2-hole rubber stopper, one opening of which carries a 25-cm. (10-inch) reflux condenser and the other a thistle tube equipped with a 3-way stopcock. The lower end of the thistle tube is drawn to a small point, which is placed very close to the bottom of the flask. To the straightaway end of the stopcock is attached a small funnel for the introduction of acid to the flask. The other opening of the stopcock is attached to receive air from a purifying tube containing soda-asbestos (ascarite) or other suitable carbon dioxide absorbent. The top of the reflux condenser is attached first to a drying tube containing a dehydrating agent such as concentrated sulfuric acid or magnesium perchlorate, and then to a weighed tube containing ascarite and magnesium perchlorate, and a second containing concentrated sulfuric acid. This train is attached to a protective U-tube containing calcium chloride. The U-tube is attached to an aspirator.

Procedure. Set up the apparatus, leaving out the weighed train, and aspirate with a slow stream of the dry carbon dioxide-free air until the apparatus is freed from carbon dioxide. Insert the train and continue the aspiration for 0.5 hour. Check the weight of the train to determine if the air is passing through too fast, or if the system is free from carbon dioxide. The system must be free from leaks. Weigh out 1 or 2 grams of the sample into the Erlenmeyer flask, cover with 20 cc. of freshly boiled distilled water and close the apparatus with the train in place. Add 20 cc. of dilute hydrochloric acid (1 to 1) through the funnel very slowly, with no heat being applied to the flask. The rate of adding acid should be carefully controlled so that the gas does not pass through the train too rapidly. As soon as the acid is added, start aspiration gently. When the absorption begins to slacken, start heating gently and continue until the contents of the flask have boiled 15 to 20 minutes. Stop heating and continue aspirating until the flask has cooled down. Remove the train and weigh. The increase of weight represents carbon dioxide, which multiplied by 2.41 equals sodium carbonate.

XII. DETERMINATION OF PHOSPHATES (*2*). If a qualitative test has shown the presence of phosphates and their determination is desired, the matter insoluble in alcohol C-II (1) or the ash from the incineration of an original sample can be used. An original sample should always be used when the highest accuracy is desired.

(1) *Reagents.* (a) Molybdate Solution. Dissolve 100 grams of molybdic acid in dilute ammonium hydroxide (144 cc. of ammonium hydroxide, sp. gr. 0.90, and 271 cc. of water); pour this solution slowly and with constant stirring into dilute nitric acid (489 cc. of nitric acid, sp. gr. 1.42, and 1148 cc. of water). Keep the final mixture in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

(b) Ammonium Nitrate Solution. Dissolve 100 grams of commercial ammonium nitrate, phosphate-free, in water, and dilute to 1 liter.

(c) Magnesia Mixture. Dissolve 55 grams of crystallized magnesium chloride ($MgCl_2 \cdot 6H_2O$) in water, add 140 grams of ammonium chloride and 130.5 cc. of ammonium hydroxide (sp. gr. 0.90), and dilute to 1 liter.

(d) Dilute Ammonium Hydroxide for Washing. Dilute 50 cc. of ammonium hydroxide (sp. gr. 0.90) to 1 liter.

(2) *Determination.* Weigh out a 2-gram (±0.01 gram) sample of the alcohol-insoluble or ash, and proceed as in C-X for removal of silica, saving the filtrate. Make up to 250 cc., concentrating if necessary. Pipet an aliquot corresponding to 0.50 or 1 gram into a 250-cc. beaker; add ammonium hydroxide in slight excess; and barely dissolve the precipitate formed with a few drops of nitric acid, stirring vigorously. Add about 15 grams of dry ammonium nitrate or a solution containing that amount. Heat to about 60° C. and add 70 cc. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) present.

Digest at about 65° C. for an hour, and determine if the phosphoric acid has been completely precipitated by adding more molybdate solution to the clear supernatant liquid. Filter, and wash with cold water, or preferably, ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide (1 to 1) and hot water, and wash into a beaker, keeping the volume under 100 cc. Neutralize with hydrochloric acid, using litmus paper or bromothymol blue as an indicator, cool, and from a buret add slowly (about 1 drop per second), stirring vigorously, 15 cc. of magnesia mixture for each decigram of phosphoric acid (P_2O_5) present. After 15 minutes add 12 cc. of ammonium hydroxide (sp. gr. 0.90). Let stand till the supernatant liquid is clear (2 hours is usually enough), filter, wash the precipitate with the dilute ammonium hydroxide until the washings are practically free from chlorides; dry, burn first at a low heat and ignite to constant weight, preferably in an electric furnace, at 1050° to 1100° C.; cool in a desiccator, and weigh as $Mg_2P_2O_7$. Calculate and report the result as percentage of P_2O_5 or alkaline phosphate known to be present.

XIII. DETERMINATION OF SULFATES. For most determinations the matter insoluble in alcohol obtained under C-II may suffice. If a determination of the highest accuracy is desired, ignite a 10-gram (±0.1 gram) sample of the soap and use the ash from the ignition. Digest with 100 cc. of water, cover with a watch glass, and neutralize carefully with hydrochloric acid. When neutralized, add 5 cc. excess of hydrochloric acid, filter, and wash the residue thoroughly. (Evaporation to dryness is unnecessary unless gelatinous silica should have separated, and should never be performed on a bath heated by gas, *9*.) Make up the filtrate to 250 cc. in a beaker, and boil. To the boiling solution add 15 to 20 cc. of 10 per cent barium chloride solution slowly drop by drop from a pipet. Continue boiling until the precipitate is well formed, or digest on a steam bath overnight. Set aside overnight or for a few hours, filter through a prepared Gooch crucible, ignite gently, and weigh as barium sulfate. Calculate to sodium sulfate, or the alkaline sulfate known to be present.

XIV. DETERMINATION OF GLYCEROL, SUGAR, AND STARCH. (1) *Determination of glycerol in the absence of sugar.* The solutions required are: potassium dichromate, 74.552 grams per liter; sodium thiosulfate, 0.1 *N;* potassium iodide, 10 per cent.

Dissolve an accurately weighed sample of the soap equivalent to not more than 3.0 grams of glycerol in 200 cc. of hot water in a 600-cc. beaker. [If starch is present, it will be necessary to remove the matter insoluble in water as described under C-II (1) and (3). Combine the alcohol and water solutions, evaporate off the alcohol, and proceed.] Decompose with 25 cc. of sulfuric acid (1 to 4). If alcohol is present, volatilize it by boiling for 20 to 30 minutes. Cool, remove, and rinse the cake of fatty acids, transfer the acid water and rinsings to a 500-cc. graduated flask, and add about 0.25 gram of silver sulfate to precipitate traces of chlorides and soluble fatty acids. Make up to volume and mix contents thoroughly.

Transfer a filtered, accurately measured 50-cc. aliquot of the above to a 400-cc. beaker, and to this add 75 cc. of accurately measured potassium dichromate solution, followed by 25 cc. of sulfuric acid (sp. gr. 1.84). Cover with a watch glass, and oxidize by heating to 90° to 100° C. for 3 hours. Conduct a blank in like manner but using 100 cc. of water, 25 cc. of sulfuric acid (sp. gr. 1.84), and 25 cc. of accurately measured potassium dichromate. Cool and make up the solutions to 1000 cc. in graduated flasks. The excess of potassium dichromate is determined by taking 50-cc. aliquots of the above, adding 50 cc. of water and 20 cc. of 10 per cent potassium iodide solution, and titrating the liberated iodine with 0.1 *N* thiosulfate, using starch solution as indicator.

Calculate the percentage of glycerol (1 cc. of the potassium dichromate solution equals 0.0100 gram of glycerol).

(2) *Determination of sugar.* Dissolve 10 grams (±0.01 gram) of the soap in 200 cc. of hot water in a 600-cc. beaker. Decompose with 25 cc. of sulfuric acid (1 to 4), boil gently for 20 minutes to invert the sucrose completely. Cool, remove, and rinse the cake of fatty acids. Extract the acid liquid with 25 cc. of ether. Neutralize the acid liquid with sodium hydroxide solution and transfer to a 500-cc. graduated flask, make up to volume and mix thoroughly. Determine invert sugar in 50 cc. of this solution by the Munson-Walker Method (*11*). To calculate sugar (sucrose) multiply the amount of invert sugar found by 0.95. [If starch is present, first remove as described under C-XIV (1) and then proceed as above.]

(3) *Determination of glycerol in the presence of sugars* (*10*). Proceed as above under (1), taking a sample so that the sum of the glycerol and sugar is not more than 3.0 grams. [If starch is present, this must first be removed as described in C-XIV (1).] The solution must be boiled in all cases at least 20 minutes to ensure complete inversion of sucrose. Determine the amount of potassium dichromate solution required to oxidize both the sugar and glycerol. Determine also the sugar by the method given in (2).

Calculate the percentage of glycerol after deducting the amount of potassium dichromate required by the sugar.

1 cc. of potassium dichromate equals 0.0100 gram of glycerol
1 cc. of potassium dichromate equals 0.01142 gram of invert sugar

(4) *Determination of starch* (*3*). Separate the matter insoluble in water as under C-II (3), using a sample of soap that will give not more than 3 grams of starch. Transfer the insoluble matter, without drying, to a beaker and heat for 2.5 hours with 200 cc. of water and 20 cc. of hydrochloric acid (sp. gr. 1.125) in a flask provided with a reflux condenser. Cool, and nearly neutralize with sodium hydroxide. Complete the volume to 250 cc., filter, and determine the reducing sugars by the gravimetric method as given under method for the determination of sugar.

Calculate the amount of dextrose (*d*-glucose) equivalent to the cuprous oxide obtained. This multiplied by 0.90 equals the amount of starch.

XV. DETERMINATION OF VOLATILE HYDROCARBONS (*13*). This method requires a source of dry, oil-free steam which is passed through the sample treated with acid, sufficient to liberate the fatty acids from the soap. The steam is next passed through strong caustic solution to scrub out any volatile fatty acids, while the volatile hydrocarbons are condensed with the steam in a suitable arrangement which allows the excess water to flow away, leaving the volatile hydrocarbons in the measuring buret. The method may be applied to samples containing substances immiscible with water and volatile with steam. For solvents heavier than water a Bidwell-Sterling tube should be used.

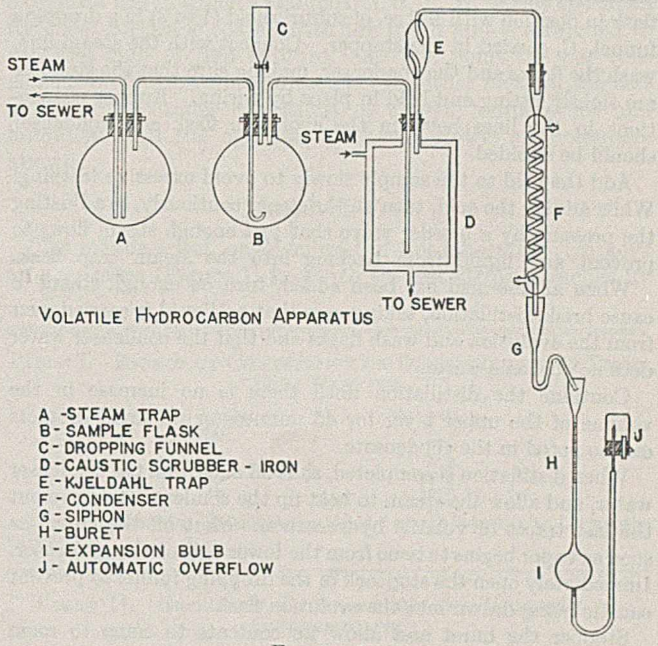

FIGURE 1

Apparatus. The apparatus and its arrangement are shown in Figure 1. The following are the important items.

Steam trap, *A*, a 1-liter round-bottomed ring-necked flask equipped with a siphon tube to the drain from the bottom of the flask and provided with a means of regulating the steam flow into the flask.

Evolution or sample flask, *B*, a 1-liter round-bottomed ring-necked flask. In case large samples are desirable the size of this flask may be increased.

Caustic scrubber flask, *D*, a steam-jacketed metal flask is preferred, but a 1-liter Florence flask provided with a steam coil of 0.32-cm. (0.125-inch) copper tubing around the upper half may be used. If the glass flask is used, it should be provided with a safety bucket below it and should be renewed frequently since the strong caustic dissolves the glass rather rapidly. This flask should be connected to the condenser by a Kjeldahl connecting tube, *E*, or similar safety device.

The inlet tubes for the steam into the evolution and scrubber flasks should extend nearly to the bottom of the flasks and be bent at right angles and parallel to the sides of the flask.

Condenser, *F*, a 30.5-cm. (12-inch) or longer spiral condenser of sufficient bore so that the condensate will not readily close it.

Measuring buret, *H*, a 10-cc. buret calibrated to 0.1 cc. and carrying a bulb, *I*, approximately 100-cc. capacity, at the lower end.

The stoppers used should be of a good grade of rubber and should have been thoroughly cleaned free from any surface sulfur and should be given a steam-distillation in position for several hours before use on a sample.

Insulating the flasks and tubing to reduce condensation aids distillation and its control.

Determination. Place 150 cc. of sodium hydroxide solution (about 1.47 sp. gr.) and several sticks of solid sodium hydroxide to provide against dilution in the scrubber flask. Rinse out the condenser and buret with acetone. Attach a rubber tubing to the lower end of the buret, fill the buret and tubing with water, and raise the outer end of the tubing so that the water level in the buret is near the top of the scale when the water is flowing to the drain from the automatic overflow, *J*. Be sure the connections are tight and that the tubing contains no air bubbles. Place the condenser in position so that the lower end extends directly into the upper end of the buret just above the water level or connect to an adapter siphon, *G*, which discharges into the buret. The cooling water should be 15.5° C. or colder. Ice water may be desirable for low-boiling hydrocarbons.

Weigh 100 grams (±0.5 gram) of the soap (cut into cubes of about 1-cm. edges) or 50 grams (±0.3 gram) of soap powder and transfer to the evolution flask. Add about 10 grams of gum arabic (commercial) and 100 cc. of distilled water. Place the flask in position with 100 cc. of sulfuric acid (1 to 3) in a dropping funnel, *C*, carried in the stopper. Connect with the steam line, wash the flasks and the condenser, making sure that the stoppers are tightly fitting and held in place by wiring. Rubber connections in the lines between the evolution flask and condenser should be avoided.

Add the acid to the sample slowly to avoid excessive frothing. While adding the acid, turn on the steam cautiously, so adjusting the pressure by a bleeder valve that just enough steam flows to prevent any liquid from backing into the steam trap flask. When all the acid has been added, turn on enough steam to cause brisk distillation, taking care that no liquid is carried over from the evolution and wash flasks and that the condenser water does not become warm.

Continue the distillation until there is no increase in the volume of the upper layer for 45 minutes or no small droplets can be noted in the condensate.

When distillation is completed, shut off and drain the condenser water, and allow the steam to heat up the condenser to drive out the last traces of volatile hydrocarbon. Shut off the steam as soon as vapor begins to issue from the lower end of the condenser. Immediately open the stopcock of the dropping funnel to prevent caustic being drawn into the evolution flask.

Stopper the buret and allow its contents to come to room temperature or bring them to a definite temperature by immersing the buret for 1 to 2 hours in a water bath held at 25° C.

Read the volume of the upper layer to the nearest 0.01 cc. The volume multipled by the specific gravity equals the weight of the volatile hydrocarbon. The specific gravity should be determined at the temperature at which the volume is read. A small Sprengel tube made of 3-mm. glass tubing is convenient for this purpose.

Calculation.

$$\frac{\text{cc. of volatile hydrocarbon} \times \text{specific gravity} \times 100}{\text{weight of sample}} = \text{per cent of volatile hydrocarbon}$$

For some samples the volatile hydrocarbon content may be so low that a larger sample than 50 or 100 grams is desirable. The size of the evolution flask may need to be increased if larger samples are used. The amount of water in the evolution flask and acid used should also be correspondingly increased.

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A Simple Laboratory Ozonizer

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A QUICKLY assembled ozonizer that can be operated for relatively long periods to give satisfactory yields is shown in Figure 1, which is self-explanatory. It has been constructed of a 600-mm. Pyrex condenser with extended side arm, and from other materials available in a laboratory. It is simple in construction, quickly assembled, relatively inexpensive, and can be dismantled into service as a standard condenser.

The transformer used was obtained from a neon sign. Several were tried, ranging from 10,000 volts upwards; all were satisfactory, and although not a stockroom item with most laboratories, they can be readily obtained from any neon sign agency. Used transformers are always available.

The units are supported in ordinary ring stands, insulation being provided by means of cork or rubber between the outer foil and the support. Several can be used in series by making the proper sealed connection.

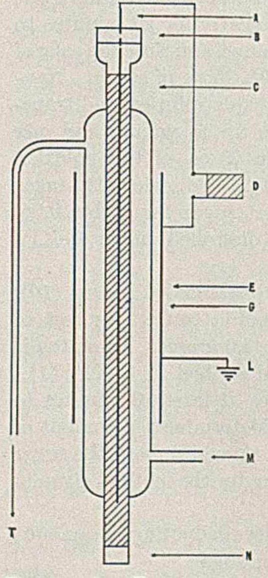

Figure 1. Diagram of Apparatus

A. Brass wire
B, N. Rubber stoppers
C. 5 per cent sulfuric acid
D. 15,000-volt transformer
E. Aluminum foil
G. 600-mm. condenser
L. Ground
M. Oxygen
T. Ozone (oxygen)

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Measurement of Distensibility of Organic Finishes

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ONE of the most important physical characteristics determining the serviceability of an organic finish is distensibility. This property perhaps more than any other furnishes an excellent means of following the ravages of age on a finish. By comparing their rates of change of distensibility with time, otherwise seemingly similar finishes can often be readily differentiated. In the case of oleoresinous varnishes and enamels, differences in oil length are clearly reflected in the degree of distensibility, and progressive embrittlement with age is readily followed. In the case of cellulose-ester finishes the effects of varying the amount and kind of plasticizer are revealed by distensibility measurements. In this paper the several variables that affect the flexibility of a finish will be briefly discussed. Two test devices for measuring the distensibility of organic finishes will be described in detail and the results obtained with them compared.

The variables that determine the distensibility of an organic finish are: (1) composition of the film-forming material, (2) thickness of the organic finish, (3) age and exposure history of the finish, (4) temperature and humidity at time of test, and (5) the rate of stress application.

These constitute the major variables that any distensibility method must take into consideration. Some idea of the relative importance of several of these factors can be had by examining the illustrative experimental values shown in Tables I, II, III, and VII. The per cent elongation shown in these tables was determined by stretching finish specimens to point of rupture, by a method described at a later point in this paper.

Methods of Test

There are two general methods of measuring the distensibility of organic finishes. One is the free-film method, and the second is by bending or stretching a metal specimen coated with an organic finish. In the first method, a suitably shaped and detached film of the finish is stretched between two clamps, and the tensile strength and per cent elongation up to the point of rupture are directly determined. The value of this test was clearly shown by Nelson (*1, 3–6*) and his coworkers a number of years ago. More recently Hunt and Lansing (*2*) have published an interesting and important paper in which the same method was used to determine the significance of the change of the humidity and temperature coefficients of distensibility with age.

In this laboratory the authors have for several reasons preferred to measure distensibility of actual finish specimens, even though this is attended by a limitation of the test to flexible base materials. The distensibility of a paint film attached to its basis material is affected by both cohesional and adhesional factors. The relation between these factors is not as yet quantitatively known. However, the user of paint materials is interested in the degree to which a given finish may actually be bent or stretched. In the case of those finishes in which the adherence of the organic coating is of a very low order, distension tests using a finish specimen yield distensibility values approximating those obtained by the free-film method at equivalent rates of distension.

Two methods of measuring the effective distensibility of organic finishes have been investigated. In each case, sample specimens of the actual finish—that is, organic coating applied to its base material—are used. One method employs an improved mandrel test, in which a number of mandrels of different diameters are used, and the other employs a direct-extension test in which a standard A. S. T. M. tensile specimen for sheet metals is coated with the finish and is stretched to the first sign of film rupture. At this point the per cent elongation is determined directly. In either method the test is performed under conditions of known temperature and humidity, and the age and thickness of the specimen are known.

Mandrel Test

The mandrel test, as developed in this laboratory, employs an apparatus (Figure 1) in which six test strips, 3 inches by

TABLE I. EFFECT OF COMPOSITION ON DISTENSIBILITY OF ESTER GUM VARNISH

Oil Length *Gal.*	Elongation *%*
10	3.2
25	36.5
40	43.8

Thickness of coatings, 0.0005 inch. Aged 1 month indoors plus 1.5 months outdoors.

TABLE II. EFFECT OF TEMPERATURE AND HUMIDITY ON DISTENSIBILITY

	Per Cent Elongation					
	Temperature, 77° F.			Relative Humidity, 50 Per Cent		
Material	26%[a]	50%[a]	90%[a]	55° F.	77° F.	95° F.
10-gallon ester gum varnish	1.5	4.2	49.9	0.6	4.2	54.0
Synthetic enamel (air dry)	15.0	15.1	54.9	2.4	15.1	53.2
Lacquer enamel (highly plasticized)	22.5	24.5	31.2	12.8	24.5	31.6
Synthetic enamel (baked)	43.0	42.3	46.6	12.5	42.3	48.9

[a] Relative humidity.

In all cases coatings are 2 weeks old. All films are approximately 0.001 inch thick.

TABLE III. EFFECT OF THICKNESS AND AGE ON DISTENSIBILITY

Material	Thickness	Per Cent Elongation		
		I[a]	II[b]	III[c]
	0.001 inch			
10-gallon ester gum varnish	0.5	8.5	2.4	2.9
	1.0	8.2	2.1	2.1
	3.0	4.7	...	3.2
	6.0	4.2	...	7.1
25-gallon ester gum varnish	0.5	>60	25.5	49.7
	1.0	59	48.3	54.4
	3.0	>60	>60	>60
	6.0	58.6	>60	>60
Lacquer A	0.5	19.4	2.9	13.7
	1.0	19.6	6.0	9.8
	2.5	9.4	1.7	2.4
	4.0	11.2	2.7	3.0
Lacquer B	0.5	35.1	2.7	22.4
	1.0	30.9	5.6	21.1
	3.0	23.0	8.7	19.5
	6.0	24.0	12.5	20.2
Baked synthetic varnish enamel A	0.5	42.2	10.3	9.6
	1.0	43.7	2.0	7.5
	3.0	38.5	2.3	3.8
	6.0	28.9	1.6	2.3
Baked synthetic varnish enamel B	0.5	58.6	3.1	>60
	1.0	>60	5.4	>60
	3.0	>60	29.0	>60
	6.0	>60	51.6	>60

[a] Test specimens aged one month at 77° F. and 50 per cent relative humidity.

[b] Same as in [a] plus 13 months outdoors.

[c] Test specimens aged 16 months as in [a].

approximately 0.5 inch, are bent either singly or simultaneously around six mandrels of diameters 0.125, 0.25, 0.375, 0.5, 0.75, and 1 inch, respectively. Each test strip is securely locked in place at the lower end and is then bent by a drawbar in a manner that assures close contact of the specimen against the mandrel surface during the entire bend of almost 180°. Smooth motion of bending is assured by the use of a worm-gear mechanism between the crank handle and the drawbar.

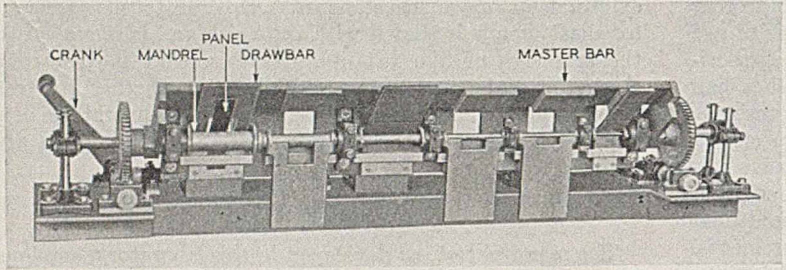

FIGURE 1. APPARATUS FOR MANDREL TEST

In this test, it is important to ascertain the degree to which the surface of the test specimen is actually stretched during the bending. This is dependent primarily on the radius of curvature of the mandrel and the thickness of the test strip. A first approximation to the actual per cent elongation of the finish as a result of bending can be computed on the assumption that the neutral surface lies halfway between the outer surfaces of the strip. This is the condition that would prevail if the stresses were within the elastic limit of the metal base. With this assumption it can be readily shown that the elongation is

$$e = \frac{t}{2r + t} = 100 \frac{t}{2r + t} \text{ per cent} \qquad (1)$$

where r is the radius of the mandrel
t is the thickness of the strip

Table IV, which is based on Equation 1, gives the values of per cent elongation for three panel thicknesses and the six mandrel sizes.

TABLE IV. VARIATION IN DISTENSIBILITY WITH PANEL THICKNESS

(Per cent elongation)

Panel Thickness	Mandrel Diameter in Inches					
	0.125	0.25	0.375	0.5	0.75	1
Inch	%	%	%	%	%	%
$^{1}/_{64}$	11.1	5.9	4.0	3.0	2.0	1.5
$^{1}/_{32}$	20.0	11.1	7.7	5.9	4.0	3.0
$^{1}/_{16}$	33.3	20.0	14.3	11.1	7.7	5.9

Actually the elastic limit is definitely exceeded in most of the bending operations, the neutral surface shifts toward the compressed side of the specimen, and the elongation of the stretched surface therefore increases. This increase in elongation cannot be calculated directly, but must be determined experimentally. The authors have performed such an experiment for $^{1}/_{32}$-inch panel stock and for three commonly used metals in order to determine the magnitude of this increase in elongation.

To do this a special jig shown in Figure 2 was devised in which metal strips were securely bent around mandrels of several sizes. Each strip prior to bending was marked with two finely scratched lines. The distance between lines was determined with a comparator to an accuracy of 0.00008 inch (0.0002 cm.). With the strip in position on the mandrel, the angle subtended at the center by the distance between the hair lines was determined to within ±5 seconds of arc. The total distance between the center of the mandrel and the surfaces of the specimen was next measured and the new extended length between gage marks calculated. Using this method, values for all but the 0.125-inch mandrel were determined. The values for the 0.125-inch mandrel were obtained by extrapolation (values plotted on double logarithmic paper) from the values for the other mandrels. The values obtained for the per cent elongation of $^{1}/_{32}$-inch sheet stock of hard and annealed brass and of cold-rolled mild steel are shown in Table V.

It is of interest to note that the annealed metal which has the least elastic range shows the greatest deviation from the values given in Table IV.

The values recorded in Table V are considerably higher than those computed from Equation 1 (see Table IV), particularly for the smaller mandrel sizes. However, since a high degree of accuracy is not necessary for most finish investigations, the computed values of Table IV may be used where the true values are unavailable.

TABLE V. ACTUAL PER CENT ELONGATION AT VARIOUS MANDREL SIZES

Material	Mandrel Diameter in Inches					
	0.125	0.25	0.375	0.5	0.75	1
	%	%	%	%	%	%
$^{3}/_{4}$ hard brass	29.1	14.2	9.6	6.9	4.6	3.4
Annealed brass	33.5	15.9	10.3	7.5	4.9	3.6
Cold-rolled steel	28.0	13.8	9.0	6.7	4.4	3.3

In the authors' studies of the physical characteristics of finishes it was of interest to ascertain the effect of change of thickness of the organic coating on distensibility. Since the organic coatings increase the effective mandrel diameter, it is necessary to apply a correction factor to the previously determined values to get the true surface elongation of the finish. This correction becomes more important as the thickness of the coating increases. On the assumption that the paint coatings are comparatively weak in tensile properties and therefore exert a negligible effect on the bending resistance of the specimen, a correction formula for coating thickness was developed. It can be shown that the elongation, e', of the outer surface of the finish is given by

$$e' = e + \frac{t'(1 + e)}{r + t}, \text{ where } t' \text{ is the thickness of coating} \qquad (2)$$

Table VI lists the corrections, as computed from Equation 2, in per cent elongation per 0.001 inch of coating to be added to the elongation values of Table V. Equation 2 may also be used to correct the values of Table IV for coating thickness. Since the corrections to be added are small in comparison to

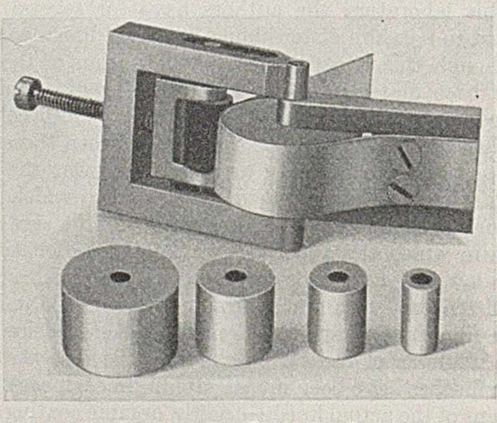

FIGURE 2. SPECIAL JIG

the normal values of elongation, they may be neglected for coating thickness up to 0.001 inch. However, as the coating thickness is increased the corrections become increasingly important, particularly for the smaller mandrel sizes, and therefore cannot be neglected.

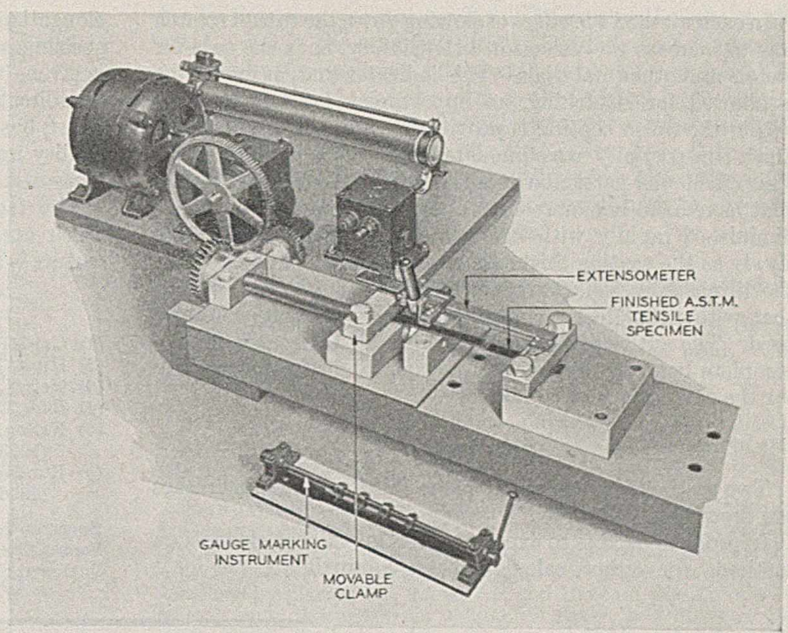

Figure 3. Apparatus for Direct-Extension Method

Direct-Extension Method

The mandrel test has the inherent drawback of being a discontinuous process—that is, with a convenient number of mandrel sizes, in order to cover a moderate range of values, the elongations are measurable only at fairly wide intervals. One way of overcoming this is by increasing the number of mandrels. Another way is to use a means of extension in which any degree of elongation can be directly measured. This has been accomplished with the apparatus shown in Figure 3. The finish to be tested is applied to a standard A. S. T. M. tensile specimen for sheet metal which is then fastened between two jaws, one of which is pulled at a slow even rate by means of a screw driven through reduction gears by a motor. During stretching, the surface of the finish is observed with a low-power microscope, and the elongation is measured at the point of film rupture. This is done by measuring the change in length of 1-inch gage marks which had been scratched on the surface of the specimen with the aid of the marking instrument also shown in Figure 3. The measurements are made with the aid of an extensometer, which consists of a vernier caliper, to the measuring head of which is attached a small microscope with a cross-hair eyepiece. The cross hair is focused on each of the gage marks and the corresponding vernier readings are noted, from which the elongation can be directly determined. Regarding the precision of the direct extension method, it was found that the average deviation from the mean elongation values was ±8 per cent on the basis of several hundred determinations.

In this test, as in the mandrel test, a qualitative measure of the adherence of the distended film to the base metal is provided. The distensibility of the coating determines the point of failure, and the adherence, the character of the failure. With good adherence the initial rupture is in the form of many fine cracks, whereas with poor adherence the coating may tear off completely and loosen over long distances behind the point of rupture.

Table VI. Correction in Per Cent Elongation for Mandrel Distensibility Values per 0.001 Inch of Coating

Material	Mandrel Diameter in Inches					
	0.125	0.25	0.375	0.5	0.75	1
	%	%	%	%	%	%
3/4 hard brass	1.38	0.73	0.50	0.38	0.26	0.21
Annealed brass	1.43	0.74	0.50	0.38	0.26	0.21
Cold-rolled steel	1.37	0.73	0.50	0.38	0.26	0.21

In both these methods of measuring finish distensibility, granulation of the metal occurs increasingly with degree of extension. This granulation is dependent on the metal or alloy used and serves to increase the actual surface extension of the paint-metal interface. In the values for distensibility reported in this paper this secondary effect due to granulation has not been determined quantitatively.

In one study in which several hundred determinations of distensibility of the same finishes were made by both methods of distension, an opportunity was offered for a comparison of the results obtained by the two methods. The result was disconcerting but illuminating. Although the same materials over a common base metal at equivalent thicknesses of coating and at the same age were measured under identical conditions of temperature and relative humidity, it was found that about half of the values for distension as determined by the mandrel test were considerably below those obtained by direct extension. Correction for coating thickness and using the values for actual surface extension as recorded in Tables V and VI reduced the disagreement between the two methods only moderately.

The discrepancy was consistently larger for coatings combining high tensile strength and high distensibility. This suggested that the rate of stretching, being quite different in the two tests, might account for the disagreements. In the mandrel test a 180° bend is completed in about 15 seconds, whereas in the case of the direct-extension test the rate of stretching was about 0.6 inch per minute. Furthermore, there is a fundamental difference in the rate of stretch in the two methods. In the mandrel test, only a small fraction of the test specimen is under tension at any one moment, but at that moment this fraction receives the complete bending stress as it enters the bending zone. In the second test, however, the entire surface of the specimen is subjected to an even, but steadily increasing stress. It became of interest therefore to see what effect varying the rate of stretch would have on the distensibility values obtained by each of these methods. The mandrel test was performed at rates ranging from 15 seconds to 55 minutes to complete a full bend of 180° C. The rate of the direct extension test was varied from 3.3 inches to 0.2 inch per minute. The effect of varying the rate of stretch is shown in Table VII for four different finishes, compared at equivalent film thickness.

Table VII. Effect of Rate of Stretch on Distensibility of Finishes

Material	Per Cent Elongation				
	Mandrel Test		Extension Test		
	15 sec.	55 min.	0.2 in./min.	0.6 in./min.	3.3 in./min.
A	10.3–15.9	15.9–33.5	25	25	21
B	<3.6	3.6–4.9	5.9	5.9	3.9
C	<3.6	7.5–10.3	9.5	9.0	8.5
D	10.3–15.9	>33	26.0	21.0	18.0

All films are approximately 0.001 inch thick. The thickness variation between specimens of the same material was within 0.0001 inch.

In each method the effect of slowing down the rate of stretch was to increase the value for distensibility, as is the case for metals and other materials. This indicates that, as more time is allowed for stretching, an opportunity for internal flow within the finish coating is provided, by means of which the finish can partially accommodate itself to the applied stress. This effect was particularly noticeable in the case of finishes that have aged not more than about one month. The effect diminished rapidly with age with thin-finish coatings, and slowly as the coating thickness was increased. The fact that the distensibility values are influenced by rate of stretch means that with either test a constant rate of extension should be used. The authors have found the rate of 15 seconds for the complete bend in the mandrel test and 0.6 inch per minute for the extension test satisfactory.

Summary

Two methods of measuring distensibility of organic finishes are described.

In order to be able to express results in per cent elongation, methods for either calculating an approximate per cent elongation value or determining actual elongation of mandrel specimens are described. A correction for thickness of finish is given.

A direct-extension method for coated specimens is described which has the advantage of permitting any degree of distensibility up to rupture of the supporting base material to be measured.

The factors that affect the distensibility of an organic finish are discussed and the relative importance of these factors is illustrated by experimental values.

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A Photoelectric Method for the Determination of Phosphorus[1]

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WITH existing quantitative methods for detecting phosphorus it is not possible to determine with a high degree of accuracy quantities as small as 0.001 mg. The device herein described was constructed to give a sensitive, simple and rapid, yet accurate, method for phosphorus determinations when applied to the methods of Fiske and Subbarow (*1*), Kuttner and Cohen (*5*), or Kuttner and Lichtenstein (*6*).

The apparatus has been entirely satisfactory when applied to the determination of blood sugar by Folin's method (*2*), the study of phosphatase activity by Jenner and Kay's (*4*) modification of the Kuttner and Cohen procedure, and the determination of yeast population by turbidity measurements.

The use of the photoelectric cell for colorimetric and turbidity estimations is not new. It has been applied by Osborn (*7*), Greene (*3*), and Samuel and Shockey (*8*).

The apparatus described makes use of the circuit outlined by Samuel and Shockey (*8*) modified to permit the use of a sensitive galvanometer, and a smaller light source.

The modified circuit of the apparatus is given in Figure 1. A single light source of low intensity directed vertically upward through a 50-ml. flat-bottomed Nessler tube containing the solution to be tested, and impinging on the photronic cell, causes a deflection of the galvanometer, the amount of the deflection being a function of the quantity of light allowed to pass through the solution.

The circuit used in the apparatus described has two decided advantages over previously described photocolorimeters: The use of a light source of small intensity eliminates temperature effects, the solutions can remain in the apparatus for extended periods without being influenced by temperature. The use of a variable resistor (R_3) instead of a fixed resistor makes it possible to maintain a constant spread on the galvanometer scale, since by its use compensation for battery depletion is regulated.

A number of precautions in the use of this photoelectric colorimeter are essential, when great accuracy is desired. Cleanliness of Nessler tubes, light bulb, photoelectric cell, and the apparatus in general is necessary. The effect of finger marks is appreciable and, unless the Nessler tube is kept clean, is reflected in deflection of the galvanometer to the extent of 1 to 2 mm. It is customary, prior to making a determination, to clean the tube with chromic acid solution, followed by washing with distilled water. Before each reading is made, the outside of the tube is wiped dry and free from finger marks.

The resistance R_1 must be capable of carrying 10 amperes; otherwise temperature changes of the resistance will cause fluctuations in the galvanometer, producing erroneous results.

It is essential to use the same Nessler tube for all determinations, since the authors have not found two tubes characterized by the same calibration curve. This will be seen by comparing Tables I, II, and III with Figure 2, three different Nessler tubes having been used.

TABLE I. REPRODUCIBILITY OF CALIBRATION CURVE

Phosphorus	Blank	0.00093 mg.	0.001868 mg.	0.00467 mg.	0.00934 mg.
Readings[a]	42.2	37.5	30.6	19.5	10.4
	43.2	37.6	31.6	20.2	10.6
	42.0	36.4	31.4	19.9	10.6
	43.2	35.2	30.4	19.5	10.2
	43.6	37.6	30.8	...	10.8
Mean	42.84	36.86	30.98	19.78	10.52

[a] Photronic cell No. 9. Nessler tube No. 3.

Photronic cells vary appreciably in the current output relative to a given change in depth of color. Therefore, each photronic cell must have its own calibration curve.

Because of the sensitivity of the equipment to minute changes in depth of color, it is always essential to follow the identical procedure in developing the color in a series of determinations that was employed in establishing the calibration curve. The same precaution applies to turbidity measurements.

The characteristics of the photronic cell are such that colorimetric methods involving transmitted light of yellow or orange color

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[1] Since presentation of this method a similar photoelectric colorimeter has been described (*9*).

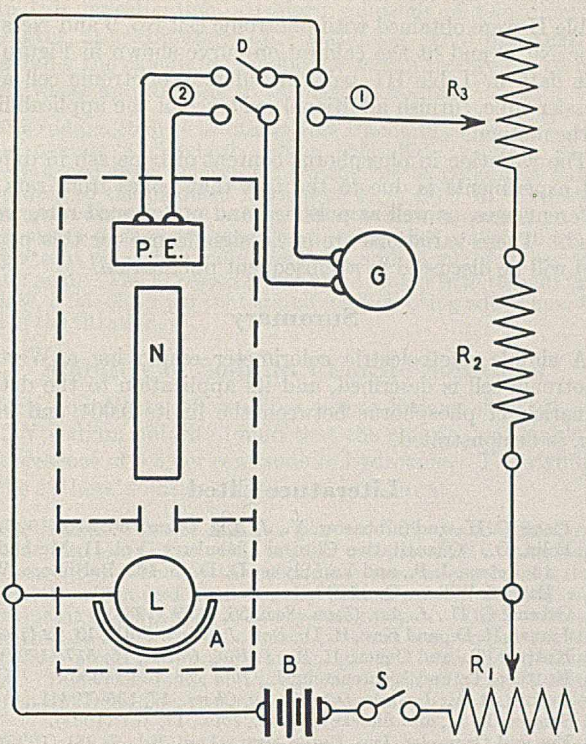

FIGURE 1. SCHEMATIC DIAGRAM

N.	Nessler tube, flat bottom
B.	6-volt storage battery
S.	Single-pole single-throw switch
L.	3-candle power 6-volt automobile bulb
A.	Reflector
D.	Double-pole double-throw switch
P.E.	Weston 594 photronic cell
G.	L.N. box galvanometer (0.025 microamp. per mm.), scale replaced by scale 70 mm. long graduated in 1 mm.
R_1.	3-ohm, 10-amp. variable resistor serially connected to 3-ohm, 10-amp. fixed resistor
R_2.	1.5-megohm fixed radio resistor
R_3.	200,000-ohm variable radio resistor
---	Light-tight box with two separate light-tight compartments; a round 3.75-cm. (1.5-inch) diameter opening is made between *N* and *L* to allow light to pass through Nessler tube

are less satisfactory than methods based on changes in blue. A spectrally pure blue-green filter inserted between the light source and the solution to be tested will be found helpful in the case of yellow solutions.

If it is desired to reduce the sensitivity of the instrument, a shunt can be placed in the galvanometer circuit, or a 0–100 microammeter can be substituted, in which case it becomes necessary to reduce the amount of resistance in R_2 and R_3.

Operation of Colorimeter

Five minutes before a determination is to be made the switch is closed, allowing the apparatus to attain equilibrium. A clean Nessler tube filled with distilled water is placed in position. With switch *D* open, the galvanometer is set at 0. With the double-pole double-throw switch in position 1, the deflection on the galvanometer is set at some arbitrary reading by the use of the resistor R_3. The greater the spread, the greater will be the sensitivity of the apparatus, and the more accurately the unknown substance can be determined. The double-pole double-throw switch is then placed in position 2, and R_1 is adjusted until the galvanometer again gives the same reading as selected in the first operation. It may be necessary to readjust R_3 again, until both positions give the same desired deflection. If the current source is constant there is no further need of adjustment.

TABLE II. PHOSPHORUS IN BONE ASH

Experiment No.	Age of Rat	Weight of Ash	Dilution Factor	Scale Reading[a]	Phosphorus		Variation of Duplicate Reading[b]
	Days	*Mg.*		*Mm.*	*Mg.*	%	%
98	24	11.2	1000	33.0	0.00199	17.76	1.51
				32.8	0.00202	18.03	1.50
102	39	6.8	500	22.2	0.00422	31.03	0.47
				22.0	0.00424	31.17	0.47
107	50	16.7	1000	23.4	0.00395	23.65	2.28
				23.8	0.00386	23.12	2.33
113	52	38.9	2000	23.5	0.00394	20.25	1.78
				23.0	0.00401	20.61	1.75

[a] Photronic cell No. 9, Nessler tube No. 2.

[b] $\frac{\text{Difference in mg.} \times 100}{\text{mg.}}$.

Procedure for Determination of Phosphorus

The method for the determination of phosphorus as finally modified by Kuttner and Lichtenstein (*6*) was used. The following reagents are necessary:

STOCK SOLUTIONS. (1) Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), 7.5 per cent; (2) 10 *N* sulfuric acid, 282 cc. of concentrated acid (sp. gr. 1.84) per liter; and (3) stannous chloride, 40 per cent in concentrated hydrochloric acid.

STANDARD SOLUTIONS. Dissolve 0.0879 gram of dried monopotassium phosphate (KH_2PO_4) in 1 liter of distilled water, and add a few drops of chloroform. One cubic centimeter of this solution contains 0.02 mg. of phosphorus. Make five standard solutions by placing 1.0, 2.5, 5, 7.5, and 10 cc. of the above solution in each of five 100-cc. volumetric flasks, and filling to the mark with distilled water. These standards contain 0.001, 0.0025, 0.0050, 0.0075, and 0.010 mg. of phosphorus in 5 cc., respectively.

The color of the standards is produced as follows:

A molybdic acid solution is freshly prepared by adding 20 cc. of distilled water to 10 cc. of 7.5 per cent sodium molybdate (solution 1), and then 10 cc. of 10 *N* sulfuric acid (solution 2). A dilute stannous chloride solution is freshly prepared by diluting 0.25 cc. of 40 per cent stannous chloride (solution 3) to 50 cc. with distilled water. To 5 cc. of each standard, 4 cc. of the molybdic acid solution are added and, while stirring constantly and regularly, 1 cc. of the dilute stannous chloride is added. One hour is allowed for the maximum color development.

After the apparatus has been adjusted for the desired sensitivity, the blue colored standards are transferred successively to the Nessler tube and made up to the mark. After placing the tube in the apparatus and closing the light-tight box, the gal-

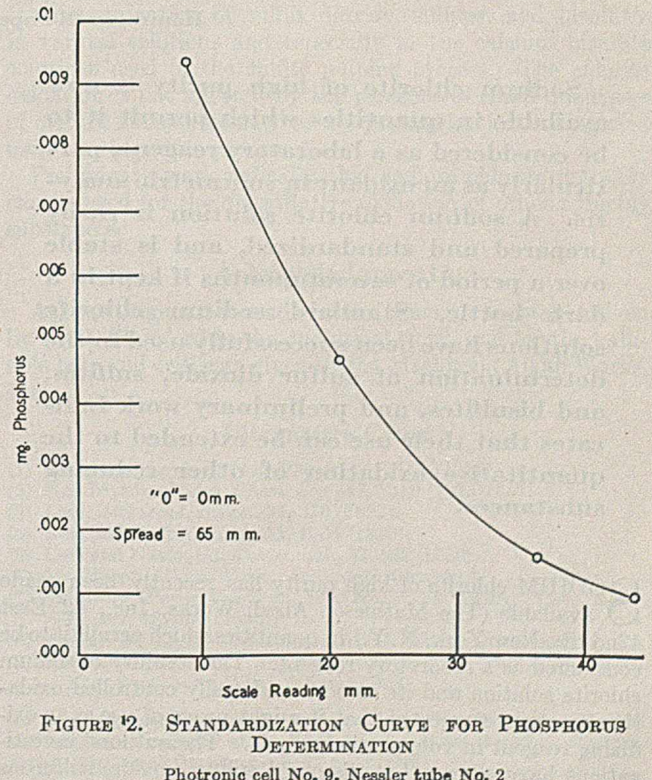

FIGURE 2. STANDARDIZATION CURVE FOR PHOSPHORUS DETERMINATION

Photronic cell No. 9, Nessler tube No. 2

vanometer deflection is noted. Five standards suffice to plot a calibration curve, as shown in Figure 2, which automatically eliminates any error due to traces of impurities in a given set of reagents.

Analysis is accomplished by taking 5 cc. of a solution in which the amount of phosphorus lies within the range of 0.001 to 0.010 mg. The color is developed and the galvanometer deflection obtained as in the case of the standards. From the position of the galvanometer reading on the calibration curve the quantity of phosphorus present may be read off.

TABLE III. PHOSPHORUS IN BONE ASH

Experiment No.	Age of Rat	Weight of Ash	Dilution Factor	Scale Reading[a]	Phosphorus		Variation of Duplicate Reading[b]
	Days	*Mg.*		*Mm.*	*Mg.*	%	%
61	10	2.4	100	32.9	0.00115	4.79	2.61
				33.3	0.00112	4.67	2.68
62	6	1.4	50	24.1	0.00205	7.32	8.29
				25.7	0.00188	6.71	9.06
64	20	15.6	1000	32.4	0.00120	7.69	1.67
				32.2	0.00122	7.82	1.65
66	11	5.1	200	15.2	0.00395	15.49	1.26
				15.4	0.00390	15.29	1.28

[a] Photronic cell No. 1, Nessler tube No. 1.

[b] $\frac{\text{Difference in mg.} \times 100}{\text{mg.}}$.

The character of the calibration curve is conditioned by the particular photronic cell, Nessler tube, and set of reagents employed. With these three factors constant, the reproducibility of the calibration curve for photronic cell No. 9, tube No. 3, was determined by noting the galvanometer reading of five sets of standards. Table I lists the mean and individual galvanometer readings for the blank and four solutions containing known concentrations of phosphorus.

The results of a number of typical analyses for phosphorus in bone ash are given in Tables II and III. The data in Table II were obtained with photronic cell No. 9 and Nessler tube No. 2 and fit the calibration curve shown in Figure 2. The data in Table III, using a different photronic cell and Nessler tube, furnish additional evidence of the applicability of the method.

The variation in phosphorus content of bone ash in different experiments is due to the fact that bones from rats of different ages, as well as poisoned and unpoisoned rats, were used. These variations are of no significance for this paper and will be discussed in a subsequent publication.

Summary

A simple photoelectric colorimeter employing a Weston photronic cell is described, and its application to the determination of phosphorus between the limits 0.001 and 0.01 mg. is demonstrated.

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Sodium Chlorite as a Volumetric Oxidizing Agent

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Sodium chlorite of high purity is now available in quantities which permit it to be considered as a laboratory reagent, particularly as an oxidant in volumetric analysis. A sodium chlorite solution is easily prepared and standardized, and is stable over a period of several months if kept in a dark bottle. Standard sodium chlorite solutions have been successfully used in the determination of sulfur dioxide, sulfites, and bisulfites, and preliminary work indicates that their use can be extended to the quantitative oxidation of other reducing substances.

SODIUM chlorite of high purity has recently been made available (The Mathieson Alkali Works, Inc., 62 East 42nd St., New York, N. Y.) in quantities which permit it to be considered as a laboratory reagent. The stability of sodium chlorite solution and its smooth and easily controlled oxidation reactions suggested that it might prove of use as an oxidizing reagent in volumetric analysis. The authors' investigations have shown that dissolved sulfur dioxide, sulfurous acid, and sulfites can be satisfactorily determined by oxidation with sodium chlorite. Preliminary work indicates that it can probably be applied to the volumetric determination of certain other reducing substances.

There are but few references in the literature to the use of chlorites (*1, 3, 4, 5*) and only one to their use as a quantitative analytical reagent. Levi and Ghiron (*4*) made use of the reaction between calcium chlorite and a permanganate in a neutral solution to determine the permanganate.

The sodium chlorite as obtained is a white, finely crystalline material. Being slightly hygroscopic, it takes up some moisture when exposed to air. The salt dissolves readily in water, its solubility being 91.3 parts in 100 parts of water at 30° C. (*6*). The freshly prepared solutions are entirely clear and colorless. The more concentrated solutions gradually turn yellow and yellow-green if allowed to stand exposed to light.

An analysis (*8*) of a sample of sodium chlorite showed the following percentages: $NaClO_2$, 97.6; NaCl, 0.7; NaOH, 1.5; $NaClO_3$, 0.0; and H_2O (by difference), 0.2.

Preparation and Standardization of Solutions

The equivalent weight of sodium chlorite (as an oxidizing agent in an acid solution) is one-fourth of its molecular weight:

$$ClO_2^- + 4H^+ + 4\,(-) \longrightarrow Cl^- + 2H_2O$$

In this investigation, standard solutions of two different strengths, approximately 0.1 *N* and 0.3 *N*, were prepared by dissolving the calculated amount of salt in freshly boiled distilled water and diluting to the desired volume.

The sodium chlorite solutions were standardized by comparing them against a standard sodium thiosulfate solution whose strength had been determined by the use of potassium iodate according to the modified method of Than (*9*). An accurately measured volume of the sodium chlorite solution was run into an Erlenmeyer flask containing 75 ml. of distilled water, 15 ml. of 10 per cent potassium iodide solution, and 15 ml. of 30 per cent acetic acid. The liberated iodine was titrated with sodium thiosulfate, 5 ml. of a 1 per cent starch solution being added near the end of the titration.

Stability of Sodium Chlorite Solutions

Levi and Natta (*5*) working with solutions of 0.2 *N* and 0.02 *N* sodium chlorite found that the chlorite was stable in the presence of 0.5 per cent sodium hydroxide. The stability of the authors' solutions was tested as follows:

The sodium chlorite solution was carefully standardized and divided into two parts. One portion was placed in a clear, glass-stoppered Pyrex bottle; the second portion was placed in a similar bottle which had been heavily coated on the outside with black paint and wrapped in heavy black paper. The two bottles were then stored in the laboratory (at room temperature) so that they were protected from direct sunlight but exposed to ordinary light. Tests were made on the chlorite solutions (as in the standardization) from time to time. The results are shown in Table I.

TABLE I. THIOSULFATE EQUIVALENT TO 1 ML. OF SODIUM CHLORITE SOLUTION

Elapsed Time	Solution Protected from Light	Solution Exposed to Light
Days	*Ml.*	*Ml.*
0	1.00	1.00
1	1.00	1.00
2	1.00	0.94
5	1.00	0.92
8	1.00	0.92
21	1.00	0.88
30	1.00	0.83
90	1.00	..
210	1.00	..

The sodium chlorite solution is entirely stable over a period of several months when stored so that light is excluded.

Determination of Sulfites

A standard solution of sodium chlorite has been used to determine the sulfites in calcium bisulfite, sodium sulfite, sulfurous acid solutions, and the cooking acid used in the sulfite pulping process. The latter solution contains lignin derivatives, sugars, and other organic matter. The sodium chlorite solution has been found satisfactory in each case.

Hendrixson (*2*) has shown that the oxidation of sulfite by iodate is quantitative. Palmrose (*7*) has shown that the iodate oxidation is not affected by the presence of organic matter in the solution being tested. In this investigation, the results obtained by the iodate titration were taken as the standard and the results of the sodium chlorite titrations compared with them.

Procedure

A measured amount of the solution being tested (or an aliquot part of the diluted solution) was transferred, with the usual precaution to avoid loss of gas, to an Erlenmeyer flask containing 100 ml. of distilled water, 15 ml. of 10 per cent potassium iodide solution, 15 ml. of 30 per cent acetic acid, and 5 ml. of 1 per cent starch solution. The standard chlorite solution was then run in rapidly until near the end point and then drop by drop until the blue starch-iodine color persisted. It is best to avoid shaking the solution until most of the chlorite has been added.

The reaction $ClO_2^- + 2SO_3^{--} \longrightarrow Cl^- + 2SO_4^{--}$ probably takes place if chlorite is allowed to react with sulfite alone. It appears, however, to be a time reaction and seems to go fairly slowly. In the presence of potassium iodide the reactions probably are:

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow Cl^- + 2I_2 + 2H_2O$$
$$2H_2O + 2I_2 + 2SO_3^{--} \longrightarrow 2SO_4^{--} + 4I^- + 4H^+$$

When all the sulfite has reacted, the free iodine gives the deep blue color to the starch, indicating the end of the reaction.

Results

Most of the authors' work has been done on solutions of calcium bisulfite containing from 0.3 to 6.0 per cent of total sulfur dioxide (free and combined). Some of the results obtained are given in Table II. The agreement among different operators was good, the results usually checking within 4 parts per thousand.

TABLE II. DETERMINATION OF TOTAL SULFUR DIOXIDE IN SOLUTIONS OF CALCIUM BISULFITE

Sample No.	Sulfur Dioxide Iodate method	Sulfur Dioxide Chlorite method
	%	%
1	0.537	0.539
2	0.497	0.492
3[a]	4.18	4.18
4	5.66	5.65
5	5.71	5.71
6	5.21	5.19
7	5.25	5.27
8[a]	3.14	3.14
9[a]	3.07	3.07
10	5.07	5.06
11	5.52	5.51
12	5.32	5.33
13	4.88	4.90
14	5.68	5.68
15	5.03	5.02

[a] Solutions did not contain organic matter.

Conclusions

Sodium chlorite gives an easily prepared, easily standardized volumetric oxidizing solution which is stable when properly protected from the light. The analytical procedure is simple and rapid.

Sodium chlorite solutions have been found satisfactory for the determination of sulfur dioxide, sulfites, and bisulfites in various solutions and especially in the calcium bisulfite solutions used in the sulfite pulping process. The chlorite oxidation is not affected by the presence of small quantities of organic substances such as are present in the cooking acid used for the sulfite process.

Preliminary work indicates that sodium chlorite probably can be used for the quantitative oxidation of other reducing substances.

Acknowledgment

Acknowledgment is made for the generous assistance given by C. H. Steinford in the analytical work, and for the valuable help and criticism given by the Mathieson Alkali Works, Inc.

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Odor Concentration in Air-Conditioned Structures

Determination by the Freezing-Out and Osmoscope Method and Reduction by Activated Carbon

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IN AIR CONDITIONING any structure where certain percentages of fresh air and recirculated air are utilized, in time the odor concentration will increase to the point where it is very objectionable, and may present a health hazard and industrial problem. It then becomes necessary to remove the odor or its cause. If complete removal is impossible, the odor concentration should be reduced to the point where it is no longer noticeable.

Complete air conditioning involves the control of temperature, humidity, dust, and odors. These factors cannot be controlled satisfactorily unless we have scientific and practical proof as to the efficiency of the equipment. Temperature can be observed on a thermometer, humidity on the hygrometer, and dust by suitable dust-counting apparatus. Methods are known whereby odorous substances known to exist in the air can be determined quantitatively, but information obtained in this way is not satisfactory for obvious reasons. The odors may be so complex and derived from so many different sources that simple chemical determinations of one or more odoriferous substances may represent only a small percentage of the total amount present.

Solution of the problem resolves itself into the following steps: (1) to determine the total odor concentration by a scientific and practical method; (2) to reduce the concentration effectively by some efficient and economical material; and (3) to prove by the developed method how much the odor concentration is reduced by using this material.

A railroad car of the club-lounge type (the use of which was made possible through the courtesy of The Pullman Company) was reserved for the purpose of conducting the tests. In the car selected eating, drinking, smoking, and sleeping were in almost constant progress while the car was in use. The air was composed of about 25 per cent fresh air and 75 per cent recirculated. Large proportions of tobacco smoke, and the odors of food, liquor, and human bodies from the bedrooms and lounge were drawn directly into the recirculated air intake. The condition of the atmosphere during and after a trip is best described by likening it to that of an improperly ventilated room where persons have been eating, drinking, and smoking while playing cards.

Determination of the total odor concentration and quantitative estimation of certain odor-bearing materials were attacked in the following manner:

Known amounts of air were drawn slowly through absorption towers filled with activated carbon. The air was sampled immediately above the recirculated-air grille, thus assuring the same composition as existed in the car. Samples were drawn through a rubber tube into the towers by means of a small Buffalo blower and suction pump connected by a flexible shaft to a small 32-volt motor. The velocity of the air was controlled by a glass stopcock inserted in a rubber tube connecting the second absorption tower with the pump. In 45 hours about 200 cubic feet of air had passed through.

This method was unsatisfactory because the odors could not be recovered from the carbon for identification. Further efforts involved drawing the air successively through washing towers containing, first, dilute sulfuric acid and then dilute alkali. This, too, was unsatisfactory because very little odor could be recovered and it was apparent that chemical action had changed or destroyed the odorous material originally present.

Freezing-Out Method

The freezing-out method followed the discouraging results previously mentioned. For this purpose the following apparatus and tests were devised:

A box of 3-inch cork was constructed according to the dimensions in Figure 1 because it was calculated that this size was necessary to hold enough solid carbon dioxide (dry ice) to last 40 to 45 hours. A 1-inch Pyrex glass tube about 19 inches long, containing a chromel wire spiral to serve as a condenser, was inserted through closely fitting holes bored in each end of the box as near as possible to the bottom inside. This tube was fitted with one-hole rubber stoppers at each end,

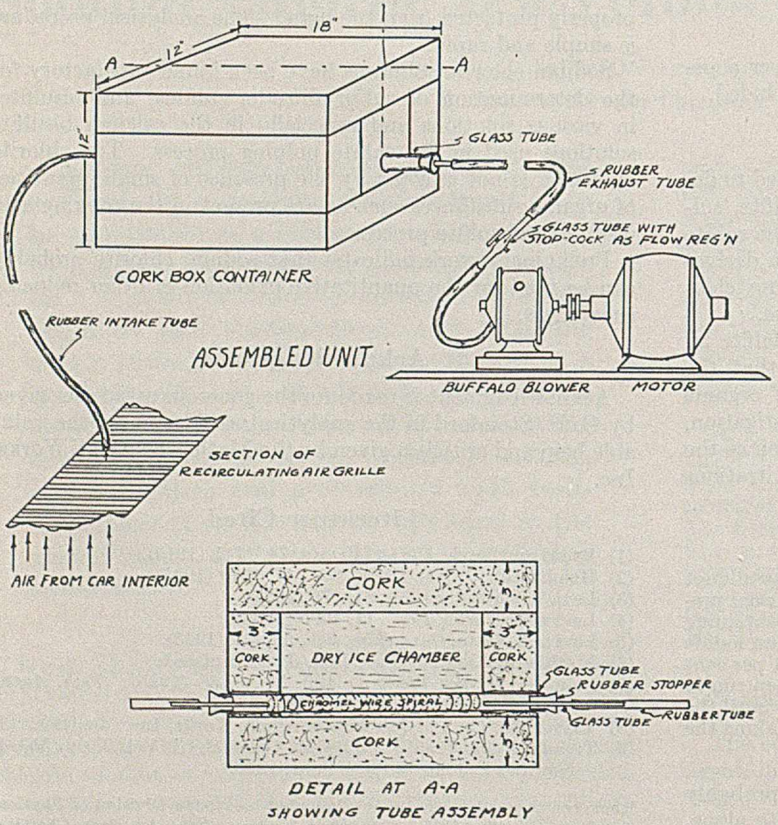

FIGURE 1. APPARATUS FOR FREEZING-OUT METHOD OF ODOR DETERMINATION

through which passed smaller glass tubes for connecting to rubber tubing. Pulverized dry ice was packed in the bottom of the box, enough to cover the condenser tube, and 2 solid cakes were sawed to fit and completely fill the remaining space inside the box. The box was tightly strapped and any noticeable leaks were stopped with asbestos fiber.

This container was placed over the hatch in the ceiling of the outside vestibule. A long rubber tube was connected to the intake end of the condenser tube and was allowed to hang over the recirculated-air grille inside the car. To the outlet end of the condenser tube another rubber tube was connected which led to a glass tube containing a stopcock for regulating the rate of air flow. This was connected by rubber tubing to the intake nozzle of a small Buffalo compressor and blower, which was connected by a flexible shaft to a small 32-volt motor. Thus a sample of recirculated air was drawn through the condenser tube, and the moisture and odor were frozen out as a cone of porous ice 3 or 4 inches long. To determine the flow of air, a calibrated manometer containing colored alcohol was connected on the outlet side of the condenser tube. The glass stopcock was so adjusted that the rate of flow was 61.02 cubic inches (1 liter) per minute, and then the manometer was disconnected. Knowing the length of time that the test was allowed to run it was a simple matter to calculate the amount of air that had passed through the tube.

A rate of 1 liter per minute was used because tests in the laboratory showed that such gases as ammonia, methyl amine, acetone, alcohol, and hydrogen sulfide were completely condensed in the first fourth of the intake side of the tube and no traces could be detected coming from the outlet end.

At the end of about 45 hours the rubber tubes were disconnected and the condenser tube was tightly stoppered and taken to the laboratory in the box containing the remaining dry ice. The tube was then taken out of the box and the frozen odor and moisture were placed in a wide-mouthed bottle, properly fitted with a cork collar through which was inserted a Fair osmoscope (*1*). The ice was allowed to melt and the liquid was shaken to saturate the air in the bottle with the odor of the liquid.

By setting the instrument at its highest reading, a sniff through the nosepiece will draw in one volume of odor-laden air from the bottle and 63 volumes of fresh air. The odor will thus be diluted 1 to 64 or 2^{-6}. If the odor is not sensed in this dilution, its pO value (relative odor value, or intensity of odor) is less than pO 6. In this case the setting is changed to its next higher position, and so on until the point is reached where the odor is barely detectable, which reading is the relative odor value (*1*).

Thus a new and very practical use has been found for the osmoscope. Previously it had been used to determine the odor value of water, but now it can be used to determine this value in air by first freezing out the water and odor in the air. After determining the relative odor value, the total amount of condensate was reserved for identification tests and quantitative determinations of the detectable odorous substances.

With a practical method for determining the intensity of odor it is hardly necessary to attempt a thorough chemical analysis. The wide variety and structural complexity of substances which impart odor render direct quantitative determinations of little significance. In Table I only four substances were determined and these only because they could be detected and were known to exist. They serve only as a check on the relative odor value, for certainly their combined odor intensity is only a small percentage of the total.

Removal of Odor

Many methods for removing odors have been tried, such as various sprays which at best give only temporary relief by masking the odor. Ozonators must be accurately controlled in order to avoid increasing the concentration of ozone to the point where it becomes toxic. Ozone deodorizes by oxidizing, but the odor of some substances is more unpleasant after oxidation than before unless oxidation is complete. The odor of ozone itself is unpleasant to most individuals. Electrostatic precipitators become inactive and act as a source of odor after the plates have become coated with the precipitated material.

Activated carbon was chosen as the material to reduce effectively the odor concentration in the car. After considerable experimental work on the odor-adsorbing power and pressure-drop from one side of a filter to another, a decision was reached to use for this work Nuchar (manufactured by the Industrial Chemical Sales Co. of New York, N. Y., which kindly furnished all activated carbon used in this work). The gas-adsorbing power of this carbon is about 85 per cent of that of the more expensive nutshell carbon and it costs about one-eighth as much. It is extremely porous, thus offering a very large exposed surface to odor-laden air and very little resistance to the flow of air in the ordinary ventilating ducts.

For experimental purposes only, eleven V-type screen filters were constructed. Each filter contained four V's and there was a 0.5-inch space between the screens. The filters were filled with Nuchar and installed in the car in such a way that all air coming into it passed through them. The pressure drop at 200 feet per minute was 0.10 inch of water. After a round trip between Chicago and New York, individuals who entered the car and tested the air by smelling reported no objectionable odor. Previous to the installation of carbon odor-filters, these same individuals had stated that the odor was objectionable.

It is regretted that these experiments could not be carried on for a longer period. The original plan was to make two tests on the same day, one before the installation of odor-filters and another while the carbon was new. Subsequent tests were to be made at intervals of 2, 4, 6 months, etc., until the adsorptive power of the carbon had decreased to the point where the odor was again objectionable. No test could be made while the carbon was new, because of inclement weather which caused an undue amount of ice to freeze on the generator belts. Changes in the ventilating ducts necessitated removing the filters at the end of 4 months while the carbon was still functioning efficiently. Therefore, it is impossible to state what the life of the carbon would have been under these conditions.

Table I gives the results of tests before and after installation of activated carbon filters.

Table I. Tests on Recirculated Air

	Unfiltered	Filtered through Activated Carbon	
		After 2 months' use	After 4 months' use
Relative odor value (of 200 cu. ft.)	40	2	10
Ammonia (NH_3), p. p. m.	0.06	0.004	0.02
Nitrite (NO_2), p. p. m.	0.0008	0.00003	0.00013
Alcohol (C_2H_5OH), p. p. m.	0.3	0.015	0.09
Phenolic bodies, p. p. m.	0.006	0.0004	0.002
Odor removed, per cent	0	95	75

For convenience of comparison, the relative odor value was either determined or calculated on 200 cubic feet of air, the amount which actually passed through the apparatus. The value of 40 was calculated from a reading of 4 obtained on an aliquot representing 20 cubic feet; 2 was the value of the whole condensate from 200 cubic feet; and the value of 10 was calculated from a reading of 2 obtained from an aliquot representing 40 cubic feet.

The ammonia and nitrite present are apparently derived from one or both of two sources: the decomposition of other nitrogenous products, or the effects of oxidation and ultraviolet rays on the nicotine in tobacco smoke as found by Gant (*2*). The absence of nicotine and sulfur compounds may be accounted for by the ease with which they are oxidized in such thin films, or they may escape detection because of the minute degree of concentration. The alcohol is undoubtedly due to the consumption of alcoholic beverages by passengers. The phenolic bodies are apparently derived from the smoke of the locomotive. The condensate also had a distinct petroleum-like odor, which may be accounted for by the fact that the train passed through a district where large oil refineries were located, or it may have been due to lubricating oil on machinery in and about the car.

Summary

A freezing-out method has been developed for determining the concentration of odors in air-conditioned structures.

Solid carbon dioxide, contained in a properly insulated box, was the refrigerant used to freeze out moisture and odor in an efficient condenser tube through which measured amounts of air were drawn at a low velocity. Liquid air was not used on account of the expense and danger involved.

The osmoscope was employed to determine the relative odor value of the condensate by the air-dilution method. Values obtained in this manner were verified by quantitative chemical determinations and also by individuals who entered the car and tested the air by smelling.

Activated carbon was demonstrated to be a safe, very efficient, and economical means of removing the odor in an air-conditioned structure.

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An Air-Bomb Aging Test for Tread Compounds

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The comparative age-resisting properties of tire tread compounds are determined in the laboratory by either oxygen-bomb or Geer-oven aging tests. The conditions under which these tests are carried out are standardized and from their results reliable predictions are made concerning the natural aging life of the tread compounds.

A few years ago oxygen-bomb aging tests, comparing first-quality tread compounds, could be satisfactorily carried out in from 39 to 48 hours, in which time the tread compound lost about 50 per cent of its original tensile. Today, largely because of the development of better antioxidants and organic accelerators, oxygen-bomb aging tests carried out under the same conditions require between 4 and 10 days to cause the same percentage loss in tensile, and the time necessary to carry out a Geer-oven aging test has been correspondingly increased. Therefore it is very desirable to develop a shorter laboratory aging test which can be correlated with the oxygen bomb or the Geer oven and which should be indicative of natural aging results.

The use of the air bomb as a laboratory method of carrying out aging tests has been previously suggested (*1*, *2*). However, papers recognized that the conditions therein employed were too severe to permit reliable comparisons of the aging properties of tread compounds.

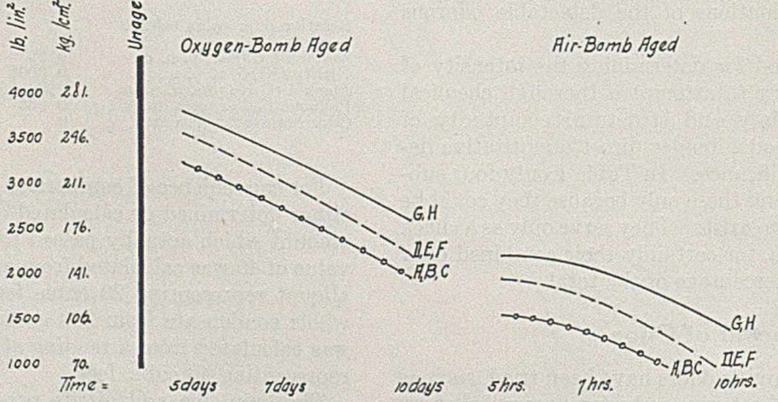

Figure 1. Aging Tests

Cure, 75 minutes at 274° F. (134° C.).
Base stock: smoked sheets, 100.00; carbon black, 50.0; zinc oxide, 5.0; stearic acid, 3.0; pine tar, 2.0; antioxidant, 1.5.

Added to base stock:

	Sulfur	Accelerator		Sulfur	Accelerator
A	2.25	1.25	*E*	1.25	2.20
B	2.00	1.50	*F*	1.00	2.40
C	1.75	1.75	*G*	0.80	2.80
D	1.50	2.00	*H*	0.60	2.80

Experimental Procedure

The procedure recommended by the American Society for Testing Materials, designated as D412-35T, was followed in carrying out the milling, vulcanizing, and testing of the rubber compounds described in this paper, and the D428-35T recommendations were followed in carrying out the oxygen-bomb and Geer-oven aging tests, with the exception that in both cases only two test pieces were broken instead of three, and in the case of the oxygen-bomb and Geer-oven aging tests one-half of the usual press-cured sheet was employed instead of the usual dumbbell test pieces.

The air-bomb aging conditions referred to as being too severe consist in placing the usual dumbbell test piece in a rack, and elongating 50 per cent; the rack is then placed in the air bomb, and a temperature of 260° F. (126.7° C.) and an air pressure of 100 pounds per square inch (7 kg. per sq. cm.) are maintained for the duration of the test. These conditions were employed in carrying out the first series of tests in which the ratio of sulfur to rubber was varied. The results are shown in Figure 1.

In the second series of tests the elongation was varied between 0 and 50 per cent, the air pressure between 50 and 100 pounds per square inch (3.5 and 7 kg. per sq. cm.), and the temperature between 210° and 260° F. (98.9° and 126.7° C.). Only a single variation was made in any one test and the duration of the test was kept constant at 5 hours, as shown in Figure 2. From the data obtained in these as well as additional tests, the following conditions were adopted as more suitable for the comparing of tread compounds: elongation, 0; pressure, 50 pounds per square inch (3.5 kg. per sq. cm.); temperature, 220° F. (104.4° C.); and time, 10 hours. These "modified" conditions were employed in carrying out all the later tests shown.

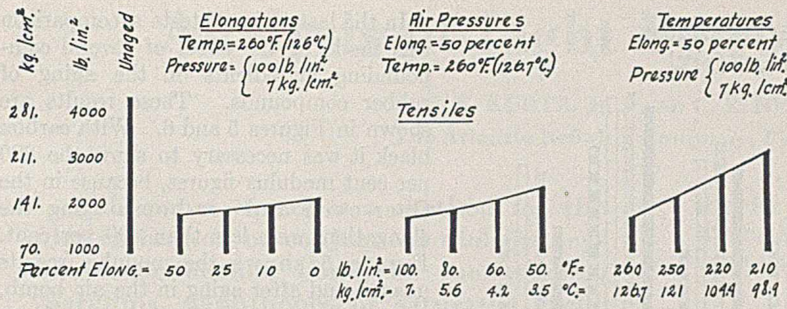

FIGURE 2. EFFECT OF VARIATIONS IN CONDITIONS OF AIR-BOMB AGING

Cure, 60 minutes at 274° F. (134° C.) Aging time, 5 hours. Base stock: smoked sheets, 100.0; carbon black, 50.0; zinc oxide, 5.0; sulfur, 2.75; stearic acid, 3.0; pine tar, 2.0; accelerator, 1.25; antioxidant, 1.50.

In the third series of tests the oxygen concentration was varied by dilution with nitrogen. The usual dumbbell test pieces were employed here and the end point of the test was the time necessary to cause a loss of 40 per cent in tensile.

Discussion

The results of previous laboratory comparisons of heat-resisting inner-tube compounds, which were carried out in the air bomb, established the theory that a low ratio of sulfur to rubber was necessary (*1*). Therefore the first series of tests in this study was carried out to determine whether or not tread compounds with low sulfur ratios aged better than tread compounds containing normal sulfur ratios and to present data to show that these air-bomb aging conditions were too severe to permit reliable comparisons of tread compounds. The results are shown in Figure 1.

It is known that tread compounds such as those shown in Figure 1 are not practical because of their poor resistance to flex cracking and abrasion. The unaged results are not shown, but to maintain the same rate of cure for all the compounds it was necessary to increase the accelerator ratio as the sulfur ratio was decreased. A range of cures was carried out and aging tests were made on several cures. However, the 75-minute cure at 274° F. (134° C.) was chosen to make up this chart because it was the optimum cure. The unaged tensiles of all the compounds were the same within the usual laboratory error of ±5 per cent. The unaged modulus figures varied between about 3000 pounds per square inch (211 kg. per sq. cm.) in the case of the *A* compound to about 2300 pounds per square inch (161.7 kg. per sq. cm.) in the *H* compound. Figure 1 represents the results of the *A*, *B*, and *C* compounds as being alike, but actually the results shown are the averages of the three results. The same is true, in the case of the *D*, *E*, and *F* and the *G* and *H* compounds. This was done in order to present a clearer picture.

The results show that reducing the sulfur ratio has improved the age-resisting properties of the tread compounds in the case of both the air-bomb and the oxygen-bomb aging, the improvement being greater in the case of the air bomb. However, even the *G* and *H* compounds show a loss of about 50 per cent in tensile due to 7 hours' aging in the air bomb, whereas previous tests showed that a heat-resisting inner-tube compound lost only about 30 per cent in tensile through aging 18 hours under the same conditions (*1*). Therefore, these air-bomb aging conditions are too severe, and since the main difference between the composition of the heat-resisting inner-tube compounds and tread compounds *G* and *H* is the use of P33 black and carbon black, respectively, the conclusion seems obvious that carbon black does not age as well as some of the other compounding ingredients. Schoenfeld (*3*) recognized the relatively poor aging properties of carbon black and attributed them to oxygen or oxygen compounds in the carbon black.

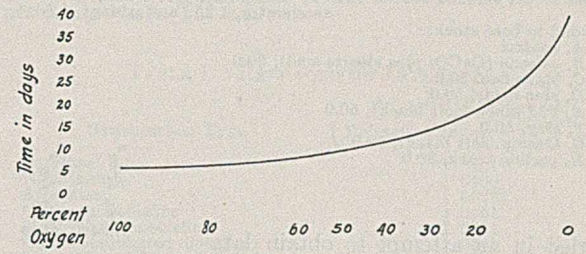

FIGURE 3. EFFECT OF OXYGEN CONCENTRATION

Same base stock as in Figure 2. End point, loss of 40 per cent of original tensile. Total pressure, 300 pounds per square inch (21.1 kg. per sq. cm.). Temperature, 158° F. (70° C.). Oxygen concentration varied from 0 to 100 per cent.

The second series of tests was carried out to determine which of the air-bomb aging conditions had the greatest effect on the results. The data shown in Figure 2 indicate that the temperature employed has the greatest effect. These results, together with a few confirming tests, led to the adoption of the "modified" air-bomb aging conditions given above.

The compound employed here and in all the later tests is probably higher in accelerator and antioxidant ratio than is usual in commercial compounds. The accelerator employed in all the compounds in this paper is dibenzothiazyldimethylthiol urea and the antioxidant employed is a ketone–primary aromatic amine reaction product. This compound has an excellent range of cure, showing no indications of overcure up to the 105-minute cure. The abrasion index and flex cracking resistance are excellent. The 400 per cent modulus figure of the cure shown was about 3200 pounds per square inch (225 kg. per sq. cm.) and the tensile was about 4400 pounds per square inch (309 kg. per sq. cm.).

In the third series of tests the oxygen concentration was

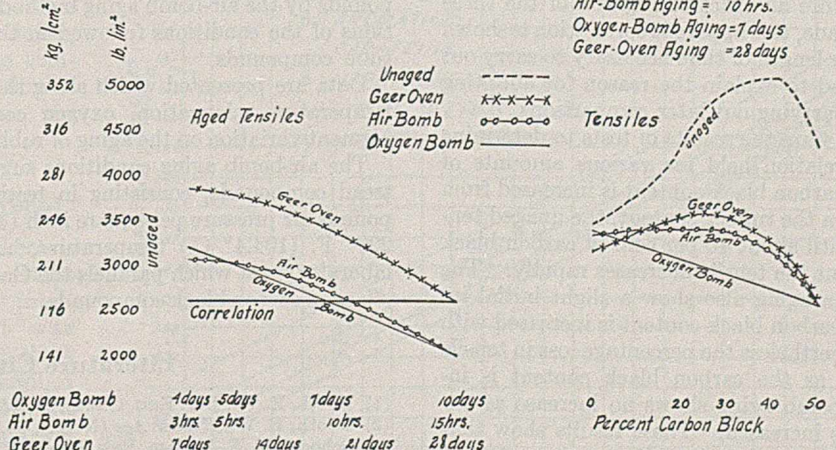

FIGURE 4. COMPARISON OF OXYGEN-BOMB, AIR-BOMB, AND GEER-OVEN AGING

Left, base stock, same as in Figure 2
Right, same stock except carbon black varied from 0 to 50 parts
Cure, 60 minutes at 274° F. (134° C.)

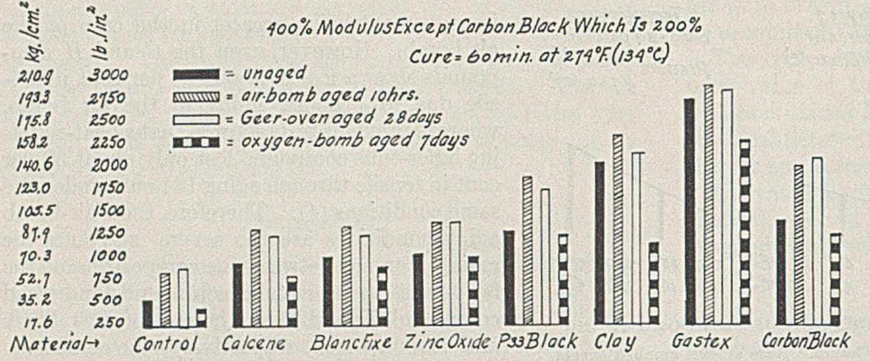

FIGURE 5. EFFECT OF COMPOUNDING INGREDIENTS

Base stock, smoked sheets, 100.00; zinc oxide, 5.0; sulfur, 2.75; stearic acid, 3.0; pine tar, 2.0; accelerator, 1.25; antioxidant, 1.50.

Added to base stock:
A, control
B, calcene ($CaCO_3$ plus stearic acid), 50.0
C, blanc fixe, 50.0
D, zinc oxide, 50.0
E, P33 black (soft black), 50.0
F, clay, 50.0
G, Gastex (soft black), 50.0
H, carbon black, 50.0

varied in an attempt to obtain data which would explain the differences between the results of the oxygen-bomb and the Geer-oven aging tests and perhaps suggest better conditions under which to carry out comparisons of tread compounds. The results are shown in Figure 3. The only obvious conclusions that can be made from these results are that a temperature higher than 158° F. (70° C.) is necessary materially to shorten the time necessary to carry out aging tests, even though the oxygen concentration is 100 per cent.

In the fourth series of tests a comparison was made of air-bomb, oxygen-bomb, and Geer-oven aging, and the results are shown in Figure 4. The "modified" air-bomb aging conditions were employed in this comparison. The results show a correlation of the three aging methods. A horizontal line was drawn which represents a loss of 40 per cent in tensile (indicated as "correlation") and shows that about 10 hours' aging in the air bomb has brought about the same loss of tensile as about 7 days' aging in the oxygen bomb or 28 days' aging in the Geer oven. Realizing that many more tests must be carried out before an exact correlation of the three aging methods can be made, this apparent correlation is shown to emphasize the shorter length of time necessary to carry out air-bomb aging tests and to explain the reason for adopting these various times in carrying out later comparisons.

Also shown in Figure 4 are the results of tests to determine whether the same correlation held for various amounts of carbon black. As the carbon black content is increased from 0 to 50 per cent based on the rubber content, the unaged tensile increases rapidly until about 40 per cent of carbon black is present. At this point the tensile decreases rapidly. The air-bomb and Geer-oven aging also show a slight initial increase in tensile as the carbon black content is increased with a later decrease, but nevertheless the percentage loss in tensile increases progressively as the carbon black content is increased. The oxygen-bomb aging shows no increase as the carbon black content is increased. These results show that the correlation is not exact for these various aging methods when different amounts of carbon black are employed. However, the air-bomb and Geer-oven aging are probably within the limit of experimental error.

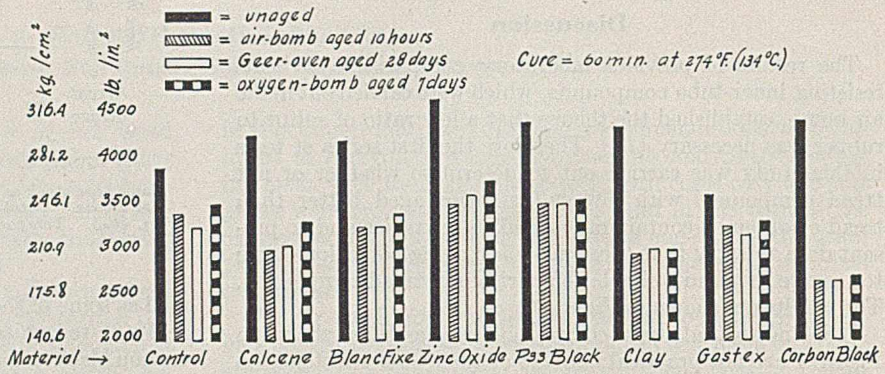

FIGURE 6. TENSILE RESULTS WITH COMPOUNDS IN FIGURE 5

In the last series of tests a comparison was made of the effect of several compounding ingredients on the aging of rubber compounds. These results are shown in Figures 5 and 6. With carbon black it was necessary to show the 200 per cent modulus figures, because in the Geer-oven and air-bomb aging the elongations were less than 400 per cent. Figure 5 shows the modulus results unaged and after aging in the air bomb, oxygen bomb, and Geer oven. Each compound shows an increase of the aged modulus over the unaged modulus for air-bomb and Geer-oven results, while the modulus decreases after oxygen-bomb aging. Figure 6 shows the tensil eresults obtained with the same compounds. These results show definitely that, irrespective of pigment used, the "modified" air-bomb aging conditions parallel the Geer-oven results, but show considerable variation from the oxygen-bomb results. In other words, the higher temperature employed for a shorter length of time in the air bomb has practically the same effect on continuing vulcanization and oxygen deterioration as is obtained in the Geer-oven tests.

Conclusion

Data here presented demonstrate that study of tread compounds by the air-bomb aging method must include modifications of the conditions followed in the comparison of inner-tube compounds.

Data are presented which show the effect of air pressure, temperature, elongation, oxygen concentration, time, and pigment variation on the aging of rubber compounds.

The air-bomb aging conditions suggested for the study of tread compounds, consisting in testing at 0 elongation, 50 pounds air pressure per square inch (3.5 kg. per sq. cm.), and 220° F. (104.4° C.) temperature, have provided a shorter laboratory test which parallels the Geer-oven aging test in its effect on carbon black compounds.

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(1) Booth, E. W., IND. ENG. CHEM., 24, 555 (1932).
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Analysis of Light Petroleum Fractions

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This paper describes a method for the determination of conjugated diolefins, cyclic monoölefins, noncyclic monoölefins, paraffins, naphthenes or saturated cyclic compounds, and aromatics, in light petroleum fractions boiling from 40° to 200° C.

The method involves chemical treatment of the material with maleic anhydride and sulfuric acid, fractionation into 30° C. cuts, and measurement of density and refractive index of the cuts. Calculation of results depends on graphical methods and is bettered by use of a new constant, the refractivity intercept.

IT IS OFTEN helpful in industrial research to have information on the chemical nature of the major types of hydrocarbons occurring in petroleum mixtures, even though the determination of individual hydrocarbons is impracticable. Such a classification is less satisfactory for the higher molecular weight fractions where a large proportion of the molecules undoubtedly is composed of several hydrocarbon types, but is quite suitable for the lighter fractions where the molecules must be relatively simple in structure.

The authors have combined chemical and physical methods to yield an analytical method for the estimation of the following hydrocarbon types in petroleum fractions boiling from 40° to 200° C.: conjugated diolefins; cyclic olefins; noncyclic olefins; aromatics; naphthenes or saturated cyclic compounds; and paraffins.

In this classification aromatic compounds by definition are those which contain one or more aromatic rings, and the naphthenes are those containing a 5 or 6 carbon-saturated ring structure. The terms "paraffin" and "olefin" are used in the conventional sense subject to the above limitations. Cyclic olefins, however, refer only to compounds wherein the double bond is located within the ring structure.

Refractivity Intercept

In this method there is used a new physical constant called the refractivity intercept. This constant was originally developed in these laboratories and is described in detail by Kurtz and Ward (*3*). Its nature, therefore, will be but briefly treated here. From Figure 1 it is evident that for a given structural type of hydrocarbons the refractive index varies linearly with the density. The refractivity intercept is the intercept constant b in the equation:

$$\text{Refractive index} = 0.5 \text{ density} + b$$

Hydrocarbon types differ, in this respect, only in the numerical value of b and are therefore distinguishable by the value of this constant. These values for a number of hydrocarbon types are given in Table I.

TABLE I. REFRACTIVITY INTERCEPT

Hydrocarbon Type	Refractivity Intercept[a] $\left(\text{Refractive Index} - \frac{\text{Density}}{2}\right)$
Paraffins	1.0461
Naphthenes	1.0400
Aromatics	1.0627
Cyclic monoölefins	1.0461
Noncyclic monoölefins	1.0521
Cyclic conjugated diolefins	1.0643
Noncyclic conjugated diolefins	1.0877
Cyclic nonconjugated diolefins	Insufficient data
Noncyclic nonconjugated diolefins	1.0592

[a] Numerical values from Kurtz and Ward (*3*).

Graphical Analysis

The use of the refractivity intercept in the general analytical method depends on the graphical comparison of the density and the refractivity intercept of a chemically treated or untreated fraction with those of various hydrocarbon types of the same boiling range. For this purpose the density and refractivity intercept of the unknown are plotted with like points for not more than three hydrocarbon types of the same boiling range as, and present in, the unknown as illustrated in Figure 2. The refractivity intercept values for the hydrocarbon types are taken from Table I, while the density values are taken from Figures 3 and 4 where average density and

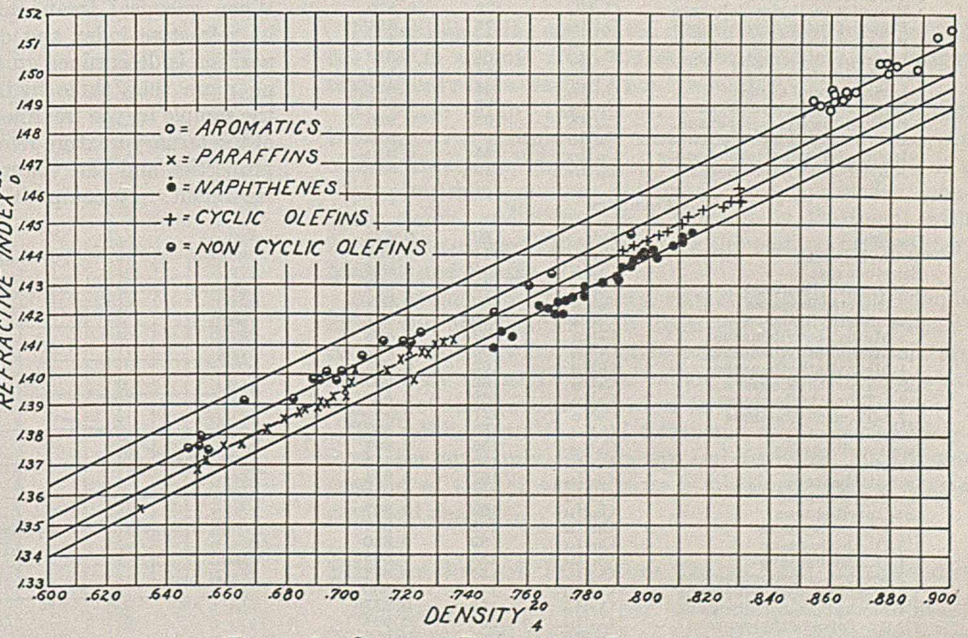

FIGURE 1. ORIGIN OF REFRACTIVITY INTERCEPT

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[1] Present address, Sun Oil Co., Marcus Hook, Pa.

Table II. Boiling Points and Densities of Noncyclic Olefins, Cyclic Olefins, and Aromatics

Compound	Formula	Boiling Point at 760 mm., ° C.	Density $\frac{20^\circ}{4}$
Noncyclic Olefins			
1-Pentene	C_5H_{10}	40	0.647
2-Pentene	C_5H_{10}	36	0.651
2-Methyl-2-butene	C_5H_{10}	38	0.666
1-Hexene	C_6H_{12}	64	0.683
2,3-Dimethyl-1-butene	C_6H_{12}	73	0.712
3,3-Dimethyl-1-butene	C_6H_{12}	41	0.653
2,3-Dimethyl-2-butene	C_6H_{12}	74	0.708
3-Methyl-1-pentene	C_6H_{12}	62	0.682
3-Methyl-2-pentene	C_6H_{12}	70	0.698
2-Methyl-2-pentene	C_6H_{12}	67	0.692
2-Ethyl-1-butene	C_6H_{12}	67	0.6914
1-Heptene	C_7H_{14}	97	0.702
3-Ethyl-2-pentene	C_7H_{14}	98	0.721
2,3-Dimethyl-2-pentene	C_7H_{14}	95	0.719
4,4-Dimethyl-2-pentene	C_7H_{14}	84	0.688
3,3-Dimethyl-1-pentene	C_7H_{14}	77	0.696
1-Octene	C_8H_{16}	123	0.720
4,4-Dimethyl-2-hexene	C_8H_{16}	106	0.720
2,2-Dimethyl-3-hexene	C_8H_{16}	100	0.705
Diisobutylene	C_8H_{16}	101	0.720
4-Methyl-3-heptene	C_8H_{16}	120	0.724
2-Nonene	C_9H_{18}	150	0.752
4-Methyl-4-octene	C_9H_{18}	139	0.748
1-Decene	$C_{10}H_{20}$	172	0.748
2,3-Dimethyl-2-octene	$C_{10}H_{20}$	162	0.748
2-Methyl-5-ethyl-5-heptene	$C_{10}H_{20}$	138	0.745
Diamylene	$C_{10}H_{20}$	156	0.768
1-Undecene	$C_{11}H_{22}$	188	0.763
2-Undecene	$C_{12}H_{24}$	193	0.761
Triisobutylene	$C_{12}H_{24}$	175	0.760
Tetraisobutylene	$C_{16}H_{32}$	250	0.794
Cyclic Olefins			
Cyclopentene	C_5H_{10}	44	0.776
Cyclohexene	C_6H_{12}	83	0.810
1,2-Dimethylcyclopentene	C_7H_{14}	103	0.792
2-Ethylcyclopentene	C_7H_{14}	108	0.796
1-Methylcyclohexene	C_7H_{14}	110	0.809
2-Methylcyclohexene	C_7H_{14}	110	0.810
3-Methylcyclohexene	C_7H_{14}	104	0.805
4-Methylcyclohexene	C_7H_{14}	103	0.799
6-Methylcyclohexene	C_7H_{14}	103	0.799
1-Ethylcyclohexene	C_8H_{16}	136	0.826
1,2-Dimethylcyclohexene	C_8H_{16}	135	0.826
2,4-Dimethylcyclohexene	C_8H_{16}	127	0.803
1,4-Dimethylcyclohexene	C_8H_{16}	127	0.800
1,5-Dimethylcyclohexene	C_8H_{16}	127	0.802
4,6-Dimethylcyclohexene	C_8H_{16}	126	0.798
5,5-Dimethylcyclohexene	C_8H_{16}	119	0.803
1-*n*-Propylcyclohexene	C_9H_{18}	156	0.824
1-Isopropylcyclohexene	C_9H_{18}	153	0.828
1-Ethyl-2-methylcyclohexene	C_9H_{18}	157	0.830
2-Ethyl-4-methylcyclohexene	C_9H_{18}	152	0.813
1-Ethyl-4-methylcyclohexene	C_9H_{18}	152	0.812
1-Ethyl-3-methylcyclohexene	C_9H_{18}	149	0.813
1,5-Trimethylcyclohexene	C_9H_{18}	129	0.800
2,5-Trimethylcyclohexene	C_9H_{18}	140	0.804
1,6-Trimethylcyclohexene	C_9H_{18}	148	0.824
1,2,6-Trimethylcyclohexene	C_9H_{18}	150	0.828
2,4,6-Trimethylcyclohexene	C_9H_{18}	140	0.800
2,4,5-Trimethylcyclohexene	C_9H_{18}	145	0.805
1-*n*-Butylcyclohexene	$C_{10}H_{20}$	182	0.826
1-Propyl-2-methylcyclohexene	$C_{10}H_{20}$	177	0.830
2-Propyl-4-methylcyclohexene	$C_{10}H_{20}$	173	0.814
1-Propyl-4-methylcyclohexene	$C_{10}H_{20}$	174	0.813
4-Isopropyl-1-methylcyclohexene	$C_{10}H_{20}$	168	0.812
1-*n*-Amylcyclohexene	$C_{11}H_{22}$	204	0.829
1-Isoamylcyclohexene	$C_{11}H_{22}$	195	0.824
1-Butyl-2-methylcyclohexene	$C_{11}H_{22}$	198	0.831
2-Butyl-4-methylcyclohexene	$C_{11}H_{22}$	195	0.820
1-Butyl-4-methylcyclohexene	$C_{11}H_{22}$	197	0.816
2-Isobutyl-4-methylcyclohexene	$C_{11}H_{22}$	185	0.810
1-Amyl-2-methylcyclohexene	$C_{11}H_{22}$	219	0.832
Aromatics			
Benzene	C_6H_6	80	0.879
Methylbenzene	C_7H_8	111	0.866
Ethylbenzene	C_8H_{10}	134	0.868
1,2-Dimethylbenzene	C_8H_{10}	144	0.879
1,3-Dimethylbenzene	C_8H_{10}	139	0.864
1,4-Dimethylbenzene	C_8H_{10}	138	0.861
1,2-Methyl-ethylbenzene	C_9H_{12}	162	0.882
1,3-Methyl-ethylbenzene	C_9H_{12}	163	0.867
1,4-Methyl-ethylbenzene	C_9H_{12}	162	0.862
1,3,5-Trimethylbenzene	C_9H_{12}	162	0.863
1,2,4-Trimethylbenzene	C_9H_{12}	169	0.876
1,2,3-Trimethylbenzene	C_9H_{12}	177	0.895
Propylbenzene	C_9H_{12}	156	0.862
Isopropylbenzene	C_9H_{12}	155	0.864
Butylbenzene	$C_{10}H_{14}$	180	0.864
Isobutylbenzene	$C_{10}H_{14}$	167	0.854
sec-Butylbenzene	$C_{10}H_{14}$	175	0.860
tert-Butylbenzene	$C_{10}H_{14}$	169	0.867
1,2-Diethylbenzene	$C_{10}H_{14}$	185	0.866
1,3-Diethylbenzene	$C_{10}H_{14}$	182	0.860
1,4-Diethylbenzene	$C_{10}H_{14}$	183	0.865
1,2-Methyl-isopropylbenzene	$C_{10}H_{14}$	157	0.856
1,3-Methyl-isopropylbenzene	$C_{10}H_{14}$	175	0.860
1,4-Methyl-isopropylbenzene	$C_{10}H_{14}$	175	0.857
1,2,3,4-Tetramethylbenzene	$C_{10}H_{14}$	204	0.901
1,3,5-Triethylbenzene	$C_{12}H_{18}$	218	0.863
1,2,4-Triethylbenzene	$C_{12}H_{18}$	218	0.882

boiling point have been correlated for hydrocarbons of several types. The basic data for Figures 3 and 4 are given in Tables II and III.

Assume the refractive index, refractivity intercept, and density of hydrocarbons to be additive on a volume per cent basis. Then if the points A, B, and C in Figure 2 represent three hydrocarbon types and a point D lying within the triangle represents the unknown which consists solely of A, B, and C, it follows that the composition of D may be computed from the geometrical properties of the triangle. In the special case of a binary mixture, say of A and B, D will lie on the line AB and its composition is apparent.

Referring to Figure 2, the composition in volume per cent of the unknown D would be found by comparing the length of the lines indicated in the equations below.

$$A = \frac{DE}{EA}\,100$$

$$B = \frac{CE}{BC}\,(100 - A)$$

$$C = 100 - A - B$$

The assumption of the additivity of the refractive index and density of hydrocarbons on a volume per cent basis is justified by the work of MacFarlane and Wright (*4*). It follows that the refractivity intercept is therefore also additive.

It should be emphasized that even though the refractivity intercept is independent of boiling point, the points A, B, and C on the graphical analysis diagram will vary for different boiling points because of the corresponding change in density illustrated in Figures 3 and 4. Because of this variation, graphical analysis is made only on fractionated cuts of about 30° C. in boiling range. These analyses are made on different diagrams for each cut and the composition of the original sample is computed from the composition of the cuts.

Chemical Treatment

Analysis by the above means alone is limited to three components, and is further limited by the fact that the three components must form a triangle on the graphical analysis diagram. In order to use this method of analysis on mixtures of more than three components, resort is made to chemical treatment which will segregate or remove three or less of those hydrocarbon types which can be analyzed graphically. When chemical treatment leaves such a ternary mixture, its refractive index and density are measured and its composition is determined graphically. On the other hand, when no more than three hydrocarbon types are removed from the sample by the treatment, the refractive index and density of the ternary mixture removed may be calculated from those properties and the volume of the sample before and after treatment. Its composition may then be determined graphi-

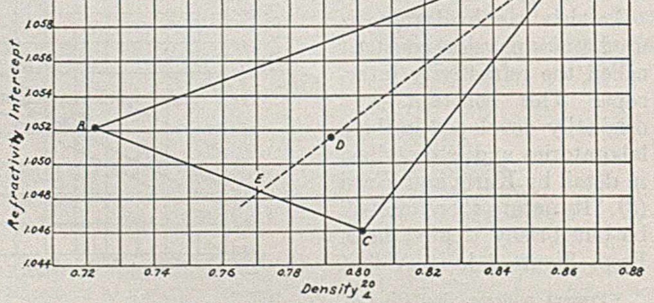

Figure 2. Graphical Analysis Diagram

cally. It is thus seen that this method does not require the isolation of a ternary mixture of hydrocarbon types in order to obtain knowledge of the composition of the mixture.

The principles of the chemical treatment are given below and the details are discussed later in the procedure.

MALEIC ANHYDRIDE TREATMENT. Removal of conjugated diolefins is brought about by treatment of the sample with maleic anhydride according to the method of Diels and Alder (*1*). Table IV gives the results of a typical treatment and illustrates how the reaction is complete after 1 hour of treatment with 10 per cent of maleic anhydride at 100° C.

TABLE III. BOILING POINTS AND DENSITIES OF PARAFFINS AND NAPHTHENES

Compound	Formula	Boiling Point at 760 mm., ° C.	Density $\frac{20°}{4}$
	Paraffins		
n-Pentane	C_5H_{12}	36	0.631
2-Methylbutane	C_5H_{12}	28	0.621
n-Hexane	C_6H_{14}	69	0.6595
2-Methylpentane	C_6H_{14}	60	0.6542
3-Methylpentane	C_6H_{14}	63	0.6647
2,2-Dimethylbutane	C_6H_{14}	50	0.6498
2,3-Dimethylbutane	C_6H_{14}	58	0.6613
n-Heptane	C_7H_{16}	98	0.6836
2-Methylhexane	C_7H_{16}	90	0.6789
3-Methylhexane	C_7H_{16}	92	0.6870
3-Ethylpentane	C_7H_{16}	93	0.6984
2,2-Dimethylpentane	C_7H_{16}	79	0.6737
2,3-Dimethylpentane	C_7H_{16}	90	0.6952
2,4-Dimethylpentane	C_7H_{16}	81	0.6745
3,3-Dimethylpentane	C_7H_{16}	86	0.6934
2,2,3-Trimethylbutane	C_7H_{16}	81	0.6900
n-Octane	C_8H_{18}	125	0.702
2,2-Dimethylhexane	C_8H_{18}	107	0.6953
2-Methylheptane	C_8H_{18}	116	0.6985
3-Methylheptane	C_8H_{18}	122	0.707
4-Methylheptane	C_8H_{18}	118	0.722
3-Ethylhexane	C_8H_{18}	119	0.713
2,3-Dimethylhexane	C_8H_{18}	114	0.720
2,4-Dimethylhexane	C_8H_{18}	109	0.703
2,5-Dimethylhexane	C_8H_{18}	109	0.696
3,4-Dimethylhexane	C_8H_{18}	117	0.721
2-Methyl-3-ethylpentane	C_8H_{18}	114	0.704
2,2,3-Trimethylpentane	C_8H_{18}	111	0.717
2,4,4-Trimethylpentane	C_8H_{18}	99	0.691
n-Nonane	C_9H_{20}	150	0.718
3-Methyloctane	C_9H_{20}	143	0.719
4-Methyloctane	C_9H_{20}	142	0.727
4-Ethylheptane	C_9H_{20}	139	0.737
2,4-Dimethylheptane	C_9H_{20}	133	0.716
2,5-Dimethylheptane	C_9H_{20}	136	0.714
2,6-Dimethylheptane	C_9H_{20}	132	0.707
2,2,5-Trimethylhexane	C_9H_{20}	126	0.707
n-Decane	$C_{10}H_{22}$	174	0.727
2-Methylnonane	$C_{10}H_{22}$	160	0.724
3-Methylnonane	$C_{10}H_{22}$	167	0.735
5-Methylnonane	$C_{10}H_{22}$	166	0.732
4-Propylheptane	$C_{10}H_{22}$	162	0.736
2,6-Dimethyloctane	$C_{10}H_{22}$	161	0.729
2,7-Dimethyloctane	$C_{10}H_{22}$	160	0.722
3,6-Dimethyloctane	$C_{10}H_{22}$	161	0.730
2,2,6-Trimethylheptane	$C_{10}H_{22}$	152	0.721
Undecane	$C_{121}H_{24}$	195	0.741
Dodecane	C_1H_{26}	216	0.749
	Naphthenes		
Cyclopentane	C_5H_{10}	50	0.754
Cyclohexane	C_6H_{12}	81	0.779
Methylcyclopentane	C_6H_{12}	73	0.750
Methylcyclohexane	C_7H_{14}	100	0.767
1,1-Dimethylcyclopentane	C_7H_{14}	88	0.755
1,2-Dimethylcyclopentane	C_7H_{14}	93	0.751
1,1-Dimethylcyclohexane	C_8H_{16}	120–125	0.781
1,2-Dimethylcyclohexane	C_8H_{16}	127	0.790
1,3-Dimethylcyclohexane	C_8H_{16}	121	0.772
1,4-Dimethylcyclohexane	C_8H_{16}	123	0.775
Ethylcyclohexane	C_8H_{16}	130	0.785
n-Propylcyclohexane	C_9H_{18}	155	0.791
Isopropylcyclohexane	C_9H_{18}	152	0.797
1,2-Methylethylcyclohexane	C_9H_{18}	153	0.803
1,3-Methylethylcyclohexane	C_9H_{18}	149	0.789
1,4-Methylethylcyclohexane	C_9H_{18}	151	0.789
1,3,5-Trimethylcyclohexane	C_9H_{18}	140	0.775
1,3,4-Trimethylcyclohexane	C_9H_{18}	140	0.789
1,1,3-Trimethylcyclohexane	C_9H_{18}	138	0.790
1,2,4-Trimethylcyclohexane	C_9H_{18}	140	0.778
n-Butylcyclohexane	$C_{10}H_{20}$	180	0.797
Isobutylcyclohexane	$C_{10}H_{20}$	171	0.795
sec-Butylcyclohexane	$C_{10}H_{20}$	179	0.799
tert-Butylcyclohexane	$C_{10}H_{20}$	170	0.811
1,2-Methyl-*n*-propylcyclohexane	$C_{10}H_{20}$	176	0.808
1,2,4,5-Tetramethylcyclohexane	$C_{10}H_{20}$	161	0.785
1,3-Methyl-*n*-propylcyclohexane	$C_{10}H_{20}$	172	0.794
1,4-Methyl-*n*-propylcyclohexane	$C_{10}H_{20}$	176	0.796
1,3-Diethyl-*n*-propylcyclohexane	$C_{10}H_{20}$	174	0.798
1,4-Diethyl-*n*-propylcyclohexane	$C_{10}H_{20}$	175	0.800
1,3-Dimethyl-5-ethylcyclohexane	$C_{10}H_{20}$	169	0.793
n-Amylcyclohexane	$C_{11}H_{22}$	202	0.802
Isoamylcyclohexane	$C_{11}H_{22}$	194	0.798
tert-Amylcyclohexane	$C_{11}H_{22}$	194	0.819
1,2,3,5,6-Pentamethylcyclohexane	$C_{11}H_{22}$	190	0.785
1,2-Methyl-*n*-butylcyclohexane	$C_{11}H_{22}$	197	0.811
1,3-Methyl-*n*-butylcyclohexane	$C_{11}H_{22}$	195	0.801
1,4-Methyl-*n*-butylcyclohexane	$C_{11}H_{22}$	196	0.807
1,2-Methyl-*n*-amylcyclohexane	$C_{12}H_{24}$	218	0.814
1,3-Dimethyl-5-isobutylcyclohexane	$C_{12}H_{24}$	194	0.810

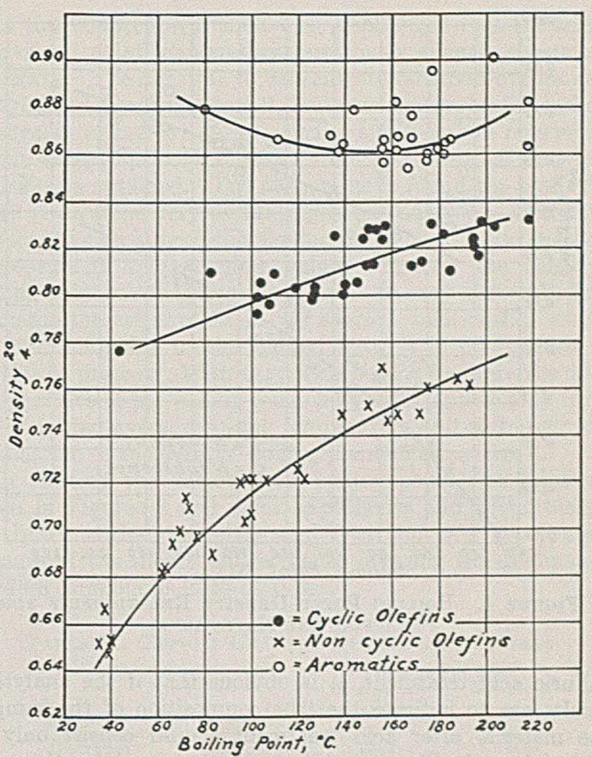

FIGURE 3. BOILING POINT–DENSITY RELATIONSHIP FOR NONCYCLIC OLEFINS, CYCLIC OLEFINS, AND AROMATICS

TABLE IV. MALEIC ANHYDRIDE TREATMENT

Time of Treatment	Maleic Anhydride Concentration	Density $\frac{20°}{4}$	Refractive Index $\frac{20°}{D}$	Refractivity Intercept
Hours	%			
0	0	0.7825	1.4418	1.0505
1.0	10	0.7870	1.4420	1.0485
2.0	10	0.7869	1.4420	1.0485
3.0	10	0.7869	1.4420	1.0485

Estimation of the conjugated diolefin content is made from the loss in volume after the reaction products and excess reagent have been washed from the sample.

SULFURIC ACID TREATMENT. After maleic anhydride treatment the sample may contain cyclic olefins, noncyclic olefins, aromatics, naphthenes, and paraffins. Removal of a three-component mixture comprised of cyclic olefins, noncyclic olefins, and aromatics is effected by treatment with 91 and 98 per cent sulfuric acid by the method of Faragher, Morrell, and Levine (*2*).

Measurement of the density, refractive index, and volume before and after sulfuric acid treatment permits the calculation of the density and refractive index of the ternary mixture removed by the acid. These values, then, allow a graphical analysis of this mixture according to Figure 2.

The residue from the acid treatment, when freed of polymers, contains only naphthenes and paraffins. The composition of this binary mixture is obtained from a second graphical analysis.

Elimination of Polymers from Acid Treatment

In view of the fact that part of the analysis is calculated from the physical properties of the sample before and after

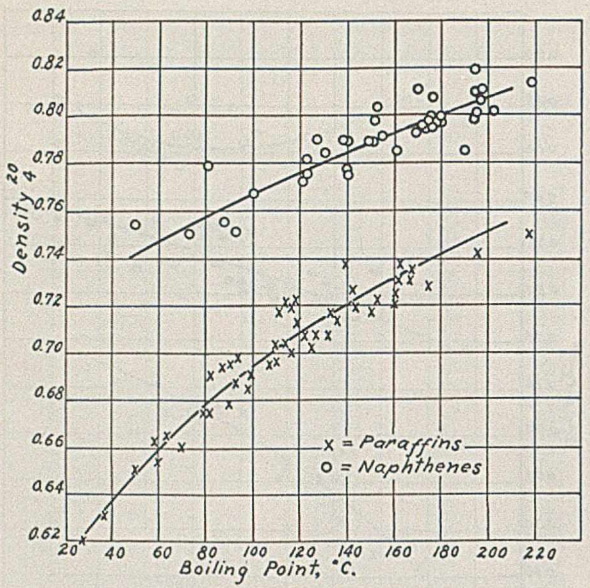

FIGURE 4. BOILING POINT–DENSITY RELATIONSHIP FOR PARAFFINS AND NAPHTHENES

sulfuric acid treatment, it is obvious that if the analytical results are to indicate the true composition of the sample, the material after acid treatment should consist only of material originally present less that removed by the acid. During acid treatment, however, polymerization and condensation take place and fractionation of the treated material to its original end point may not be sufficient to remove all polymers so formed. For instance, if two molecules of pentene polymerize to the dimer, its boiling point of about 165° C. may fall within the boiling range of the material treated.

In order to eliminate such polymers from the sulfuric acid–treated sample, it is treated in two fractions, the first boiling up to 125° C. and the second boiling from 125° to 210° C. After acid treatment both fractions are refractionated to their original end points and combined. The boiling points of the dimers of the lowest boiling compounds in each fraction will fall above the boiling range of the fractions and so will be eliminated in the redistillation.

Procedure

In order to eliminate very volatile materials in density and refractive index measurements, the sample is stripped of all material boiling below 40° C. by fractionation. Six hundred cubic centimeters of the stripped sample are then treated with 60 grams of freshly distilled maleic anhydride by heating in a 1-liter flask on a steam bath for 1 hour. A reflux condenser maintained at −10° C. with cold brine is used to prevent loss due to vaporization. At the end of an hour the sample is cooled, the hydrocarbon layer decanted from the maleic anhydride, and enough 10 per cent sodium hydroxide solution added to the maleic anhydride remaining in the flask to dissolve it. This solution is then added to the hydrocarbon layer in a 1000-cc. separatory funnel and after gentle shaking and settling is drawn off and discarded. One hundred cubic centimeters of fresh 10 per cent sodium hydroxide solution are then added to the hydrocarbon in the funnel, shaken, and drawn off, followed by two 100-cc. water washes. Handling losses should be determined by carrying out a blank treatment and have been found by authors to be of the order of 1 per cent.

Five hundred cubic centimeters of the maleic anhydride-treated material are then carefully fractionated into cuts of the following boiling ranges: 40° to 70° C., 70° to 100° C., 100° to 125° C., 125° to 150° C., 150° to 180° C., and 180° to 210° C.

The volume percentage as well as the refractive index $\left(\frac{20°}{\text{D}}\right)$ and density $\left(\frac{20°}{4}\right)$ are measured for each cut and the cuts discarded. The errors in physical property measurements should not be greater than 0.0005 in the case of the density and 0.0002 for the refractive index.

A portion of the stripped untreated sample is fractionally distilled to a vapor temperature of 125° C. and the overhead and bottoms are then treated twice with their own volume of 91 per cent sulfuric acid following the procedure of Faragher, Morrell, and Levine (*2*). Each treatment is carried out in 250-cc. centrifuge tubes, and the sludge and acid are separated by centrifuging at 1800 to 2000 r. p. m. for 10 minutes. The acid layer is withdrawn by suction.

After the second application of 91 per cent acid the naphtha is washed in the treating tube with 70 per cent methanol to remove sulfonic acids. Each fraction is then distilled through a small Hempel column to a temperature 5° C. above the end point of the original naphtha to eliminate polymers.

The two fractions are now combined and the resulting sample is treated twice with its own volume of 98 per cent sulfuric acid and centrifuged. If serious emulsions are encountered it is treated with 70 per cent methanol. The sample is washed with two volumes of 2 per cent sodium hydroxide solution and then with two volumes of water. If methanol is used, it must be thoroughly water-washed from the sample in order to prevent interference in refractive index measurements.

Sufficient sample should be taken for distillation and sulfuric acid treatment to yield residues of treated hydrocarbon totaling at least 200 cc. The overhead portions are then combined and subjected to exactly the same fractionation as the maleic anhydride–treated material, cutting the material again into the same 6 cuts by temperature and measuring the volume per cent, density, and refractive index of each cut. Handling losses should be evaluated and suitable corrections applied to the acid treating loss. The authors have found these handling losses to be of the order of 4 per cent.

Calculation of Results

Calculation of results is simplified by means of the steps enumerated below. All results are reported on the basis of a sample boiling within the range 40° to 210° C.

CONJUGATED DIOLEFINS.

1. Calculation of conjugated diolefin content on the basis of the sample stripped of volatile material.

Volume per cent of conjugated diolefins = (volume per cent loss on maleic anhydride treatment) − (volume per cent handling loss)

AROMATICS, CYCLIC OLEFINS, AND NONCYCLIC OLEFINS.

2. Conversion of first fractionation (after maleic anhydride treat) to the stripped sample basis.

$$(\text{Volume per cent of each cut}) \times \frac{(100 - \text{volume per cent conjugated diolefins})}{100}$$

3. Conversion of second fractionation (after sulfuric acid treat) to the stripped sample basis.

$$(\text{Volume per cent of each cut}) \times \frac{[100 - (\text{volume per cent acid treating loss} - \text{volume per cent handling loss})]}{100}$$

4. Calculation of volume per cent aromatics plus olefins in each cut, on the basis of the cut from the first fractionation, by subtraction of the results in per cent of steps 2 and 3.

$$\frac{(\text{Volume per cent in 1st fractionation}) - (\text{volume per cent in 2nd fractionation})}{\text{volume per cent in 1st fractionation}} \times 100$$

5. Calculation of the density and refractive index of the aromatics plus olefins in each cut by means of these properties of the cuts before and after acid treatment and the result obtained in step 4.

$$A = \frac{(100B) - [C(100 - D)]}{D}$$

where
A = density or refractive index of aromatics plus olefins
B = density or refractive index before acid treatment
C = density or refractive index after acid treatment
D = volume per cent aromatics plus olefins from step 4

6. Calculation of refractivity intercept for aromatics plus olefins in each cut from the density $\left(\frac{20°}{4}\right)$ and refractive index $\left(\frac{20°}{\text{D}}\right)$ obtained in step 5.

Refractivity intercept = refractive index − 0.5 density

7. Graphical analysis of the aromatics and olefins by locating on a separate chart similar to Figure 2 for each cut the refrac-

tivity intercept from Table I and the density from Figure 3 for pure aromatics, cyclic olefins, and noncyclic olefins. The density and refractivity intercept of the cut are then located on these charts and the graphical analyses carried out as described previously.

8. Conversion of graphical analysis results of each cut to the stripped sample basis for each component type.

$$\text{Concentration in each cut} = (\text{result of step 2} - \text{result of step 3}) \times \left(\frac{\text{result of step 7}}{100}\right)$$

9. Addition of aromatic, cyclic olefin, and noncyclic olefin contents from step 8 to obtain concentration of each type in stripped sample.

NAPHTHENES AND PARAFFINS.

10. Graphical analysis similar to step 7 for naphthenes and paraffins in each cut by means of the densities and refractivity intercepts of the cuts from the second distillation. Refractive intercepts for this analysis are taken from Table I and densities from Figure 4.

11. Conversion of graphical analysis results on each cut, from step 10, to the stripped sample basis for each component type.

$$\text{Concentration in each cut} = (\text{result of step 3}) \times \left(\frac{\text{result of step 10}}{100}\right)$$

12. Addition of naphthenes and paraffin contents from step 11 to obtain concentration of each type in stripped sample.

Discussion

This method does not provide for the determination of nonconjugated diolefins of either the cyclic or the noncyclic type. They are removed during the sulfuric acid treatment along with monoölefins and aromatics, but it is believed that their concentration in most petroleum fractions is negligible. On the graphical analysis triangle the point for the noncyclic nonconjugated diolefins falls near that for the noncyclic monoölefins, while the point for the cyclic nonconjugated diolefins falls near that for the aromatics; therefore, when present they will be included with the noncyclic monoölefins and aromatics, respectively, in the analytical results. On the other hand the conjugated diolefins are very far removed, on the graphical analysis diagram, from these other groups and consequently their presence even in low concentrations might materially affect the physical properties of the mixture; hence the necessity for their removal.

Cyclic olefins wherein the double bond is located in a side chain were not included in the preparation of Table I nor the density–boiling point relationships. The latter relationship for these compounds, however, has been found to be very close to that for the cyclic olefins included in Table II for the range covered. The refractivity intercept of these compounds is slightly higher than the value for cyclic olefins given in the table. Results for cyclic olefins would therefore be slightly low if an appreciable concentration of these compounds were present.

In the analysis of fractions of high conjugated diolefin content, values for both the cyclic and noncyclic types may be obtained by a calculation of the refractive index and density of the material removed by maleic anhydride followed by a graphical analysis. In fact, the intercepts of these two hydrocarbon types are so far apart that a simple interpolation instead of a graphical analysis is sufficient for the result.

In view of the preliminary stripping to 40° C., the analysis is limited to materials boiling above this point, unless special precautions for handling these light materials are taken. Also, there may be a small distillation residue boiling below 210° C., due to vapor hold-up in the flask. If desirable this residue can be taken overhead by adding to the flask some kerosene from which the naphtha residue can be fractionated. The kerosene should have an initial boiling point of at least 250° C. to avoid naphtha contamination.

In this connection it should be emphasized that the selection of cut point temperatures previously given is somewhat arbitrary. The aim was to concentrate 6-carbon cyclics and 7-carbon noncyclics in cut 2, 7-carbon cyclics and 8-carbon noncyclics in cut 3, 8-carbon cyclics and 9-carbon noncyclics in cut 4, etc., although it is not absolutely essential that this division be obtained. The authors have found the temperatures given to be very useful in gasoline analyses. Fractions should have an appreciable boiling range because the method is dependent upon average values wherever the density–boiling point relationship is involved. In very narrow boiling fractions the assumption of an average relationship would be less valid, due to the limited number of compounds of each type present. With very wide boiling fractions the mid-temperature of the boiling range may differ appreciably from the weighted average boiling temperature and so impair the application of the density–boiling point relationship.

In relating the density and boiling point, the relations given in Figures 3 and 4 for naphthenes and cyclic olefins are based entirely upon 5- and 6-carbon ring compounds because of the theory and evidence favoring the dominance of these compounds in these types.

TABLE V. TYPICAL CRACKED DISTILLATE ANALYSES

	Volume Per Cent	
	Sample 1	Sample 2
Noncyclic monoölefins	10.3	42.6
Cyclic monoölefins	16.8	24.0
Aromatics	25.1	14.3
Naphthenes	6.3	11.4
Paraffins	41.5	7.7

The differences in the composition of the two cracked distillates in Table V illustrate the application of this method to two materials representing extremes in composition.

Accuracy

It is very difficult to state the accuracy that can be expected from a method of this type. Obviously this is dependent upon how closely the composition of the hydrocarbon types approaches the averages used in the density–boiling point relationship. Considerable work was done on known mixtures of hydrocarbons and on gasoline analyses. Such analyses can be reproduced to 1 or 2 per cent (arithmetical).

Acknowledgment

The authors wish to express their appreciation to J. H. Boyd, Jr., for his assistance in the preparation of this paper, to E. A. Kniel for refinement of the laboratory technic, and to The Atlantic Refining Company for permission to publish this information.

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Spectrographic Analysis of Biological Material

II. Bismuth

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A method is reported for the spectrographic determination of bismuth in biological material. The method is capable of detecting 0.00004 mg. of bismuth and can be used to determine quantities from 0.001 to 3.00 mg. with an average error of ±10 per cent. Samples as small as a fraction of a gram of tissue or 25 to 50 cc. of urine may be used.

THE quantities of bismuth present in biological material may be determined by a method similar to that described for lead (*1*, *2*). It is necessary first to isolate the bismuth in a concentrated form, since the most sensitive bismuth line (λ 3067.7) is partially masked by the iron line at λ 3067.3 when material rich in iron is being analyzed, and since the presence of a faint narrow band in the spectrum of the graphite electrodes makes it impossible to detect bismuth unless the short-wave edge of the band is enhanced by having at least 0.00004 mg. of bismuth in the arc. Bismuth is not a common contaminant of reagents and as its sulfide is one of the least soluble of the heavy metals (solubility product = 3.2×10^{-91}, *4*), its separation and concentration are not attended by great danger of contamination or loss. The disadvantage of increased manipulation is offset by the fact that the isolation of the bismuth permits the arcing of material identical in composition with the standards used to derive the working curves.

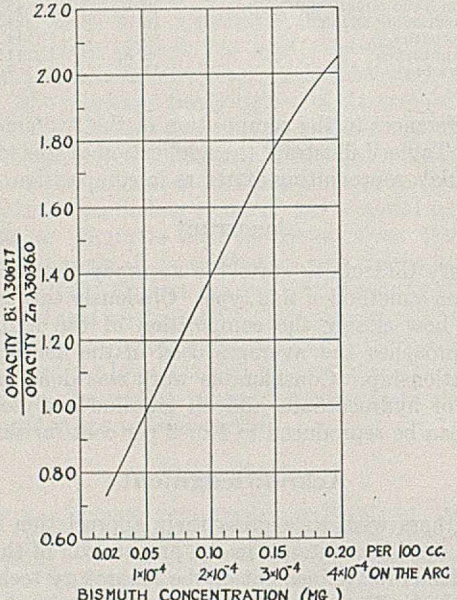

FIGURE 1

Technic

The samples, digested with nitric acid and evaporated to dryness, are ashed in a muffle furnace maintained at a temperature of 450° to 500° C. (Some difficulty due to fusing is encountered when materials rich in phosphates are ashed. Such samples, especially liver and brain, are best ashed by a wet method employing sulfuric, nitric, and perchloric acids. If care is taken to destroy the char as soon as it is formed, bismuth will not be lost during the process of ashing.) The time required for complete ashing may be shortened considerably if the gray ash produced after a few hours in the furnace is treated with nitric acid, evaporated to dryness, and again placed in the furnace for about 15 minutes. The resulting white ash is dissolved in the smallest possible quantity of nitric acid and distilled water. The excess acid is neutralized with 20 per cent sodium hydroxide and the solution made just acid to methyl orange with (1 to 2) hydrochloric acid. An excess of 3 cc. of (1 to 2) hydrochloric acid for each 50 cc. of solution is added and the solution is treated with hydrogen sulfide for 1 hour. After it has been permitted to stand overnight in order to coagulate colloidal bismuth sulfide, the sulfide is filtered off on a Munktell No. 00 filter paper and washed with a hydrogen sulfide–saturated solution of 0.1 per cent hydrochloric acid. The sulfides are dissolved from the paper with hot (1 to 1) nitric acid and the paper is washed several times with hot distilled water. The filtrates containing the bismuth are then adjusted to suitable volumes, as determined by the apparent quantity of sulfides obtained. Thus when a sample is small and when the sulfide is barely visible, the filtrate may be concentrated conveniently to 2 cc., which may then contain up to 0.06 mg. of bismuth. When the sulfides indicate the presence of considerable quantities of bismuth, any convenient concentration between 0.2 and 3.0 mg. of bismuth per 100 cc. may be employed.

Two cubic centimeters of the properly adjusted bismuth solution and 2 cc. of a stock solution of inorganic salts containing 500 mg. of zinc per 100 cc. (the zinc line λ 3036 serves as the "internal standard") are mixed in a graduated 15-cc. Pyrex centrifuge tube and evaporated to 2 cc. in a water bath. [The concentrated stock salt solution used as diluent and as base for the standard bismuth solutions is made up by dissolving 170.5 grams of sodium chloride, 63.5 grams of potassium chloride, 31.5 grams of calcium chloride ($CaCl_2 \cdot 6H_2O$), 20 grams of magnesium chloride ($MgCl_2 \cdot 6H_2O$), and 37.5 grams of sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$) in 1 liter of 10 per cent hydrochloric acid. Portions of this solution (50 cc., diluted to 100 cc. and made to contain 500 mg. of zinc) serve as the stock salt standard for mixing with the bismuth isolated from the samples and to make up the bismuth standards used to derive the calibration curves. This solu-

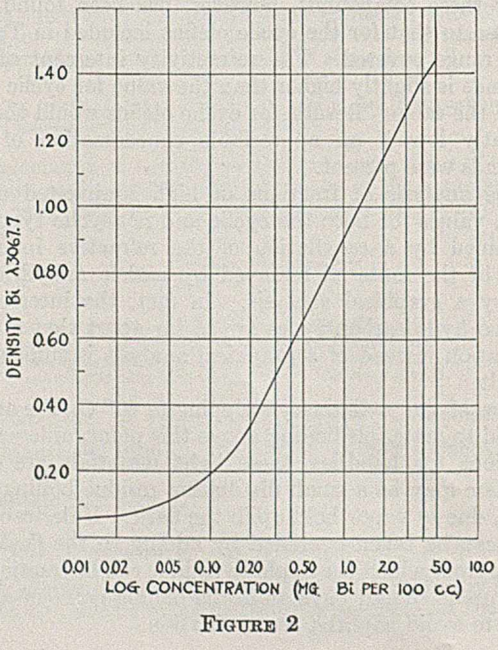

FIGURE 2

TABLE I. BISMUTH RECOVERIES

Bismuth added, mg.	Nil	0.001	0.01	0.10	0.25	0.50	1.00	2.00
Bismuth found, mg.	Nil	0.0008	0.008	0.10	0.23	0.48	0.98	1.80
	Nil	0.0008	0.009	0.085	0.27	0.50	1.08	1.80

TABLE II. RECOVERY OF BISMUTH FROM TISSUES AND EXCRETA OF A RABBIT

(Killed one week after the administration of 3.5 mg. of bismuth intravenously)

Tissue	Weight *Grams*	Bismuth Found *Mg.*
Blood	76.1	0.001
Liver	54.8	0.013
Spleen	0.7	0.000
Kidneys	11.5	0.08
Heart	4.1	0.000
Lungs	6.2	0.001
Central nervous system	14.0	0.000
Testes	1.4	0.000
Bile	...	0.000
Pancreas	2.1	0.004
Muscle	578.5	0.014
Bone	132.0	0.18
Skin	208.4	0.01
Intestinal tract	132.2	0.05
Contents of tract	164.0	0.03
Ears, tail, and feet	130.0	0.10
Remainder	348.0	0.05
Entire carcass		0.533
Urine	2.24	
Feces	0.90	
Total bismuth found in excreta		3.140
Total bismuth found		3.673

tion has proved very satisfactory, in that the salts present are good conductors and give a very steady arc when used with the technic described (*1*). Moreover it is free from the excessive creeping which may give rise to incrustations about the crater of the electrodes. Such incrustations result in spectrograms with very dark backgrounds because of the high concentration of incandescent salt particles in the arc.] Then a 0.2-cc. portion is introduced into each of 4 cratered graphite electrodes which are dried at 120° C. and arced in accordance with the technic described for lead (*1*), while the region λ2600 to λ3800 is photographed.

Following the suggestion of Lundegardh (*3*), two curves have been found useful in evaluating the densitometric values for the plates. The curve in Figure 1, in which the opacity ratios (galvanometer throw for the zinc line/galvanometer throw for the bismuth line) are plotted against the bismuth concentrations, is employed when the average opacity ratio of the four spectra indicates less than 0.0004 mg. (0.20 mg. per 100 cc.) of bismuth on the arc. This curve may also be used in estimating higher amounts of bismuth by diluting with a sufficient quantity of the diluent to reduce the bismuth concentration. The alternative, when dealing with quantities above 0.20 mg. of bismuth per 100 cc., is to determine the average density of the bismuth line corrected for variations in the density of the internal standard and to evaluate the bismuth concentration from the straight-line portion of Figure 2. These curves were plotted from the mean values of repeated observations on a series of solutions prepared by adding known quantities of bismuth and the required quantity of the "internal standard" to suitable volumes of the stock salt solution.

Applicability, Sensitivity, and Accuracy of Method

The recoveries for known amounts of bismuth added to digested portions of beef are tabulated in Table I. In Table II are recorded the results obtained from the tissues and excreta of an experimental animal. The weights of tissue available have been recorded in order to indicate the size of samples which can be utilized. The error of analysis, as shown in Table I, naturally depends on the quantity of bismuth encountered. For amounts above 0.20 mg. the error is ±10 per cent. For quantities from 0.01 to 0.20 mg. the error is about ±0.01 mg. The greatest proportional error naturally occurs with quantities below 0.01 mg., but the errors in the estimation of extremely small amounts down to 0.001 mg. rarely exceed ±20 per cent. (Although much smaller quantities can be detected, at least as low as 0.00004 mg., quantitative estimations below 0.001 mg. do not appear sufficiently accurate to be useful because of mechanical losses, such as those caused by adsorption, and the passage of colloidal bismuth sulfide through the filter paper.) In the case of material free from iron and containing very little ash, the separation of bismuth is of course unnecessary, and it may well be that quantities as low as 0.0002 mg. of bismuth can be dealt with by further concentrating the solution of the ash.

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Determining Calcium in Blood Serum

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IN THE determination of blood serum calcium by the Rymer and Lewis (*1*) modification of the Tisdall (*2*) method, the separation and washing of the calcium oxalate by successive centrifuging are very time-consuming. There is also possible loss while decanting and from creeping of the precipitate.

By the use of 30-cc. sintered-glass Büchner funnels (designation 3 G. 4), this centrifuging and decanting can be avoided.

Place 2 ml. of serum in the test tube, dilute with 2 ml. of water and 0.5 ml. of saturated ammonium oxalate, shake, and allow to stand overnight. Filter on the glass filters, and wash with ammonia water (4 cc. of concentrated ammonia to 250 ml.). After removing the funnel, rinse out the portion below the filter, place the funnel on top of test tube in the suction flask, dissolve the precipitate through the filter with three 2-ml. portions of hot *N* sulfuric acid, applying suction after each addition of acid, and wash the filters with water. Remove and rinse the test tube and lower portion of filter into a 50-ml. beaker, heat to boiling, and titrate with dilute permanganate from a Koch automatic microburet.

Very satisfactory results were obtained with this method which lends itself well to fast routine work.

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RECEIVED September 1, 1936.

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Spectrographic Determination of Platinum by the Constant-Pair Method

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WHILE investigating minute impurities in dental alloys by means of the spectrograph, the authors were able to develop a rapid method for the determination of platinum. The present method of cupellation and subsequent chemical analysis, although more precise, is long and tedious, besides being expensive. The spectrographic method is not only simple of execution but the most rapid by which the platinum content of precious metal alloys, jeweler's scrap, etc., may be obtained. It is the authors' belief that this method can be extended to include such metals as palladium, gold, silver, rhodium, etc., with all the advantages mentioned above.

Inasmuch as the authors' method has been evolved from a study of many methods previously established, it is desirable to give a brief account of these other methods.

A previous method for the spectrographic determination of platinum in silver alloys, as developed by de Laszlo (*2*), is based on the fading out of weak lines at certain concentrations of platinum. At threshold concentrations weak lines disappear until, as the concentration becomes smaller, only the persistent lines or *raies ultimes* remain on the photographic plate. The degree of correlation existing between the number of fine lines appearing in the spectrum and the concentration of platinum is one of the main factors governing the accuracy of this method. Undue stress, however, is not placed on the reproducibility of arc conditions, in going from one spectrum to the next. The de Laszlo method, as used in the routine analysis of alloys containing small amounts of platinum, has an accuracy of ±20 per cent of the amount present.

The authors have found that greater accuracy can be obtained by counting the number of lines in a given spectrum than by direct visual comparison of line intensities. This latter method, which enjoys widespread application, requires very rigorous control of arc conditions in order to reproduce the background present in the standard plate.

Method of Constant Internal Standard

It remained for Gerlach and Schweitzer (*1*) to show "that it is not practical to establish on general principles an absolute system of analyses which is based solely upon the measurement of the intensity of spectrum lines of the element which is to be quantitatively determined." Thus they compare in the same spectrum lines of the impurity with lines of the main constituent, where the latter is assumed to be present in constant amount or to vary only as the result of the variation in the amount of the impurity to be determined. This arrangement eliminates any differences arising from changes in conditions of excitation, timing, photography, etc., since these latter affect both groups of lines similarly. For alloys having elements with many lines of decided intensity variation this method is excellent. In cases of elements having few lines, however, it becomes a matter of considerable difficulty to find enough suitable pairs to compile a reference table of any value. In precious metal alloys where gold is the main constituent (present in varying amounts), the above method cannot be used.

Nitchie and Standen (*3*) modified Gerlach and Schweitzer's method by adding to the sample in solution a constant amount of an element not originally present. The added element furnished spectrum lines of constant intensity which served as a comparison standard in estimating the percentages of the constituent to be determined. Using a microphotometer, the intensity of the added element was compared with that of the element being estimated, and from known amounts of the latter, in standards, a calibration chart was constructed. This calibration chart could then be used in future analyses.

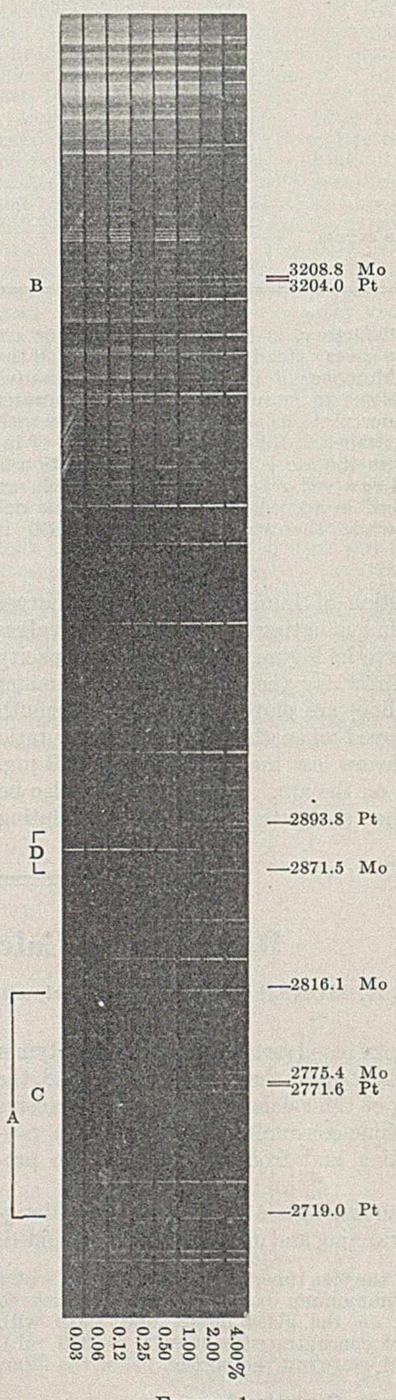

FIGURE 1

Constant-Pair Method

In the case of dental alloys the method of Gerlach and Schweitzer (*1*) cannot be used because the main constituents are not present in constant amount. The method of Nitchie and Standen (*3*) can be employed where a microphotometer is available.

Obviously if an element could be found which behaved like platinum in its arc spectrum, the amount of platinum in the sample could be estimated from the concentration of such an element. Some of the lines of this element would have the same intensity as some of the platinum lines if both were present in equal amounts. By noting the concentration of the added element at which equal intensities are obtained, the percentage of platinum could be found. Such a method would require no calibration curve and would secure the full advantage of the internal standard method. The preliminary work necessary in the selection of a suitable internal standard is somewhat long and tedious, but once this has been done the determinations which follow are a matter of simple routine.

Selection of Internal Standard

Confining attention to the work done in the proper selection of an internal standard for platinum, the authors were able to note the following facts: The element chosen as the internal standard must be absent from the sample or alloy which is the subject of analysis. Its spectrum must contain a sufficient number of suitable lines not too far removed from the platinum lines usually employed in analysis. It must be subject to the same sampling conditions as the element being determined—the two elements must be soluble in the same acids or at least be capable of giving a clear solution when their separate solutions are mixed or diluted.

Among the elements examined as to their suitability to act as internal standards for platinum, aluminum, manganese, and nickel were eliminated because of the differences in their rates of volatilization as compared with platinum. The lack of suitable lines eliminated tungsten. Tin, bismuth, and antimony were rejected on account of their failure to meet the sampling conditions specified above. Molybdenum was found to be suitable and the final selection of this element was justified by the results explained below.

Selection of Constant Pair

Solutions were made by dissolving separately in aqua regia 2-gram samples of pure molybdenum and platinum. These solutions were diluted to various concentrations and mixed in equal volumes, so that a series of solutions containing from 0.4 to 0.03 per cent of each metal was obtained. Spectrographic examination of these solutions as shown in Figure 1 revealed the following pairs of lines.

Pair	*A*	*B*	*C*	*D*
Platinum	2719.0	3204.0	2771.6	2893.8
Molybdenum	2816.1	3208.8	2775.4	2871.5

Of these the matched constant pair marked *D* was selected because the lines were sufficiently sensitive to record small changes in composition over the range studied; they were not basic or ultimate lines subject to reversal, masking or halation effects were absent, and their close proximity to each other ensured uniform conditions in the emulsion.

In addition to *D*, the authors have selected as matched pairs *A*, *B*, and *C*, which were found to be very useful as an aid to checking results. At the higher concentrations pair *A* has the same intensity, whereas pair *B* has the molybdenum line slightly more intense than the platinum line, and in pair *C* the platinum line is more intense than the molybdenum line. These pairs are therefore useful in estimating roughly the amount of platinum present in the solution.

Apparatus and Experimental Results

The spectrum from 2450 to 3300 Å. was photographed on a 25-cm. (10-inch) plate using a Bausch and Lomb Littrow-type quartz spectrograph of 70-mm. aperture and 183-cm. focal length. Three-minute exposures were found to be sufficient to volatilize all the platinum and molybdenum contained in the crater of the graphite rod.

A 1-gram sample of the alloy dissolved in aqua regia was diluted to 25 cc. Three solutions, each of 10 cc., were prepared by taking equal volumes of alloy and molybdenum solutions, the latter at high, medium, and low concentrations. Spectra were obtained from these solutions by pipetting 0.15 cc. into each carbon crater and arcing when dry, using a current of 11.5 amperes. These spectra serve to indicate the approximate amount of platinum in the solution. A final plate was then made using the molybdenum solutions over a narrower range of concentration until a matched pair of lines was obtained. In the hands of an experienced operator five to seven solutions are required in obtaining a suitable match.

Table I shows the quantitative results obtained by the constant-pair method for a group of dental alloys. The analyses given in the second column are taken as correct, since they represent at least six determinations of platinum. These determinations were carried out by cupellation of the alloy and precipitation of the platinum from the solution as ammonium chloroplatinate after removal of the gold.

Table I. Quantitative Results with Dental Alloys

Sample	Platinum by Cupellation, etc.	Platinum by Spectrograph	Difference
AG	0.0250	0.0227	−0.0043
A7	0.0300	0.0350	+0.0050
A8	0.0115	0.0130	+0.0015
A3	0.0300	0.0280	−0.0020
A9	0.0102	0.0088	−0.0014
A1	0.0400	0.0370	−0.0030
AP	0.0129	0.0124	−0.0005

The method as carried out should give an accuracy of ±17 per cent of the total amount of platinum present, by visual comparison of line intensities. It is probable that this accuracy could be greatly improved by determining line intensities using a densitometer.

Summary

A spectrographic method has been developed in which a rapid estimation may be made of platinum in precious metal alloys, using molybdenum as the internal standard. Conditions governing the proper selection of elements used as internal standards are stated.

Acknowledgment

The authors wish to acknowledge with thanks the helpful criticism and advice of C. C. Nitchie, Bausch and Lomb Optical Co., Rochester, N. Y.

Literature Cited

(1) Gerlach and Schweitzer, "Foundations and Methods of Chemical Analysis by the Emission Spectra," p. 152, Leipzig, Leopold Voss, 1929.
(2) Laszlo, H. de, Ind. Eng. Chem., 19, 1366 (1927).
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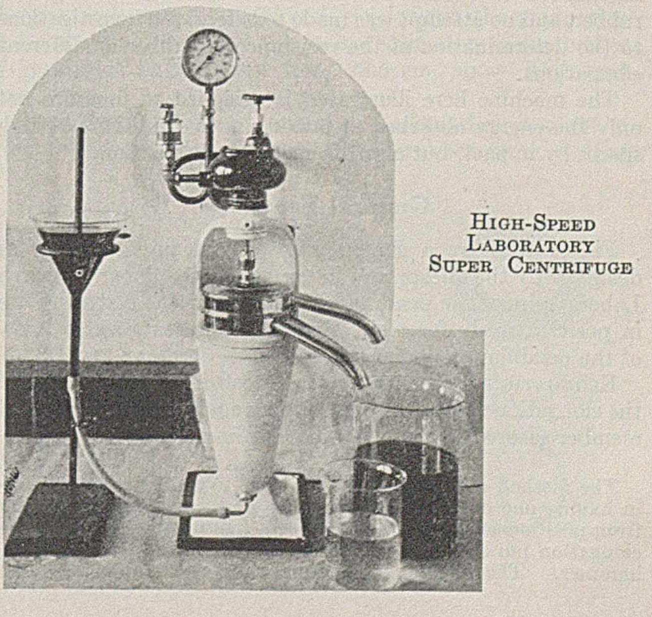

High-Speed
Laboratory
Super Centrifuge

Impact Machine for Rubber Testing

Determining the Stress-Strain Diagram at High Speed

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The main features of this impact machine are as follows: high speed of performance, 25,000 cm. per minute, as compared with 50 per minute by the ordinary methods, accurate and direct determination of the energy absorbed at a speed in reasonable agreement with performance, possibility of determining the stress-strain relationship by impact, possibility of determining the magnitude of decay on the energy storage capacity at successive cycles, possibility of determining the stress-strain characteristics of uncured stocks by emphasizing the elastic phase under conditions of high speed, and simplicity of manipulations required, leading to the possible application to routine control.

IN CONTRAST to the ordinary standard procedure at low speed, various methods have been devised to carry out tensile tests of rubber under rapid application of load, with the purpose of securing more definite indications, at a speed in agreement with actual performance. The application of those methods to the study of the tensile properties of rubber stocks goes as far back as 1910, when Beadle and Stevens (*1*) made use of the pendulum to investigate these properties. Their work applied to rubber compounds of different compositions and different loadings.

More recently, Van Rossem and Beverdam (*2*) presented a set of results tending to prove an optimum in the tensile properties, coinciding with the best cure as determined by practical observation.

However, all experiments, previous to those here reported, are limited to the determination of the tensile strength of rubber, and no attempt was made to extend the investigations to the determination of the resistance of rubber at different elongations.

The machine here illustrated is designed to measure not only the energy absorbed at break, under conditions of high speed, by impact, but also the stress-strain relation.

General Features

Figure 1 shows a general view of the impact tester as designed by the author and in use at the Goodyear Research Laboratories. The pendulum hammer and the test piece are in position ready for test. Figure 2 represents a close view of the pendulum hammer and scales.

ELONGATION FEATURES. The most important parts of the elongation system are the tripping device and the arcuated member secured to the pendulum hammer.

The method of securing the test piece to the machine consists in having one of the two supporting pins capable of dropping from position whenever the lock is set free by the impact of the elongation pin secured at the arcuated member of the pendulum hammer. The dropping pin supporting one end of the test piece is carried by a cylinder capable of rotating around a pinion. The method of arresting and releasing the rotor is illustrated by the detailed view of the tripping device (Figure 3).

To secure the release of the test piece at different elongations, an arc is attached to the pendulum hammer. To this arc is secured a removable pin, capable of releasing the tripping device at any prefixed elongation of the test piece. The arc carries a series of holes at such distances as to operate at zero elongation, at 50, 100, 150, and every 50 per cent elongation up to 400 per cent. On the present machine, holes are also provided for 10, 20, 30, 40 per cent, and also for 450 up to 650.

Experimental determinations, carried out by the use of fine metallic wire of proper lengths secured with the rubber test piece in proper position for test, tend to demonstrate that the test piece is fully released at the elongation required.

In Figure 3 the arrows indicate the direction of the motions and illustrate the coördination of the movement of the arcuated member, with the release of the trigger.

TEST PIECE. Although different experiments were carried out, using the dumbbell test piece, the ring type was finally adopted for convenience. The rings are cut from the ordinary

FIGURE 1. GENERAL VIEW OF MACHINE

A. Arcuated member on which are directly indicated settings of pin used to trip releasing device at different elongations of test piece
D. Dials
H. Pendulum hammer
I. Indicator
P, R. Pawl and rack arrangement (used only for special purposes, pawls being normally kept in a lifted position)
S. Pins securing test piece at proper position
T. Support, at back of which is secured the tripping mechanism

molded 2-mm. sheets, by the same procedure used for the dumbbell test piece. The diameter, measured at the middle of the width, is 7.0 cm.; the initial length is 11 cm. (half of the circumference). Figure 4 shows the three test pieces (6.3, 5, and 3 mm. in width) and the corresponding dies.

Operation

The procedure to be followed in the operation of the machine can be considered in three ways:

1. Procedure required to obtain the maximum of accuracy necessary to calculate the full extent of the stress-strain curves. A new test piece is required for the determination of each point.
2. Simplified procedure sufficient to determine the energy absorbed by the test pieces at two elongations, a and b (preferably 100 per cent apart), and to calculate the modulus at the elongation $(a + b)/2$.
3. Determination of the energy absorbed at break, to evaluate the relative tensile strength of the stocks and eventually their best cure.

Aside from the type of correction and the number of test pieces required, the method of operating the machine is substantially identical in all three cases. However, in determining the tensile strength, the use of the releasing pin, set at the arcuated member of the hammer, is omitted, and the tripping device is kept in locked position.

The method of operation is as follows:

Raise the pendulum to the position for impact and set the pin in the arcuated member of the hammer at the position indicated for the release of the test piece at the elongation wanted. Lubricate the test piece with castor oil, or castor oil diluted with a mixture of methanol and ether. Set the ring test piece, across the pendulum path, from the movable to the stationary pin and lock the trigger of the tripping device. Release the pendulum weight and record the readings of the dials.

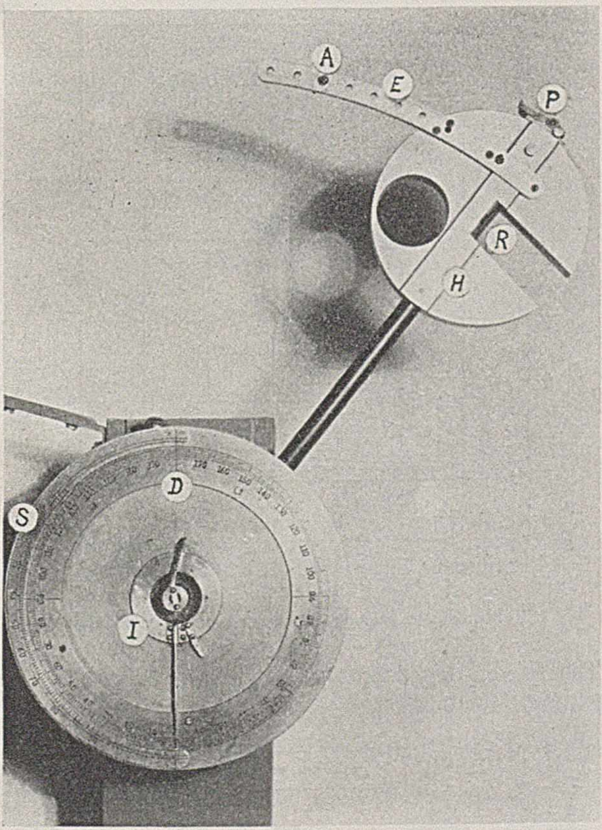

Figure 2. Close View of Pendulum Hammer and Scales

A. Arcuated member attached to pendulum hammer
D. Degree scale (divided in tenths)
E. Openings for holding releasing pin at different elongation settings
H. Pendulum hammer
I. Indicator arrangement and sliding supporting disk, pressed (at back) by a series of small springs
P. Pawls, with small adjusting cam
R. Roller at center of pendulum hammer, against which stretches central portion of lubricated test piece while pendulum advances
S. Scale for corrected readings of available kinetic energy of pendulum

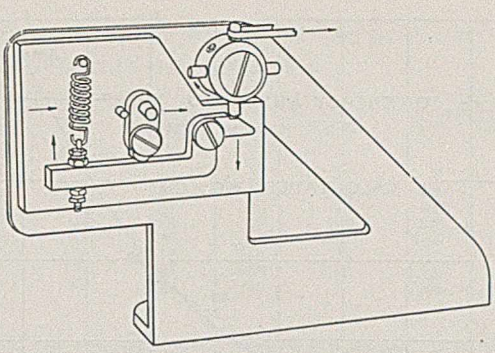

Figure 3. Tripping Device

In operating the machine, the pendulum ruptures or carries the test pieces to a definite elongation when near or at the bottom of the fall.

The difference between point H, from which the center of gravity of the pendulum is allowed to drop, and height H_1, to which it rises at the other side of the stroke, is proportional to the energy required to break or to elongate the test piece. The energy absorbed is equal to:

$$W(H - H_1)$$

where W = weight of the pendulum

Construction Details and Calculation of Results

The total drop height and available drop heights of the pendulum hammer when due allowance is made for frictional resistances are:

Distance of the center of gravity from the axis of rotation, 56.6 cm.

Maximum pendulum deviation from the vertical, 142.3°; total drop height, 101 cm.

Available drop height when correction is made for bearing and air resistance and for frictional resistance of the pointer, 100 cm.

Available drop height when further correction is made for the resistance due to the tripping device, 98.5 cm.

On the dial for the direct reading of the per cent energy absorbed, when the elongation device is used, the graduation of the scale represents the drop in centimeters of the center of gravity of the hammer from 98.5 cm. above its lowest position.

Hammers of different weights were adopted on account of wide differences in resistance of the rubber stocks. The

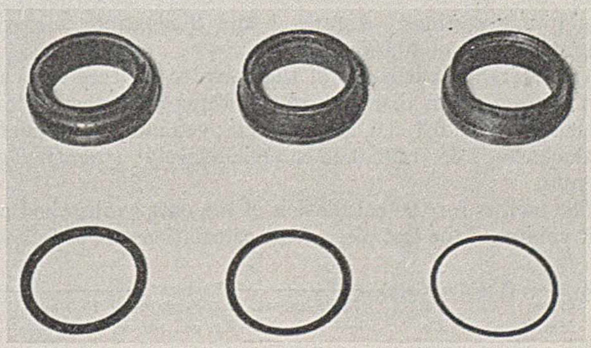

Figure 4. Test Pieces and Dies

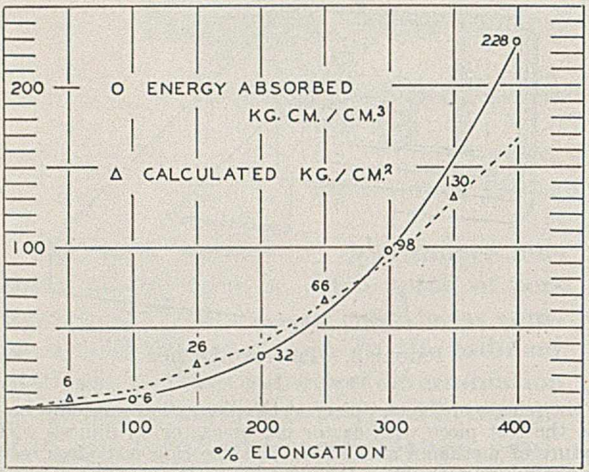

FIGURE 5. CALCULATION OF KG. PER SQ. CM. VALUES FROM ENERGY ABSORBED (KG. CM. PER CC.)

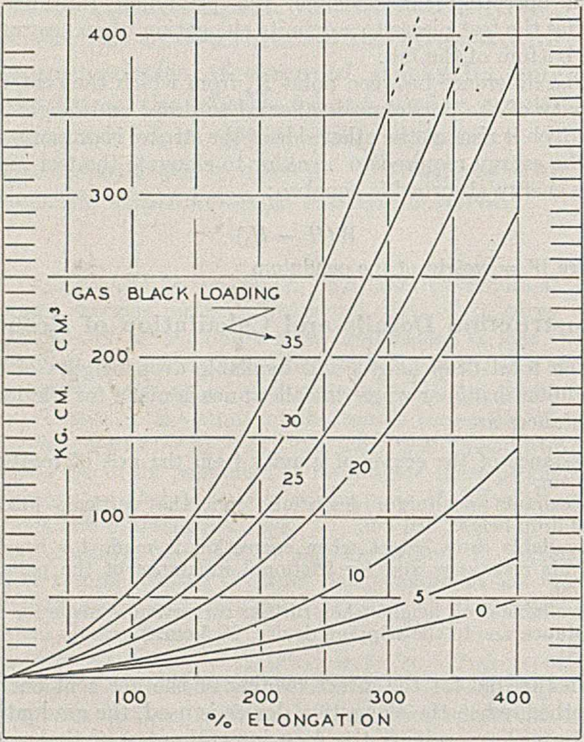

FIGURE 7. ENERGY ABSORBED AT HIGH SPEED BY IMPACT

25,000 cm. per minute

three weights used are 4,077, 10,695, and 13,325 grams. They are quickly interchangeable, being constructed of overlapping sections. Figures 1 and 2 illustrate a single-weight hammer of 10,695 grams.

The average dimensions of the three test pieces used are as follows: mean diameter of all three ring test pieces, 7.0 cm.; widths, 6.3, 5.0, and 3.0 mm.; volume per millimeter of thickness, 1.38, 1.08, 0.65 cc., respectively; average gage, 1.8 mm.

The factors for the calculation of the energy absorbed per unit volume of the test piece, from calculations are as follows:

Test Piece (1.8-Mm. Gage) Width	Vol.	Factors for: 74.08-kg. wt.	10.69-kg. wt.	13.3-kg. wt.
Mm.	*Cc.*	*Kg. cm. per cc.*		
6.3	2.49	1.61	4.23	5.26
5.0	1.95	2.06	5.40	6.72
3.0	1.17	3.43	9.00	11.20

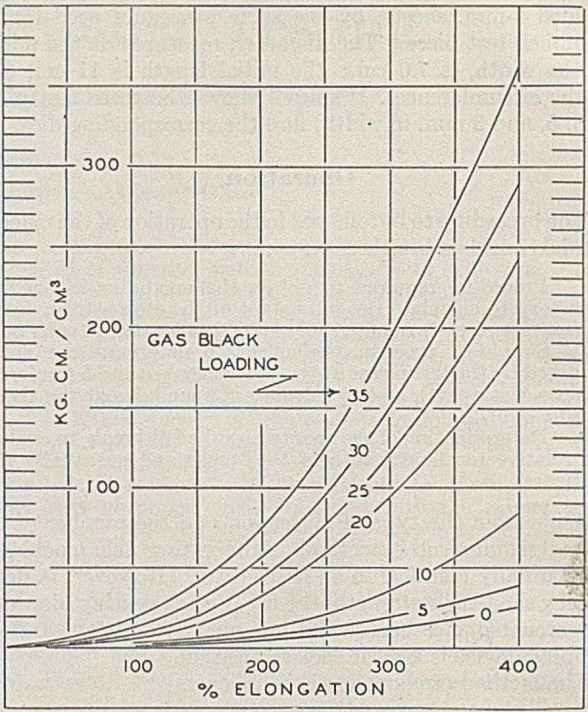

FIGURE 6. ENERGY ABSORBED AT LOW SPEED

50 cm. per minute, by usual methods

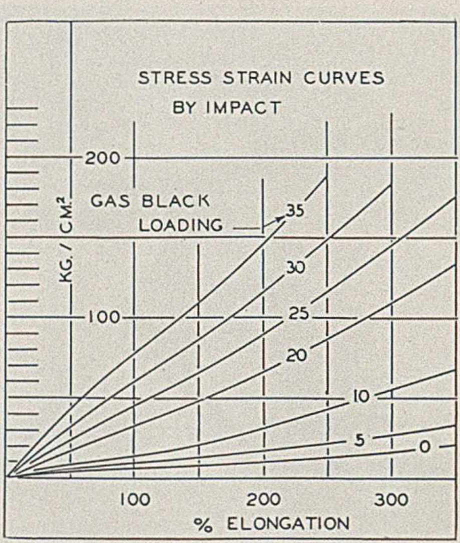

FIGURE 8. STRESS-STRAIN RELATIONSHIP BY IMPACT

Kg. per sq. cm. calculated from kg. cm. per cc. values

The factors, based on the equivalence of results, from experimental data are:

Test Piece (1.8-Mm. Gage) Width	Vol.	Factors for: 4.08-kg. wt.	10.69-kg. wt.	13.3-kg. wt.
Mm.	*Cc.*	*Kg. cm. per cc.*		
6.3	2.49	1.7	4.23	5.2
5.0	1.95	2.0	5.3	6.5
3.0	1.17	3.3	8.7	10.8

The actual drop height of the hammer at different elongations is:

Elongation	Drop Height	Elongation	Drop Height	Elongation	Drop Height
%	*Cm.*	%	*Cm.*	%	*Cm.*
20	95.2	300	99.8	500	96.2
100	96.9	400	98.4	600	94.9
200	98.1				

TABLE I. ENERGY ABSORPTION (KG. CM. PER CC.) GAS BLACK LOADINGS, VOLUMES

Elongation	Gas Black Loadings, Volumes													
	0		5		10		20		25		30		35	
%	50[a]	25,000[a]	50[a]	25,000[a]	50[a]	25,000[a]	50[a]	25,000[a]	50[a]	25,000[a]	50[a]	25,000[a]	50[a]	25,000[a]
50	..	3	1	4	1	6	2	8	3	13	5	17	7	24
100	1	6	2	9	3	12	5	22	8	32	13	43	19	57
150	2	10	4	14	6	20	15	42	20	58	30	79	41	103
200	4	14	8	21	12	34	33	70	44	98	57	128	76	166
250	8	21	12	31	21	52	60	108	78	149	97	196	126	250
300	12	27	20	43	36	76	96	156	122	214	149	278	192	354
350	18	36	28	58	58	108	140	217	178	296	216	370	272	...
400	26	48	40	76	86	144	190	290	244	384	290	...	364	...

[a] Cm. per minute.

For ordinary determinations, this correction is generally not required but was applied in calculating the results illustrated here.

The correction for frictional resistance of the test piece, at the pins, was calculated as the energy absorbed at no elongation by releasing the tripping device at such position, and recording the energy absorbed. This determination is desirable to establish the operating condition of the machine and the characteristics of the stock tested. The values range between 5 and 7 kg. cm. per cc., according to the type of stock. The results are very uniform when the test piece is previously lubricated, as indicated under "Operation."

The striking velocity of the pendulum hammer is calculated from the equation

$$V = \sqrt{2\,GS}$$

where V = velocity at end of time t, sec.
S = vertical space traversed in time t (100 cm.)
G = acceleration of gravity (980)
$V = \sqrt{2 \times 980 \times 100}$
= 443 cm. per sec.
= 26,580 cm. per min.
= 10 miles per hour

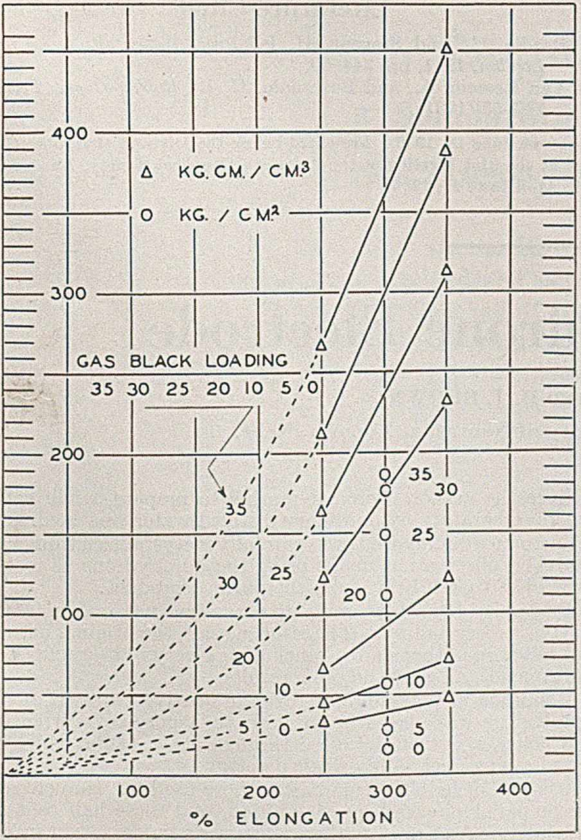

FIGURE 9. ENERGY ABSORBED BY IMPACT

At 250 and 350 per cent elongation, and calculated modulus at 300

The calculation of the stress-strain curves (in kg. per sq. cm.) from the relation between elongation and energy absorbed (in kg. cm. per cc.) is made as follows:

> The area under the stress-strain curves can, with sufficient degree of approximation, be divided into a series of trapeziums.
> The number of kg. per sq. cm. at E per cent elongation = [(kg. cm./cc. at elongation $E + A$) − (kg. cm./cc. at elongation $E - A$)] multiplied by $100/2\,A$.
> The area under the curve representing kg. cm. per cc. between 0 and 50 per cent elongation can be considered as a triangle. The number of kg. per sq. cm. at 25 per cent elongation can be considered equal to the number of kg. cm. per cc. at 50 per cent elongation.

Figure 5 illustrates graphically the procedure used to calculate the stress-strain curve from the values of kg. cm. per cc.

Experimental Applications to Vulcanized Rubber

The following is a series of tests applied to vulcanized rubber. No attempt is made to illustrate the application of the machine to uncured stock.

COMPOSITION AND CURE. The composition of the stocks tested was as follows:

Stock No.	V-92	V-93	V-94	V-95	V-96	V-97	V-98
Rubber	100	100	100	100	100	100	100
Gas black	None	9.4	18.8	37.5	47.1	56.4	65.8
Zinc oxide	5	5	5	5	5	5	5
Sulfur	3	3	3	3	3	3	3
Stearic acid	4	4	4	4	4	4	4
Captax (mercaptobenzothiazole)	0.35	0.50	0.80	1.2	1.3	1.3	1.3
Vol. gas black loading	0	5	10	20	25	30	35

Cures were 35, 50, 70, 100, and 140 minutes at 260° F. The best cure, as judged by tear and practical observation, was 70 minutes. Therefore, in the following tests (except for the application of the impact test to the determination of the best cure), only the 70-minute cure was represented.

ELONGATION AND ENERGY ABSORBED. The relation between elongation and energy absorbed at low speed by the usual methods and at high speed by impact is shown in Figures 6 and 7. The comparison between energy storage capacity at 50 and at 25,000 cm. per minute is given in Table I.

STRESS-STRAIN DATA. The stress-strain curves by impact, calculated from the relation between elongation and energy absorbed, are given in Figure 8. The stress-strain data calculated from Table I are as follows:

Elongation	Gas Black Content, Volumes:						
	0	5	10	20	25	30	35
%	*Kg. per sq. cm.*						
25	3	4	6	8	13	17	24
100	7	10	14	34	45	62	79
150	8	12	22	48	66	85	109
200	11	17	32	66	91	117	147
250	13	22	42	86	116	150	188
300	15	27	56	109	147	174	...
350	21	33	68	134	170	...	...

SIMPLIFIED DETERMINATION OF ENERGY ABSORPTION AND MODULUS. A simplified procedure limited to the deter-

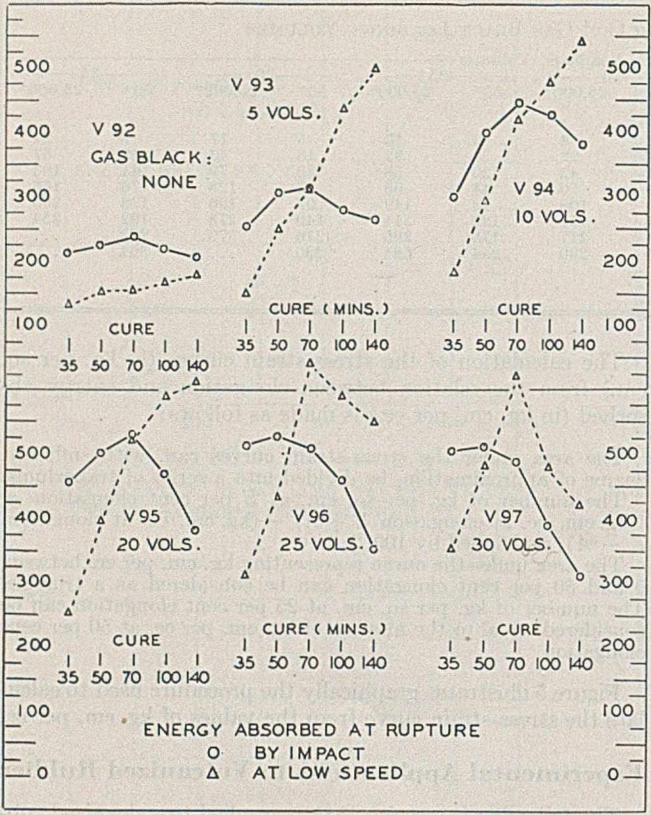

FIGURE 10. ENERGY ABSORBED AT RUPTURE, IN RELATION TO CURE

mination of the energy storage capacity at 250 and 350 per cent elongation and to modulus at 300 per cent is shown in Figure 9 and in Table II.

ENERGY ABSORPTION AT BREAK. The energy storage capacity at break in relation to best cure is shown in Figure 10.

Probably one of the most useful applications of the impact test is the determination of the best cure, from the standpoint of energy storage capacity. The difference between cure is, in some cases, not very accentuated and almost on the limit of the errors involved in the test. However, the general trend is, in most cases, sufficient to indicate the true value of the best cure.

TABLE II

Elongation %	Gas Black Content of Stock, Volumes: None	5	10	20	25	30	35
350	11.3^a	16.9^a	28.8^a	55.3^a	58.8^a	44.5^a	(52)^a
250	7.7^a	10.4^a	15.4^a	29.0^a	30.9^a	24.4^a	30.7^a
Test Piece Width, Mm.:	6.3			5	3		
Experimental Factors	4.2			5.3	8.7		
Energy Storage Capacity							
350	47^b	71^b	121^b	232^b	312^b	387^b	(452)^b
250	32^b	44^b	65^b	122^b	164^b	212^b	267^b
Modulus							
300	15^c	27^c	56^c	110^c	148^c	175^c	185^c

^{a} Scale reading (per cent energy absorbed).
^{b} Values marked ^{a} multiplied by the corresponding factors.
^{c} Modulus (kg. per sq. cm.), calculated from values marked ^{b}.

Following is a comparison of results obtained at 50 cm. per minute with those at more than 25,000 cm. by impact; the cures were 35, 50, 70, 100, and 140 minutes at 260° F.:

Stock No.	Gas Black Loading *Vol.*	Ratings in % of Lowest Cure Values: At low speed: 50-min.	70-min.	100-min.	140-min.	By impact: 50-min.	70-min.	100-min.	140-min.
V-92	None	116	118	128	132	108	113	106	101
93	5	169	228	295	340	118	123	110	104
94	10	163	234	267	297	132	152	146	126
95	20	157	207	237	243	110	116	104	83
96	25	140	206	192	178	104	99	90	68
97	30	131	178	138	119	100	98	77	62
98	35	128	147	128	112	99	97	75	47

Acknowledgment

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A Standard Quinhydrone Electrode

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IT WAS the authors' purpose to prepare an electrode readily without use of balance or volumetric apparatus. Of those studied, a quinhydrone half cell in which the solution is potassium tetroxalate, saturated at 0°, was found to be very satisfactory.

The saturated calomel electrode was used as the reference half cell. In all the determinations the calomel half cells were of the same reproducibility as those prepared by Samuelson, (*5*) and the same precautions were used in their preparation. The value $+0.2446 + 0.00020\ (t - 25)$ was used to calculate the values for the quinhydrone electrode (*1*, *2*). However, if the temperature coefficient of the hydrogen electrode at all temperatures is called zero, the temperature coefficient of the saturated calomel half cell is −0.66 mv. per degree (*6*). Values on this basis are also included.

Since the authors were attempting to prepare a half cell for general laboratory use, ordinary distilled water was used.

Eastman's quinhydrone was carefully recrystallized from water. However, observations made using the quinhydrone as received varied less than 0.1 mv. from the purified product.

A sample of the best grade of potassium tetroxalate (Merck) was twice recrystallized. The resulting salt, the original material, and salts from other sources, including a very old sample (Eimer and Amend), all gave the same results.

A solution of potassium tetroxalate nearly saturated at room temperature was placed in an ice bath, vigorously stirred for 2 or 3 hours, and then decanted through a glass tube which contained a plug of carefully washed cotton.

A "nest" of half cells, similar to those used by Samuelson (*5*), was prepared for each type of solution, and these half cells were measured against one another. The average deviation in millivolts during a series of observations is included in Table I. One of these was then compared with one of a nest of calomel half cells which had been likewise interchecked and found to have a very small average deviation.

A sufficient quantity of the tetroxalate solution for several half cells was saturated with quinhydrone, and several half cells were filled. The balance of the solution was used to wash the platinum foil electrodes, which were prepared as directed by Morgan, Lammert, and Campbell (*4*) and kept in water. Before use they were thoroughly washed with the solution of the half cell, but when transferred from one solution to another they were washed thoroughly with the latter solution only. To detect possible misbehavior of the electrodes, they were checked against one another in some of the solution before each run, and were not used until they agreed within 0.02 mv.

The liquid junction between the nest of calomel electrodes and of the quinhydrone electrodes was effected by means of "glass-stoppered" salt bridges built according to the directions of Irving and Smith (*3*).

A Leeds & Northrup Type K potentiometer equipped with a type R galvanometer was used in connection with a calibrated Weston cell.

The potential of the tetroxalate-quinhydrone electrode was calculated at 25° C. and its temperature coefficient expressed either absolutely (*1*, *2*) or relatively to the hydrogen electrode at all temperatures as zero (*6*).

The resistance of the cell was found to be comparatively low. If a current of 0.1 microampere, sufficient to deflect the galvanometer 3 cm. on the scale, flowed for 20 seconds, the maximum effect was 0.05 mv. This polarization disappeared within 20 seconds, or more quickly if stirred.

The new half cell is very easily prepared without use of balance or volumetric apparatus. The materials are easily obtainable. While the temperature coefficient is high, so is that of the half cells to be measured, and, since in ordinary work the temperature coefficients are not considered, the observed values will be more nearly true than if the comparison half cell had a lower value. For these reasons the authors believe this quinhydrone–potassium tetroxalate electrode is very suitable for ordinary laboratory work.

Table I. Quinhydrone Electrode

Temp.	E. m. f. Observed	Average Deviation	E. m. f. of Calomel		E. m. f.	
			I[a]	II[b]	I[a]	II[b]
		Mv.				
0	0.36566	0.07	0.2396	0.24625	0.60526	0.61191
25	0.35236	0.04	0.2446	0.2446	0.59696	0.59595
35	0.34743	0.06	0.2466	0.2380	0.59403	0.5854

$$\frac{\Delta E_{\text{I}}}{\Delta T} = -0.31 \text{ mv. degree}$$

$$\frac{\Delta E_{\text{II}}}{\Delta T} = -0.1.17 \text{ mv. degree}$$

[a] Absolute.
[b] Relative to hydrogen electrode.

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Determination of the Ash Content of Sugar Products

A Standardized Sulfated Ash Method

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Experiments showed that the sulfated ash method needed to be standardized as to the time and temperature of heating of the resulfated ash. A standard method was worked out, based on the thermal decomposition of pure sulfates. A technic was devised for ashing large amounts of low-ash samples. The method is suitable for ash adsorption studies, etc., where precision measurements are necessary.

THE methods for the determination of the ash content of sugar products are of two types—i. e., gravimetric and conductometric. As the latter is interpreted in terms of the former, it is obvious that gravimetric methods are the basis of all quantitative ash measurement. There are two gravimetric methods—the carbonated ash method and the sulfated ash method.

Carbonated Ash Method. Browne and Gamble (*2*) have shown that the ash content as measured by the carbonated ash method is affected by the partial and variable loss of chlorine, nitrogen, and sulfur from the sample during incineration. Thus the percentages of these constituents so lost vary according to the method of burning and the nature of the bases with which these elements are combined. This means that the method is unsuitable for the determination of comparable values of the ash content at various stages of the fabrication process or before and after treatment with some ash adsorbent. For these reasons the use of the method has been discontinued.

Sulfated Ash Method. In this method (*1*) the partly dried sample of sugar product is moistened with concentrated sulfuric acid and then incinerated till a white ash is obtained. This ash is taken up with a few drops of sulfuric acid—i. e., resulfated. The excess acid is driven off by heating and the weight of ash recorded.

All the volatile constituents of the ash are driven off by the acid treatment. Obviously, owing to the variation in the composition of the sulfatable salts as well as the amounts of the inert matter present, there is no correlation between the sulfated and carbonated ash values.

Purpose of Resulfation

In the ash obtained by the decarbonization of the sulfated sugar product, qualitative tests have shown (1) the presence

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of sulfides; this is in accord with the findings of Schweizer (*3*); and (2) the presence of chlorides in the case of low-grade products—e. g., molasses—hydrogen chloride fumes being liberated when sulfuric acid is added to the ash.

This means that resulfation of the ash effects its sulfation by the conversion of sulfides into sulfates and by driving off volatile constituents when the addition of sulfuric acid to the sugar product is ineffective, inadequate, or absent. Any sulfuric acid added to the sugar product reacts during the decarbonization process, not only with the ash but also with the decomposing sucrose; and the latter is by far the predominating component. This explains the presence of chlorides and sulfides in the ash prior to resulfation, and the discrepancy in the results when resulfation is not used.

Standardization of Method

The need for the standardization of the time and temperature of heating of the resulfated ash is brought out by the following experiment: A sample of raw cane sugar was sulfated and ashed and the ash so obtained was heated for the time and temperature specified, resulfation of the ash being performed prior to each heat treatment.

TABLE I. RESULFATION

	Temperature of Heating		Time of Heating	Weight of Ash
	° F.	*° C.*	*Hours*	*Gram*
Before resulfation	1000	538	5	0.376
Ash resulfated	580	304	4	0.450
	1200	649	2	0.387
	1480	804	1	0.384

A typical result is given in Table I, which shows that apart from the gain in weight on resulfation, the weight of the resulfated ash is a function of the time and temperature of heating; and that the rate of decomposition of the sulfates increases with increase in temperature. The most striking feature is that the result at 580° F. (304° C.) is some 17 per cent higher than the value at 1480° F. (804° C.).

Further experiments were carried out to note whether (1) the ash weights approach a constant value as the temperature rises—i. e., a weight at which the salts that tend to decompose are decomposed—and (2) the position of the ash in the muffle furnace has any bearing on its weight.

The resulfated ash from a raw sugar solution was heat-treated as shown in Table II.

TABLE II. HEAT TREATMENT OF RESULFATED ASH

Temperature	Time	Weight of Ash		
		I[a]	II	III
° F.	*Hours*	*Gram*	*Gram*	*Gram*
580	4	0.1807	0.1801	0.1812
580	20	0.1767	0.1776	0.1782
1000	2	0.1512	0.1521	0.1517
1000	20	0.1507	0.1511	0.1502
1480	1	0.1477	0.1481	0.1479
1480	16	0.1458	0.1464	0.1472

[a] Position in muffle: I, farthest in; III, near mouth.

Further data showed that samples incinerated near the mouth of the muffle possessed in practically all cases higher weights than samples heated well inside the muffle: Ash weight III > ash weight II > ash weight I. Data also showed that an 8 per cent loss in weight occurred between 1500° and 1700° F. (816° and 927° C.).

The conclusions from the above data are (a) the salts do not arrive at a constant state of composition but continue to decompose even when impracticably high temperatures are reached; (b) for a given temperature after a certain time the rate of decomposition of the sulfates is slow; and (c) resulfated samples heated near the mouth of the muffle furnace have larger weights than those heated well inside the furnace. This is explicable on the basis of a temperature gradient in the furnace mainly due to the distribution of the heat insulation.

In order to select the most suitable time and temperature for the heating of the resulfated ash, the thermal decomposition of pure sulfates was studied. The sulfates chosen were those which were known to occur in the ash of sugar products.

PROCEDURE: The weight of the pure sulfate was noted. The salt was then heated for varying times and temperatures, and the weight taken; prior to each heat treatment the sample was resulfated so as to copy the conditions used in the ash determination. The composition of the salt was determined by the ratio of the weight of partially decomposed product to the weight of the sulfate. When the decomposition of the salt was complete, this ratio became equal to that of the ratio of the formula weight of the oxide to that of the sulfate for the salt in question (Table III).

TABLE III. SUMMARY OF RESULTS

Sulfate Used	Weight of Product / Weight of Sulfate	Assumed Formula of Product	Weight of Product / Weight Corresponding to Assumed Formula
4-Hour Heat Treatment at 580° F. (304° C.)			
K_2SO_4	1.45	$K_2S_2O_7$	0.999
Na_2SO_4	1.56	$Na_2S_2O_7$	1
$CaSO_4$	1	$CaSO_4$	1
$MgSO_4$	1	$MgSO_4$	1
$Fe_2(SO_4)_3$	1	$Fe_2(SO_4)_3$	1
$Al_2(SO_4)_3$	1	$Al_2(SO_4)_3$	1
2-Hour Heat Treatment at 1200° F. (649° C.)			
K_2SO_4	1	K_2SO_4	1
Na_2SO_4	1	Na_2SO_4	1
$CaSO_4$	1	$CaSO_4$	1
$MgSO_4$	1	$MgSO_4$	1
$Fe_2(SO_4)_3$	0.40	Fe_2O_3	1
$Al_2(SO_4)_3$	0.84	Al_2O_3	2.82
1-Hour Heat Treatment at 1480° F. (804° C.)			
K_2SO_4	1	K_2SO_4	1
Na_2SO_4	1	Na_2SO_4	1
$CaSO_4$	0.98	$CaSO_4$	0.98
$MgSO_4$	1	$MgSO_4$	1
$Fe_2(SO_4)_3$	0.40	Fe_2O_3	1
$Al_2(SO_4)_3$	0.29	Al_2O_3	1

The choice of the times and temperatures was based on the following facts:

Even after 20 hours at 580° F. both ferric sulfate and aluminum sulfate were practically undecomposed.

After 2 hours at 1200° F., $Fe_2(SO_4)_3$ is converted completely into Fe_2O_3.

After 1 hour at 1480° F., $Al_2(SO_4)_3$ is completely decomposed into Al_2O_3.

The sodium and potassium salts, when heated for less than 4 hours at 580° F. after treatment with sulfuric acid, gave weights greater than required by the formulas $K_2S_2O_7$ and $Na_2S_2O_7$.

These experiments show that the order of decomposition of the sulfates in the resulfated ash as the temperature increased is as follows: (1) sodium and potassium pyrosulfates, (2) ferric sulfate, (3) aluminum sulfate, and (4) calcium sulfate, the temperature range for the decompositions being from 580° to beyond 1700° F.

TABLE IV. TYPICAL RESULTS

Samples	Ash Weights			Amount Ashed	Purity of Sample	Ash per 100 Grams of Borax in Sample
	A	B	C			
				Cc.		*Grams*
Crystallizer Remelt sirup	1.3777	1.3771	....	50[a]	74	4.5
Crystallizer	0.5113	0.5113[b]	....	50[a]	85	1.7
Remelt sugars	0.2470	0.2460	....	50[a]	...	0.8
Raw sugar	0.1248	0.1250	....	50[a]	99	0.4
Granulated sugar	0.0083	0.0083	0.0085	100[c]	99.99	0.01

[a] At 50° Brix.

[b] This sample prior to resulfation showed weights of 0.4790 and 0.4904 due to incomplete sulfation—i. e., the presence of chlorides.

[c] At 61° Brix.

Therefore the time and temperature of heating of the resulfated ash must be standardized; and the most appropriate conditions were 1480° F. for 1 hour. Thus, while reproducible results were obtained for sugar solutions at the two other time-temperature conditions stated, 1480° F. was chosen because it was rapid and because under certain conditions of heating (above about 1200° F.) the ferric oxide in the ash does not resulfate except by digestion of the ash with hydrochloric acid prior to the sulfuric acid treatment.

These experiments also explain the large difference between the ash weights of a sugar solution at 580° and at 1480° F., due mainly to the pyrosulfates of sodium and potassium. The small percentages of iron and aluminum in sugar ash cannot account for the 17 per cent increase in weight between 1480° and 580° F., whereas the percentages of alkali metals range around 30 per cent; so that when we realize that the formation of pyrosulfates can increase this value to 30 × 1.5 = 45 we find therein the main cause of the 17 per cent increase noted above.

Standardized Method

Add a few cubic centimeters of sulfuric acid to the sugar product and decarbonize in the usual way at 1000° F. Add a few drops of sulfuric acid to the carbon-free ash; and drive off the excess acid over a free flame. Heat the resulfated ash at 1480° F. for 1 hour in a muffle furnace, cool in a desiccator, and weigh.

To test this procedure on a wide variety of samples, a method was devised for the carbonization of large amounts of low-ash samples.

Drop Method. For samples of low ash content, the amount of sample carbonized and ashed must necessarily be large if an appropriate weight of ash is to be obtained.

The solution of the sugar product (say at 50° Brix) plus a few cubic centimeters of sulfuric acid was allowed to drop slowly from a pipet into a platinum dish heated over a small open flame so as to bring about the dropwise carbonization of the sample without any sputtering. In this way some 60 to 100 grams of the sample were carbonized in a dish of 100-cc. capacity. The admixture of the acid with the sample facilitated the charring of the drops in the heated dish. The rate of dropping was regulated by a screw clamp which saddled a piece of rubber tubing placed over the top of the pipet.

Precision of Standardized Method. Duplicate ash determinations agree to within 0.5 per cent. Where the ash weight was too low for this precision, the results checked within the precision of weighing. A few typical results are shown in Table IV. The method was successfully applied to char-treated liquors.

Precautions. As it is not practicable to eliminate the temperature gradient in the muffle furnace, trouble from this source must be minimized by using one zone (say two or three platinum dishes deep) in the muffle for all determinations.

Too rapid heating is the source of loss of sample by spattering in the decarbonization process, as well as in driving off the excess sulfuric acid after resulfation. Some charred matter is lost if the carbonized sample is inserted into too hot a muffle furnace [1000° F. (538° C.) is recommended].

Conclusions

The sulfated ash method using resulfation of the ash is capable of giving results differing by 17 per cent or more, depending on the time and temperature of heating of the resulfated ash.

The heating of the resulfated ash for 1 hour at 1480° F. (804° C.) yields all the sulfatable metals as sulfates except iron and aluminum, which are completely decomposed into the oxide. Duplicate results agree to 0.5 per cent when the ash weights can be determined with that precision.

Large amounts of low-ash samples can be carbonized by using the drop method. In this way ash determinations can be carried out with great precision on low-ash samples.

No account is taken of the chemistry of phosphates. There is evidence that $Ca_3(PO_4)_2$ on treatment with sulfuric acid yields sulfate and pyrophosphate, with a gain in weight depending on the amount of transformation.

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Effect of Time on the Iodometric Method of Sugar Analysis

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THE iodometric method of sugar analysis is based upon the oxidation of aldose sugars to their corresponding acids by an alkaline solution of iodine according to the following reaction:

$$RCHO + I_2 + 3NaOH \longrightarrow RCOONa + 2NaI + 2H_2O$$

Since ketose sugars are only negligibly affected under controlled conditions, a number of investigators (*1*, *2*, *5*) have in this way proposed a method of identifying and quantitatively determining aldose sugars in the presence of ketoses. There is a voluminous literature concerning the merits and demerits of various alkali media, while investigators have apparently touched only sparingly upon the question of the relative ease by which different members of aldose sugars are oxidized under identical conditions.

Using sodium carbonate as an alkaline medium, Cajori (*2*) calls attention to the fact that the oxidation of maltose by iodine proceeds more slowly than the oxidation of glucose. Where glucose was completely oxidized in 25 minutes, maltose under the same conditions required 35 minutes. This question of time is an important one and should not be overlooked. The author presents data showing the relative length of time between the oxidation of glucose and lactose by an alkaline solution of iodine under the same conditions.

Chemicals

All chemicals used were c. p. quality corresponding to the following descriptions:

Iodine-potassium iodide solution: 12.69 grams of iodine plus 16.60 grams of potassium iodide, dissolved in distilled water and diluted to a liter.

Sodium thiosulfate solution: 24.8 grams of sodium thiosulfate pentahydrate, dissolved in distilled water, heated to boiling, cooled, and diluted to 2 liters.

Sodium hydroxide solution: 0.1 *N* sodium hydroxide, prepared from the corresponding saturated solution free from carbonate.

Glucose: The $[\alpha]_D^{25°}$ of the glucose (10 grams in 100 cc. of solution) was found to be 52.45.

Lactose monohydrate: The $[\alpha]_D^{25°}$ of the lactose monohydrate was 52.90.

Sucrose: Optical measurements showed it to be 99.68 per cent pure.

Potassium dichromate solution: The potassium dichromate was recrystallized from water and dried overnight in an oven at 100° C., after which 3.8639 grams were dissolved in distilled water and diluted to 1 liter. This solution was used as a primary standard against which the thiosulfate solution was standardized.

Starch solution was prepared fresh daily.

Procedure

The procedure adopted was essentially that employed by Kline and Acree (*3*). Twenty-five cubic centimeters of the sugar solution were pipetted into a 250-cc. ground-glass stoppered flask, to which were added the iodine and sodium hydroxide solutions successively in approximately 4- and 7-cc. portions, respectively, with shaking after each addition. All the experiments were performed at 25° C. The length of time indicated in Tables I to V was reckoned from the time the iodine and alkali were added to the sugar solution until the solution was made slightly acid with sulfuric acid, the iodine unused being titrated immediately afterwards with the standard thiosulfate solution.

Some typical results obtained with the dextrose are shown in Table I. It is significant to note that 8 minutes is the optimum length of time for practically complete oxidation under the conditions employed. When a shorter length of time was allowed incomplete oxidation resulted, while on the other hand, if the oxidation was prolonged beyond 8 minutes, overoxidation was indicated.

Table I. Typical Results with Dextrose

(100.0 mg. of dextrose, 35 cc. of 0.1 *N* sodium hydroxide, and 20 cc. of 0.1 *N* iodine)

Time of Reaction	Dextrose Found	Error
Min.	*Mg.*	*Mg.*
8	99.5	−0.5
	99.3	−0.7
	99.6	−0.4
	99.6	−0.4
	99.5 ± 0.1	

Table II. Typical Results with Lactose

(100.0 mg. of lactose·H_2O, 35 cc. of 0.1 *N* sodium hydroxide, and 20 cc. of 0.1 *N* iodine)

Time of Reaction	Lactose·H_2O Found	Error
Min.	*Mg.*	*Mg.*
8	88.7	−11.3
	93.6	−6.4
	96.1	−3.9
	92.0	−8.0
	91.1	−8.9
	88.3	−11.7
	95.6	−4.4
	92.2 ± 7.8	

Table III. Results with Lactose

(100.0 mg. of lactose·H_2O, 35 cc. of 0.1 *N* sodium hydroxide, and 25 cc. of 0.1 *N* iodine)

Time of Reaction	Lactose·H_2O Found	Error
Min.	*Mg.*	*Mg.*
8	98.6	−1.4
15	100.9	+0.9
15	99.2	−0.8
15	99.4	−0.6
15	99.4	−0.6
15	99.9	−0.1
15	100.0	0.0
30	102.6	+2.6
30	102.9	+2.9
30	102.6	+2.6
30	103.0	+3.0
60	103.1	+3.1
60	103.4	+3.4
60	103.6	+3.6
60	103.4	+3.4

Table IV. Results with Glucose and Lactose

(50.0 mg. of lactose·H_2O, 50.0 mg. of glucose, 35 cc. of 0.1 *N* sodium hydroxide, and 25 cc. of 0.1 *N* iodine)

Time of Reaction	Lactose·H_2O Found	Glucose Found	Error
Min.	*Mg.*	*Mg.*	*Mg.*
15	48.9	48.9	−1.1
	49.0	49.0	−1.0
	48.9	48.9	−1.1
	49.0	49.0	−1.0
	49.0	49.0	−1.0
	49.0 ± 1.0		

Table V. Effect of Sucrose

(50.0 mg. of glucose, 50.0 mg. of lactose·H_2O, 100.0 mg. of sucrose, 35 cc. of 0.1 *N* sodium hydroxide, and 25 cc. of 0.1 *N* iodine)

Time of Reaction	Lactose·H_2O Found	Glucose Found	Error
Min.	*Mg.*	*Mg.*	*Mg.*
5	50.0	50.0	0.0
5	49.2	49.2	−0.8
5	51.9	51.9	+1.9
15	53.8	53.8	+3.8
15	54.0	54.0	+4.0
15	52.9	52.9	+2.9

Employing the same length of time for the oxidation of lactose as for the oxidation of glucose, all other conditions being equal, it was found that about 8 per cent of the lactose was not oxidized, as is shown in Table II.

The results given in Table III show that even with an increase in the amount of iodine used the lactose is not completely oxidized in 8 minutes, but requires 15 minutes for optimum oxidation. Beyond 15 minutes high results occurred, similar to those reported by Slater and Acree (*4*) when excess alkali was used.

When a mixture of equal weights of glucose and lactose monohydrate was subjected to the iodometric method of sugar analysis as outlined in this report, it was found that after 15 minutes the oxidation of each sugar, calculated on the basis that each sugar is oxidized according to its chemical equation, was about 2 per cent short of complete oxidation. Typical results are shown in Table IV.

When 100 mg. of sucrose were added to the mixture of 50 mg. of glucose plus 50 mg. of lactose monohydrate, complete oxidation was indicated within 5 minutes and overoxidation within 15 minutes. This increase in oxidation cannot be attributed wholly to sucrose alone, since under similar conditions sucrose gave only an apparent amount of dextrose equivalent to 0.3 ± 0.1 mg. (5 measurements). Results are recorded in Table V.

Summary

Experimental data show that the oxidation of lactose monohydrate by an alkaline solution of iodine proceeds more slowly than does the oxidation of glucose.

A mixture of equal weights of glucose and lactose monohydrate is more difficult to oxidize by an alkaline solution of iodine than either separately, while a mixture of these sugars in the presence of sucrose gives complete oxidation within 5 minutes and overoxidation within 15 minutes.

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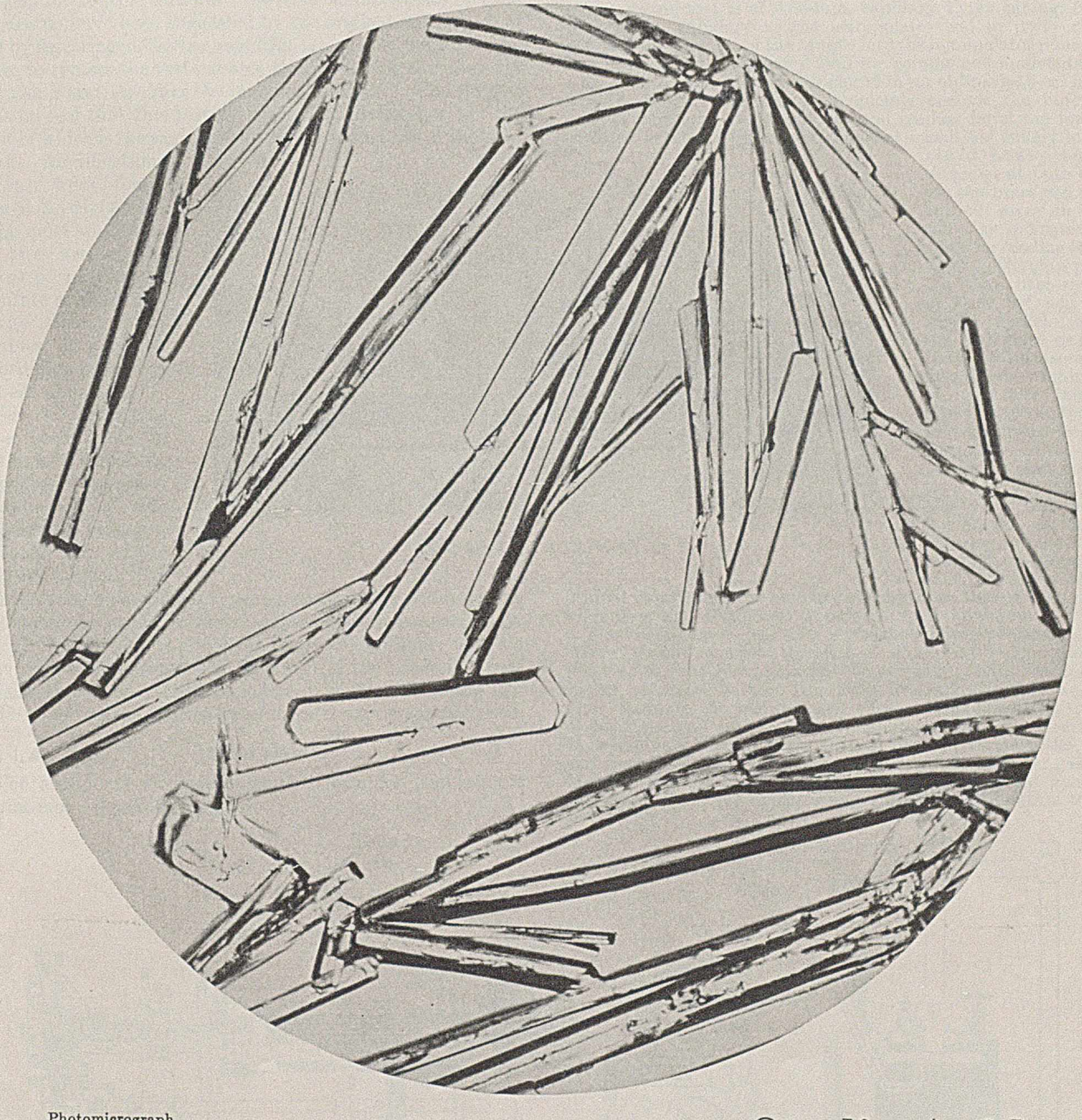
MICROCHEMISTRY



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A. A. Benedetti-Pichler

Oxalic Acid

A Micromethod of Gas Analysis Adapted for Biological Studies

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IN ADAPTING the principles of the method of microanalysis of gases, described by Blacet and Leighton (*1*), to biological studies, it became necessary to devise methods of sampling and transporting of samples which were suitable to such investigations. Whereas the original apparatus used by these authors is relatively simple, its manipulation is rather tedious for routine analysis. Several modifications of their apparatus have been suggested by the original authors (*2*, *3*) and by Swearingen, Gerbes, and Ellis (*4*), who used a horizontal buret to replace the vertical one, thus obviating the necessity of raising and lowering the mercury reservoir. The present authors feel that this feature has many advantages, not the least of which is the saving of the physical energies of the analyst. Modifications which were found over a 3-year period to be most applicable in the accomplishment of rapid and accurate analysis of a large number of samples have been incorporated into the present apparatus.

Improvements have been made in methods of sampling, transport of samples, introduction of the reagents into the gas, and activation of the mercury thread. The maintenance of a constant temperature in the water jacket eliminates one correction factor and tends to increase accuracy. Since four absorptions may be in progress simultaneously, the time ordinarily consumed in this part of the analysis is materially shortened. Certain inherent limitations of the dry method, as regards the analysis for water vapor, are discussed.

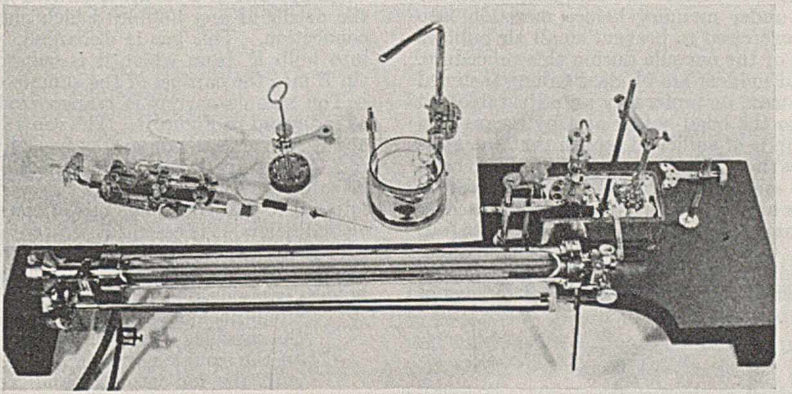

FIGURE 1. THE APPARATUS

Apparatus

The assembled analysis apparatus, sampler, and sample carrier may be seen in Figure 1.

The details of the microburet, drawn to scale, are shown in Figure 2. The whole unit is rotated around the horizontal axis of the capillary on the bearings, *NN*, by the lever, *P*. The unit may be easily removed from the bearings, for cleaning the buret, by release of the thumbscrews. The extent of rotation of the unit is limited by the adjustable stop, *H*, to prevent damage to the capillary arm. This arm is further protected by the support, *I*.

The microburet is of 0.66-mm. capillary Pyrex tubing, fused to a 2-mm. capillary at the manipulator end to prevent the accidental aspiration of the sample into the manipulator reservoir. The portion of the capillary used for volume measurements has a capacity of 0.18 cc. and is enclosed in an ordinary 50-cc. buret with scale divisions which completely encircle the buret to prevent parallax. Both capillary and reading buret are further enclosed in a heavy glass water jacket which fits snugly into a rigid brass tube, threaded at both ends for the brass end caps and cut away on both sides, as indicated, to allow for reading of the buret. The glass parts are thus held rigidly in place between two rubber gaskets when the end plate nearest the buret tip is screwed into place. Manipulation of the thumbscrew, *R*, results in pressure on the 18-gage Allegheny metal diaphragm, *L*, and activation of the mercury thread. The metal diaphragm is much superior to any of the numerous contrivances which the authors have utilized to activate the mercury thread, since there are no parts to replace and hysteresis is reduced to a minimum.

The manipulator reservoir is machined from a steel block, open at the end to receive the plate, *T*, which may be conveniently removed to allow for cleaning of the capillary. A thin cardpaper gasket, saturated with de Khotinsky wax, and sealed into place after warming the metal parts, effects a mercury-tight union of both the end plate and the diaphragm with the reservoir. In assembling, the capillary tube is inserted through the unit and spaces *VV* are filled with sealing wax over a rubber gasket. Mercury is introduced into the apparatus through the opening at the top of the manipulator reservoir and sealed with a tight-

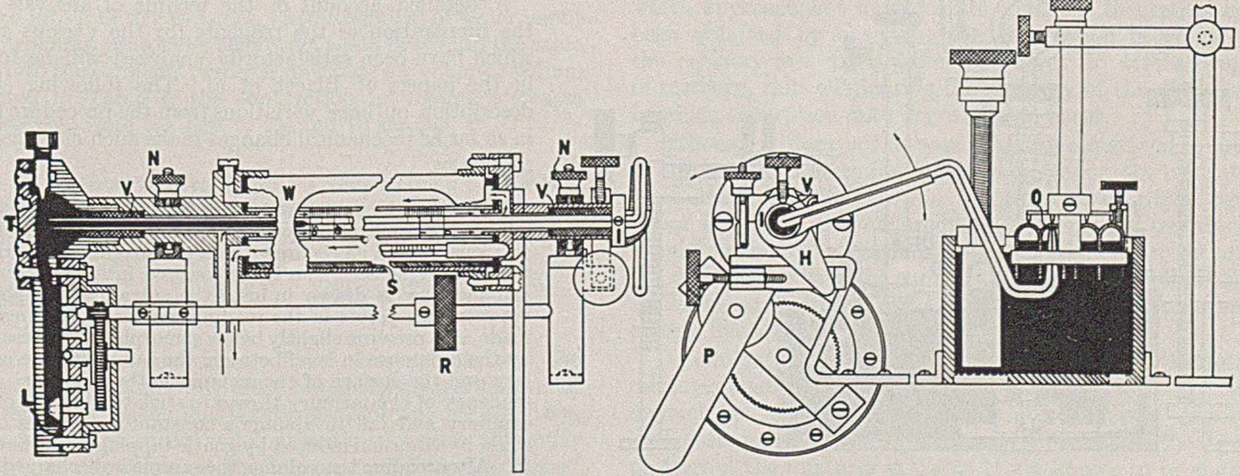

FIGURE 2. DETAIL OF BURET

fitting needle valve. As indicated by the arrows in the diagram, water from a constant-temperature bath circulates by gravity feed between the capillary and the reading buret and returns to the outlet through the space between the reading buret and the outer jacket. It empties into a reservoir from which it is elevated to the bath by a water pump. Forced pumping through the apparatus results in so much bubbling as to make reading difficult.

The relation of the microburet to the absorption reservoir is shown in Figures 2 and 3.

By rotation of the buret unit around its horizontal axis, the buret tip may be introduced into any capsule of either the sample carrier, *N*, or the capsule holder, *Q*, since the latter two have not only a vertical axis of rotation, but are free to describe an arc around their respective supporting rods.

Absorption of the various constituents is accomplished in the four capsules in the holder, *Q*, which is shaped like a segment of a circle to allow vertical passage of the bead holders when the capsules are turned toward the buret tip. The four capsules are held in the same horizontal plane by the stops, *A*. The capsules in this holder, as in the carrier, are held firmly in place by a coiled spring and ball bearing, *W*. The authors have found this to be a most satisfactory method of holding the capsules firmly and still allowing for easy removal. Steel forceps made from a sponge clamp are used to handle the capsules, which are filled by slowly inverting under mercury before insertion into the holder. Care must be exercised to prevent small air bubbles from adhering to the walls of the capsule during this procedure.

The interchangeable bead holders are of glass tubing fastened into the metal shank with wax, or preferably an adjustable rod of stainless steel fastened to the bead-holder arm by means of a set screw. The platinum tip is of sufficient length that the glass portion of the holder does not enter the sample. The bead holders are of uniform size and shape and held in fixed position by two pins upon the cross arm *T* (Figure 3) which is raised or lowered by the rack and pinion. It is thus possible to insert four beads into the absorption capsules without any bead coming in contact with the inner surface of the capsules. As reported repeatedly, such an occurrence ruins the analysis. The level of the mercury in the reservoir may be changed by raising or lowering the Bakelite block, *K*. This provision is necessary in order to maintain a constant level of mercury in the reservoir.

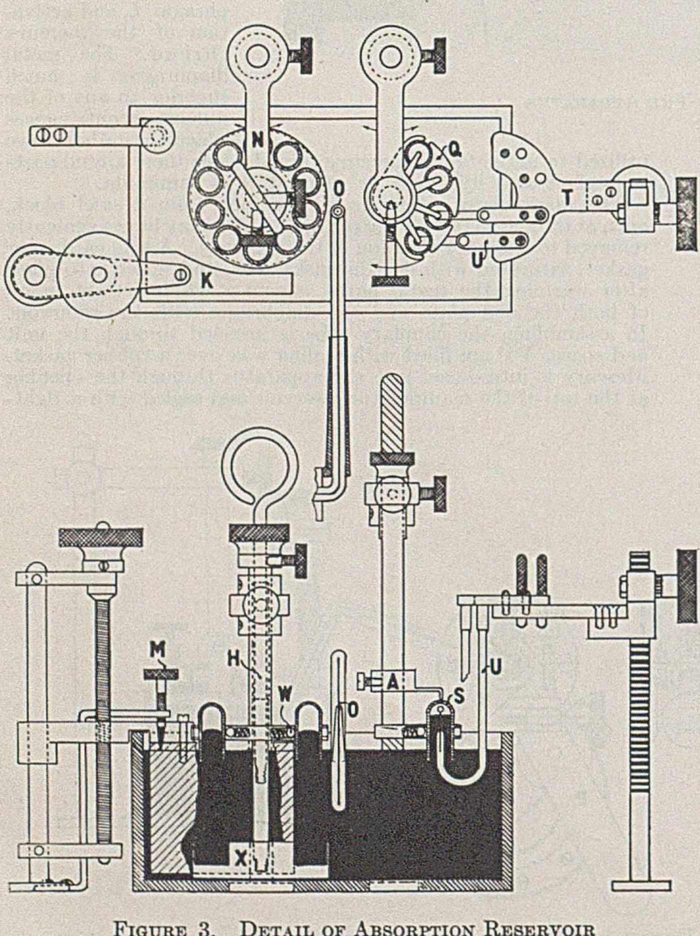

FIGURE 3. DETAIL OF ABSORPTION RESERVOIR

Sampling, Transporting, and Drying the Gas

The sampler in Figure 4 was devised for convenience in taking a large number of samples from gas depots in the skin or some body cavity where 2 or 3 cc. of gas were available for each sample. If desired, it could be made on a scale to handle smaller volumes.

The needle, *A*, with lateral openings near the tip, is fastened into the short section of glass capillary with a metallic oxide dental cement. Before sampling, the needle unit, which is detachable to allow of sterilization, is connected to the sampler by a short section of gum-rubber pressure tubing. The entire apparatus, excepting the needle, is then completely filled with mercury. The mercury is activated by pressure exerted on the heavy gum-rubber tubing enclosed in the brass tube by the thumbscrew, *G*, the action being similar to that of a fountain pen pouch in its barrel. The diagrams in Figure 4 are largely self-explanatory. Stopcock *C* is of convenience in cleaning the apparatus without dismantling the reservoir.

After the needle is introduced into the source of the gas to be sampled, 1 or 2 cc. are aspirated into bulb *M* to wash air from the needle or any bubbles which may be trapped at the rubber connection. This gas is discarded. The sample is then drawn into bulb *R*, from which it is subsequently discharged through tip *E* into the capsule of the sample carrier.

The sample carrier is transported in the mercury reservoir as indicated in Figure 4. The central shaft of the carrier rotates about its vertical axis and is fixed by the thumbscrew, *Z*. The rod, *H*, is threaded into the Bakelite shaft and trough, *X*. Release of the thumbscrew, *P*, allows the trough to be raised or lowered to seal the open ends of the sample capsules. As is discussed below, it is essential, if accuracy is not sacrificed, that all water vapor be removed prior to introduction of the sample into the microburet. By means of the rack and pinion, four bead holders carrying phosphorus pentoxide beads may be introduced simultaneously into four samples. Accurate centering of the capsules over the beads is obtained by bringing a mark on the sample carrier into a definite positional relationship with the indicator, *F*, and fixing thumbscrew *Z* prior to insertion of the bead holders into the mercury. The whole carrier may then be swung clear on its supporting shaft to allow insertion of the bead holders into the mercury.

If two sample carriers are available, dehydration of four samples may be accomplished while the analysis of four others is in progress. Extra carriers are also of value in collecting and storing numerous samples. After removal of water vapor, trough *X* is elevated into position to seal the capsules, the entire carrier is transferred into the large absorption reservoir of the analysis apparatus, and the trough is lowered away from the capsules. The level of the mercury in the reservoir is then brought to the ivory tip, *M*, by raising or lowering the Bakelite block, *K*.

The Analysis

A detailed account of the technic of analysis and the preparation of the reagents for the various gases which have been satisfactorily analyzed will be found in the papers of Blacet et al. The following short description outlines variations from the procedure only in so far as mechanical changes make such clarification necessary.

The tip of the dry mercury-filled capillary is introduced into one of the capsules of the carrier and a sample of the previously dried gas is drawn to a predetermined mark on the reading scale. The tip is lowered into the reservoir and mercury is drawn in until the entrapped sample lies between two points in the reading scale. All readings are made at a pressure slightly below atmospheric, represented by the difference in level between the sample in the capillary and the surface of the mercury in the reservoir. The tendency of the mercury thread to stick to the walls of the capillary and fail to assume a constant pressure is overcome by vibration induced by gentle tapping of the handle, *P*. After reading the volume, the sample is discharged into a mercury-filled capsule in holder *Q* (Figure 3). Four

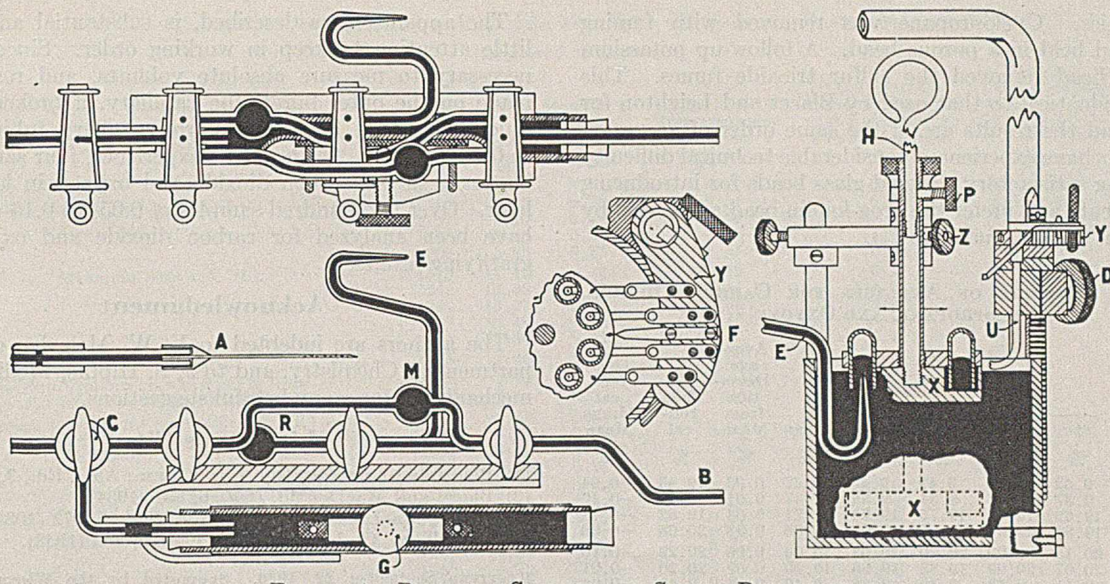

FIGURE 4. DETAIL OF SAMPLER AND SAMPLE RESERVOIR

samples are measured thus, care being taken to adjust the mercury level to the ivory tip, *M*, at each reading.

The dry reagent for the particular constituent to be removed is fused into the platinum loops of the four bead holders and they are placed in position under the mercury. Capsule holder *Q* is now rotated into position over the four bead holders and the beads are elevated into the gas sample. Following absorption, the residual gas is drawn into the buret, the volume reading made, and the gas discharged into the same capsule. Particular care at this reading is taken to see that the mercury level is the same as during the original reading. The position of the thumbscrew, *R*, in relation to the handle, *P*, is such that both raising and lowering of the buret tip and the activation of the mercury thread are accomplished without change of position of the right hand, thus leaving the left hand free to alter the position of the capsules in relation to the tip.

Discussion of Results

Blacet and Leighton stress the fact that the normal vapor pressure of water cannot be assumed to exist in these reacting systems. They did not, however, lay particular emphasis upon the necessity of keeping the microburet absolutely free from moisture, although this may be inferred from their data.

The representative results in Table I indicate the source and magnitude of the error which occurs in the analysis when a wet gas is introduced into a dry buret and vice versa. Four wet samples of identical composition were measured successively into the capillary, which was initially dry, and discharged into four dry capsules. After removal of water vapor by phosphorus pentoxide, they were again drawn, in the same order, into the capillary (which is now wet) for volume reading. As noted in Table I, the contraction in volume increases progressively from the first to the fourth sample.

TABLE I. EFFECT OF INTRODUCING A WET SAMPLE INTO A DRY BURET ON THE SUBSEQUENT ANALYSIS FOR CARBON DIOXIDE

Sample	1	2	3	4
	%	%	%	%
P_2O_5 absorption	0.20	0.50	0.72	0.83
KOH absorption	7.42	7.22	7.05	7.05

The contraction in volume of the first sample was the smallest because it not only contributed the greater portion of its water vapor to the initial saturation of the dry capillary, thus reducing the initial volume reading for that particular sample, but also took up the largest quantity of adsorbed water when reintroduced into the wet capillary after dehydration. That such an explanation is a tenable one is evident from the progressive diminution in contraction which parallels the former increase when the four samples are subsequently exposed to a potassium hydroxide bead. This bead removes not only the carbon dioxide present, but also the water vapor which was contributed during last contact of the sample with the wet capillary, thus introducing an error in the analysis for carbon dioxide. It might appear to be theoretically possible to determine the absolute quantity of water vapor in any given gas, if the analyst started with a dry capillary and made several passes and absorptions until the capillary was again dry, the result for water vapor being obtained by adding the successive contractions in volume. The authors have never succeeded, however, in even approaching the theoretical figure for water vapor in air saturated at room temperature. It appears that as the sample is drawn into the dry buret, the majority of water vapor is adsorbed onto the dry walls of the capillary arm before the reading portion of the buret is reached. The initial volume determination at this point is in reality made on the dry gas plus the small amount of water vapor which has escaped adsorption in the arm. As might be expected, only a very small contraction in volume is obtained, even though the adsorbed water vapor be subsequently removed from the arm by successive passes, since the total water present in the original sample was not included in the initial volume measurement. Values for water vapor which approach but do not quite equal the theoretical have been obtained by observing the contraction in volume in the capillary arm after sealing the buret tip with a droplet of mercury, thus eliminating the majority of the dead space in which adsorption onto dry walls can occur.

Although it does not appear that the apparatus is suited to the accurate determination of water vapor, the utilization of chemical reactions within the capsule, in which water vapor is one of the end products, is seemingly permissible providing this constituent is removed prior to aspiration of the residual gas into the capillary for volume determination. As discussed by Blacet and Leighton even this procedure has certain limitations.

Determinations were done in quadruplicate on theoretical mixtures made by diluting a given quantity of the dry commercial gas with a known volume of commercial nitrogen, both gases being measured in the microburet. The theoretical purities of the mixtures in Table II are known to be slightly in error, since the commercial gases contain small quantities of impurities. Cyclopropane was removed with fuming sulfuric acid held in a porous bead. A follow-up potassium hydroxide bead removed the sulfur trioxide fumes. This method is identical to that used by Blacet and Leighton for ethylene and the results are of the same order of accuracy. The authors have experienced considerable technical difficulty in preparing satisfactory sintered-glass beads for introducing liquid reagents and prefer the grog-kaolin bead advocated by Swearingen, Gerbes, and Ellis (*4*).

TABLE II. RESULTS OF ANALYSES FOR CARBON DIOXIDE, CYCLOPROPANE, AND OXYGEN

Gas Sample	Determinations				Mean	Average Deviation from Mean	Theoretical	Theoretical Minus Mean
	1	2	3	4				
	%	%	%	%	%	%	%	%
CO_2	9.52	9.43	9.49	9.45	9.47	0.03	9.43	+0.04
	9.37	9.38	9.34	9.38	9.37	0.01	9.47	−0.10
	19.62	19.72	19.75	19.75	19.71	0.04	19.82	−0.11
	19.84	20.00	20.07	20.09	20.00	0.08	20.08	−0.08
C_3H_6	20.15	20.09	20.00	20.02	20.06	0.05	20.22	−0.16
	20.07	20.09	19.83	19.96	19.99	0.09	20.20	−0.21
	9.41	9.43	9.40	9.35	9.40	0.02	9.46	−0.06
O_2 in laboratory air	20.77	20.71	20.73	20.80	20.75	0.03	20.90	−0.15

The apparatus, as described, is substantial and requires little attention to keep in working order. Since it is not necessary to measure absolute volumes, and readings are made on the outer buret, the capillary, if broken, may be quickly replaced by any uniform capillary tubing of 0.5- to 0.7-mm. bore. With a little experience, four samples may be analyzed for carbon dioxide and oxygen in less than 1 hour. Over five hundred samples of 0.05- to 0.15-cc. volume have been analyzed for carbon dioxide and oxygen with gratifying results.

Acknowledgment

The authors are indebted to V. W. Meloche, of the Department of Chemistry, and to J. S. Hipple, Medical School mechanician, for many helpful suggestions.

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Microdetermination of Zinc

Comparison of Spectrographic and Chemical Methods

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THIS study was undertaken to analyze various plant materials for zinc by two different methods of analysis and to compare the results. The chemical method which was followed employs an iodometric titration (*1*) and is often used for the determination of zinc in plant materials. The spectrographic method which was used (*2*) has been shown feasible for this determination, but is not so well known.

Approximately forty samples have been analyzed by both methods and the results appear in Table I. For about half the samples, there has been fair agreement, but the analyses show wide differences for many of the other samples. In nearly all cases where differences occurred, the spectrographic analyses gave higher results than did the chemical analyses. In an attempt to explain these differences, various possible sources of errors have been considered.

Particularly careful homogenization of the ash of the samples before separating into two portions for the analyses by the two methods has reduced the error from this factor to a minimum.

Possible sources of error in the spectrographic method are: (1) contamination, from the internal standard or from the graphite electrodes; (2) nonuniform distribution of the internal standard throughout the sample; (3) variation of exposure conditions (wandering of the arc, change of line voltage, etc.); (4) influence of varying major constituents of the ash on volatility and "excitability" of the zinc atoms; (5) photometric errors.

The first factor may be controlled by spectrographic examination of the tellurium and of the graphite electrodes for zinc. The influence of the second factor may be lessened by careful homogenization. The fourth factor is to be discussed in another paper, but its effect in all cases studied thus far is not as great as the third factor.

The dispersion of the results of replicate analyses is a criterion of the influence on the method of the second, third, and fifth factors. Some calculated probable errors of the spectrographic method are shown in Table II.

Three-fourths of the samples in group B in Table II had a calculated probable error of less than 10 per cent of the mean, while the average calculated probable error for all sixty-one samples was 8.3 per cent of the mean.

Possible sources of error in the chemical method are: (1) incomplete extraction of zinc, either (a) in the first extraction of the original sample, or (b) in dissolving the zinc sulfide precipitate; (2) contamination, from the various reagents; (3) incomplete precipitation of zinc; (4) precipitation by hydrogen sulfide of other metals which would affect the titration; and (5) titration errors.

As to the first factor, qualitative spectrographic examination of residues from the original hydrochloric acid extraction (the first procedure in the chemical method) of nineteen samples has shown zinc in every residue (last column of Table I, which also gives quantitative spectrographic analyses of eight of the residues). It will be noted that zinc was found in the residues of some samples even though the analyses for the total zinc by the two methods agree. This inconsistency is apparently due to one of the other error factors. Obviously, when only a very small proportion of the ash is insoluble in the acid, the hydrochloric acid extraction procedure may be sufficient, but it seems indicated that a modification of the extraction procedure will be necessary when plant samples with large proportions of acid-insoluble matter are encountered, if a true value of the zinc content is to be obtained.

In view of the data given above, studies of the influence on the chemical method of the other error factors are being held

TABLE I. COMPARISON OF ANALYSES FOR ZINC ON VARIOUS PLANT MATERIALS

(Expressed on ash basis)

Identification	Sample No.	Ash	Mean of 2 Chemical Analyses	Mean of 5–10 Spectrographic Analyses	Calculated Probable Error[a] of Mean of Spectrographic Analyses	Residue from Chemical Analyses after HCl Extraction of 1 G. of Ash	Zinc Found in Residue with Spectrograph
		%	*Mg./g.*	*Mg./g.*	%	*Gram*	*Mg.*
Test sample	1244		0.21	0.29	6.9	Not weighed	Present
Isopappus divaricatus (Nutt.) T. & G.	1266	4.45	0.26	0.38	6.5	Not weighed	Present
	1267	4.19	0.42	0.40	13.0	Not weighed	Present
	1268	5.03	0.21	0.38	11.5	Not weighed	Present
	1269	5.08	0.38	0.45	13.0	Not weighed	Present
Mexican clover, *Richardia scabra* St. Hil.	1240	14.10	0.11	0.12	5.0	Not weighed	Trace
	1242	13.38	0.11	0.11	4.5	Not weighed	Trace
	1243	13.23	0.09	0.09	4.4	Not weighed	Present
	1239	13.10	0.10	0.10	2.0	0.1991	0.04
	1241	13.36	0.14	0.15	4.0	0.1127	0.02
Pods from three species of Crotalaria	1245	3.96	0.28	0.60	5.0	0.0009	Present
Coffeeweed, *Emelista tora* (L.) Britton & Rose	1255	7.99	0.43	0.65[b]	[b]	0.0009	Present
Diodella teres (Walt.) Small	1256	8.33	0.27	>1.0[b]	[b]	0.3753	>0.37
Buzzard grass, *Heteropogon melanocarpus* (Ell.) Benth.	1257	3.96	0.51	>1.0[b]	[b]	0.0759	>0.08
Heterotheca subaxillaris (Lam.) Britton & Rusby	1263	5.82	0.43	0.22	4.3	Not weighed	Present
	1264	6.45	0.33	0.26	12.0	0.0095	0.005
	1265	6.41	0.27	0.22	5.5	0.0199	0.004
Mexican tea, *Ambrina ambrosioides* (L.) Spach.	1276	10.41	0.08	0.14	12.0	0.0211	>0.02
Crotalaria spectabilis Roth.	1258	10.18	0.22	0.18	3.3	0.0099	0.01
	1260	9.89	0.22	0.21	7.6	....	....
Crotalaria striata DC.	1246	4.70	0.26	0.29	6.9	....	....
	1247	4.34	0.15	0.10	3.0	....	....
	1248	5.73	0.21	0.34	10.0	....	....
	1249	4.52	0.25	0.57	7.5	....	....
Crab grass, *Syntherisma sanguinale* (L.) Dulac.	1250	6.94	0.26	>1.0[b]	[b]	....	....
Foxtail, *Chaetochloa lutescens* (Weigel) Stuntz.	1251	9.08	0.42	>1.0[b]	[b]	....	....
Flea bane, *Leptilon canadense* (L.) Britton	1252	5.78	0.56	0.52	3.3	....	....
	1253	6.17	0.51	0.67	6.7	....	....
	1254	5.89	0.43	1.0[b]	[b]	....	....
Crotalaria intermedia Kotschy	1261	5.59	0.25	0.77[b]	[b]	....	....
	1262	6.11	0.32	0.32	17.0	....	....
Ragweed, *Ambrosia elatior* L.	1270	7.53	0.44	0.79[b]	[b]	....	....
	1271	7.68	0.31	0.84[b]	[b]	....	....
	1272	7.39	0.28	0.57	11.5	....	....
	1273	7.15	0.20	0.24	13.4	....	....
	1274	7.30	0.10	0.43	9.1	....	....
Beggarweed, *Meibomia purpurea* (Mill.) Vail	1275	7.44	0.25	0.49	9.8	....	....

[a] Used here to indicate $0.6745\sqrt{\frac{\Sigma d^2}{n}}$.

[b] One (or more) of the replicates of this sample was off the calibration curve; hence instead of averaging the concentrations, this value was obtained by averaging the density ratios and then determining the average concentration of zinc. For the same reason no calculated probable error is given. A reasonable calculated probable error may be assumed as 15 per cent of the mean.

in abeyance until a more generally applicable extraction procedure has been developed.

Recently, Vanselow and Laurance (*4*) have proposed a modified combination of the two methods which have just been discussed. Their procedure permits the use of spectrographic methods for the determination of zinc in plant materials where only a grating spectrograph (or other spectrograph employing reflection surfaces) is available, since it employs a spectral line of zinc in the near ultraviolet (3345 Å.), whereas the spectral line of zinc employed in this study (2138 Å.) would be almost totally absorbed by the usual reflection surfaces. As pointed out previously (*2*), the zinc line at 3345 Å. is not as sensitive as the zinc line at 2138 Å. In fact, Ruthardt and Hirschmann (*3*) find that the 2138 Å. line is thirty to fifty times more sensitive than the 3345 Å. line. Thus, using the zinc line at 2138 Å., 20 p. p. m. of zinc (on the ash basis) may be determined by spectrographing the ash of the sample, but using the same technic with the 3345 Å. line, a minimum of 500 p. p. m. of zinc may be determined. Reducing the analyses from the ash basis to the dry basis obviously changes both results by the same ratio.

However, few plant ashes contain as much as 500 p. p. m. of zinc; hence to analyze plant materials for zinc using the 3345 Å. line, it is necessary to concentrate the zinc. Vanselow and Laurance find, using the 3345 Å. line and auxiliary chemical concentration, that 1 p. p. m. of zinc (on the dry basis) may be determined. Using the same technic with the 2138 Å. line, it would be possible to determine 0.04 p. p. m. of zinc.

There has never been a plant sample encountered at this laboratory which could not be analyzed for zinc by direct spectrography of the ash using the 2138 Å. line. Accordingly it has never been necessary to introduce any chemical procedure in this determination.

TABLE II. CALCULATED PROBABLE ERRORS[a] OF THE SPECTROGRAPHIC METHOD

	Sample No.	Number of Replicates	Calculated Probable Error of the Mean
			%
Group A (5 samples)	1892	30	4.4
	1893	30	3.8
	1894	28	5.1
	1895	44	8.5
	1896	30	6.1
	Different Samples	Replicates on Each Sample	
Group B (61 samples)	2	10	0–3
	13	5–10	3–5
	30	5–10	5–10
	14	5–10	10–15
	2	5	15–17

[a] Used here to indicate $0.6745\sqrt{\frac{\Sigma d^2}{n}}$

In addition to requiring ten to twenty times more sample per determination and much extra manipulation, the modification combines spectrographic error factors 1, 3, and 5, with error factors 1a, 2, and 3 for the chemical method.

Therefore, the inherent advantages of analyzing for zinc with direct spectrography of the plant ash using the 2138 Å. line (speed, sensitivity, elimination of chemical reagents, fewer manipulations, and fewer possibilities of introduction of contamination) are discarded, and the disadvantages of the chemical method are introduced by the lengthy procedure of the Vanselow and Laurance modified combination of the two methods. In fact, there seems to be no advantage in using the spectrograph for the final determination of zinc in place of the iodide titration in the chemical method.

Summary

Comparisons of analyses for zinc by a spectrographic method with analyses for zinc by a chemical method have been made on about forty samples of several varieties of plants. Agreement has been attained on only half the samples. It has been found that zinc is frequently retained in the residue from the hydrochloric acid extraction employed in the chemical method, which may explain some of the lack of agreement between the two methods. A modification of the extraction procedure seems indicated. A discussion of a modified combination of the two methods is given.

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The Microanalysis of Gases

IV. Nitrous Oxide and Methane

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THE methods of microanalysis of gases previously described (*1*, *2*, *3*) have been extended to include a new procedure for the combustion of gases. This procedure has been applied in the analysis for nitrous oxide and methane and presents the possibility of application in the case of several other gases. It is assumed that the preceding articles are available to the reader and in the interest of brevity reference to them will be made frequently.

Analysis with the aid of a combustion in which an explosion occurs (*1*) has two important limitations. In the first place, the mixture must exceed a certain minimum richness before an explosion will occur. This means that a small percentage of gases such as methane or ethane cannot be detected readily by this method. In the second place, certain gases do not burn completely upon the passage of a spark through the system containing them. These factors may be overcome, however, by carrying out the reaction on a hot surface placed in the system (*4*). This was accomplished, in the present instance, by means of a platinum loop shown in the operating position in Figure 1. Other details of the gas microanalysis apparatus have been described (*3*).

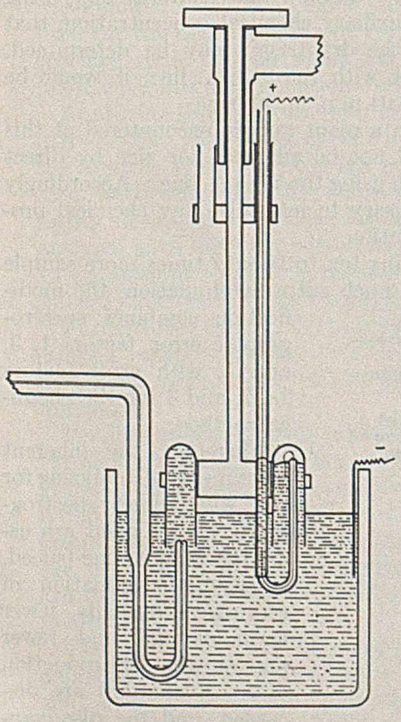

Figure 1. Combustion Coil in Operating Position

The mounting for the platinum was made from a piece of soft glass tubing of the same length and diameter as an absorbent holder (*1*, *3*). A 7-cm. length of 24-gage platinum wire was placed in the tube in such a manner that about 1 cm. of it extended beyond one end of the tube. Starting at this end, a narrow portion of the tubing was heated carefully, so that a fusion of glass to platinum occurred. By slowly moving the tube through the flame the platinum wire was encased in glass for a length of about 5 cm. It is important that no air bubbles be trapped in this process. The glass and wire were then bent to assume the shape shown in the diagram.

The exposed platinum was bent so that the top of the loop was about 1 mm. above the end of the glass and the tip of the loop could be immersed in the mercury within the gas holder. The top of the loop was worked down for a distance of 1 mm. by careful filing and the use of Crocus cloth, until the cross section was approximately one-third of the original. By placing a small amount of mercury in the unconstricted portion of the mounting, electrical contact could be made, as indicated. The large mercury reservoir served to complete the circuit.

In the use of this combustion coil, it was found convenient to have available an electrical potential of about 10 volts and to regulate the glow of the coil by means of a slide wire rheostat placed in the circuit.

In any extensive program involving gas microanalysis it is necessary to save more samples than the main analytical apparatus can accommodate. The authors have solved this problem by using gas holder clips of the type sketched in Figure 2, which will fit on the side of any mercury reservoir in the manner indicated. The clip is made of iron with one piece of watch spring to hold it in place and another to support the gas holder. By means of the pneumatic trough previously described (*2*), gas samples may be transported, without danger of loss or contamination, from a storage reservoir to the analytical apparatus or vice versa.

Specific Methods of Analysis

Nitrous Oxide. It has been suggested that a satisfactory method of microanalysis for nitrous oxide in the presence of air would be very useful in the field of anesthetics (*6*). This problem has been solved by first removing the oxygen and moisture by means of phosphorus and potassium hydroxide (*1*) and then reducing the nitrous oxide with hydrogen gas by the well-known reaction in which nitrogen gas and water are produced (*4*). The procedure up to the analysis for nitrous oxide is identical with that described for oxygen (*1*).

Thereafter, a measured volume of pure hydrogen is added to the sample and the combustion coil placed in position as shown in Figure 1. After adjusting the coil so that a small amount of the glass insulation appears above the mercury surface, the current is turned on and regulated until the thin portion of the platinum wire appears reddish orange in color. With this condition it was found that in all cases complete reduction of the nitrous oxide took place within 4 minutes. Varying the excess of hydrogen does not seem to affect the accuracy of the results in any way and has little effect on the combustion time. Upon completion of the reaction, the coil is removed and fused potassium hydroxide introduced to remove the water vapor. The volume decrease which is now obtained is a direct measure of the amount of nitrous oxide present in the original sample.

In Table I are given typical results of the analysis of a nitrous oxide sample obtained by heating ammonium nitrate and collecting the gas over mercury after removing the water vapor by means of a carbon dioxide trap. The deviation from a 100 per cent sample is to be expected in this method of preparation of the gas (*5*).

Table II gives results obtained upon analysis of a sample made by diluting the sample represented in Table I with dry air. The theoretical percentage of nitrous oxide present is 20.01, calculated on the premise that the undiluted sample is 99.25 per cent nitrous oxide as indicated in Table I. The oxygen was removed as previously described.

Methane. It is frequently desirable to estimate the amount of saturated hydrocarbons in small gas samples which do not contain enough of these substances to give an explosive mixture with oxygen. The combustion coil herein described has made this type of microanalysis possible in the case of methane and there is little doubt but that the method may be applied to certain other gases.

The procedure is essentially the same as that employed in the analysis for nitrous oxide, except that the gas to be analyzed in this case is oxidized instead of reduced and hence an excess of oxygen, or carbon dioxide-free air, is added in place of hydrogen. After the water vapor has been removed, the carbon dioxide produced in the reaction is determined in the usual way. This, of course, represents the amount of methane in the original sample. Using a reddish orange coil, it was found that methane was oxidized completely within 2 minutes.

Table I. Analysis of Nitrous Oxide Prepared by the Decomposition of Ammonium Nitrate

Determination	Volume of Sample	Volume of Hydrogen	Nitrous Oxide	Deviation from Mean
	Cu. mm.	*Cu. mm.*	%	%
1	53.73	71.77	99.05	−0.20
2	54.58	71.78	99.56	+0.31
3	54.31	71.20	98.92	−0.32
4	54.13	76.49	99.48	+0.23
		Av.	99.25	±0.27

Table II. Analysis of a Mixture of Nitrous Oxide and Dry Air

Determination	Volume of Sample	Volume of Hydrogen	Nitrous Oxide	Deviation from Mean	Deviation from Theoretical
	Cu. mm.	*Cu. mm.*	%	%	%
1	54.79	47.89	19.60	−0.24	−0.41
2	57.07	50.37	19.96	+0.12	−0.05
3	56.27	49.44	19.87	+0.03	−0.14
			Av.	±0.13	−0.20

Table III. Analysis of Methane Prepared from Sodium Acetate and Soda Lime

Determination	Volume of Sample	Methane	Deviation from Mean
	Cu. mm.	%	%
1	41.91	96.42	+0.18
2	40.15	96.00	−0.24
3	39.98	96.20	−0.04
4	39.69	96.35	+0.11
	Av.	96.24	±0.14

Table IV. Analyses of Mixtures of Methane and Air

Determination	Volume of Sample	Methane Theoretical	Methane Determined	Difference
	Cu. mm.	%	%	%
1	62.06	56.52	56.61	+0.09
2	108.53	5.81	5.90	+0.09
3	101.56	3.18	3.22	+0.04
4	101.29	3.19	3.41	+0.22

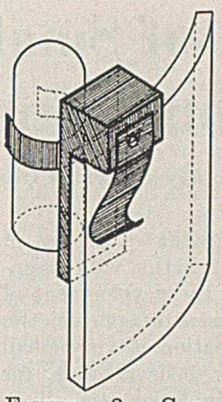

Figure 2. Gas-Holder Clip

Mounted on side of storage reservoir

In this work methane was prepared by heating a mixture of sodium acetate and soda lime and collecting the gas over mercury. Table III gives the results of the analysis of the sample thus prepared.

In order to test the value of the method when small amounts of methane are present in a sample, portions of the gas were diluted with known volumes of air and then analyzed. The data thus obtained are shown in Table IV. The theoretical percentage is based on the assumption that the analysis represented in Table III is correct. The close agreement of the experimentally determined percentage with the theoretical appears to validate this assumption.

Discussion

The requirements of the combustion coil are such that it must necessarily be fragile. An attempt was made to attach the end of the loop to the glass insulation of the incoming wire, but for some reason which is not clear, it was more difficult to get the coil up to the desired temperature when this was done. However, with reasonable care one coil will last for a long time when made as described and, when the tip does break off, the rest of the wire can be salvaged in good condition by simply heating the glass and platinum to redness and plunging them into cold water.

The coil is so constructed that the gas may be brought to the desired temperature at the surface of the wire while the mercury and surroundings are kept relatively cool. Because of this the expansion of the gas volume is not great during the course of the combustion and the contamination of the sample, by adsorbed gases which may be driven from the glass surface, is reduced to a minimum. It is important that the glass-enclosed platinum extend beyond the lower bend in the apparatus; otherwise, foreign gases may be introduced into a sample by the development of minute cracks in the glass.

There was no evidence of the oxidation of mercury during the short time required for the reactions of nitrous oxide and methane. However, continuous operation of the coil for 15 minutes or more, gave some evidence of this reaction.

It would appear that this method of analysis may be applied generally in cases where combustible gases are involved. Hydrogen may be determined by the use of oxygen and oxygen may be determined by the use of hydrogen, etc. However, an attempt to analyze for butane by this method was not quantitatively successful. The time required for the reaction to go to completion was of such length that the entire system became hot and oxidation of mercury began to take place. It is possible that further experimentation with conditions would overcome these difficulties.

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Determination of Small Quantities of Nicotine by a Silicotungstic Acid Micromethod

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THE necessity of accurately determining quantities of nicotine of the order of 0.1 mg. in connection with greenhouse fumigation experiments prompted the development of the method to be described. Colorimetric and nephelometric methods are available for the determination of very small quantities of nicotine, but the author believes that, for directness, accuracy, and ease of manipulation, the silicotungstic acid micromethod described here has much to recommend it. Although determinations are started one day and completed the next, the actual time required for making each determination is short.

The silicotungstic acid method is ideal as the basis of a gravimetric micromethod. The solubility of nicotine silicotungstate is very low, the weight of the ignited residue is more than nine times that of the combined nicotine, and since the ignited oxides are not appreciably hygroscopic they can be weighed in an open crucible.

Bertrand and Javillier (*1*) were the first to use silicotungstic acid for the determination of nicotine by a volumetric method, and they suggested the possibility of its use in a gravimetric method. Chapin (*2*) later worked out the experimental conditions for the gravimetric method now recommended by the Association of Official Agricultural Chemists. Bertrand and Javillier observed that the solubility of nicotine silicotungstate is dependent on the acid concentration of the solution from which it is precipitated, and Chapin showed that loss of nicotine due to solubility of the silicotungstate is negligible in the macroprocedure. Preliminary investigation soon made it apparent that such loss could not be neglected in the microdetermination, as it is 10 per cent when 0.1 mg. of nicotine is precipitated from a solution containing 10 ml. of 0.05 *N* hydrochloric acid. For greatest accuracy it is necessary to know both the volume and the acid concentration of the solution from which the nicotine is precipitated and to apply the appropriate correction.

The effect of dilute hydrochloric acid on the solubility of nicotine silicotungstate has been reported elsewhere (*7*). For convenient reference the results are given in Figure 1. Although the solubility of the salt is at a minimum in 0.005 *N* hydrochloric acid, it is desirable to carry out the precipitation in 0.03 to 0.1 *N* acid, since crystal formation appears to be favored in more concentrated acid. For washing the precipitate 0.005 *N* acid can be used; this is slightly lower than the concentration adopted by the A. O. A. C.

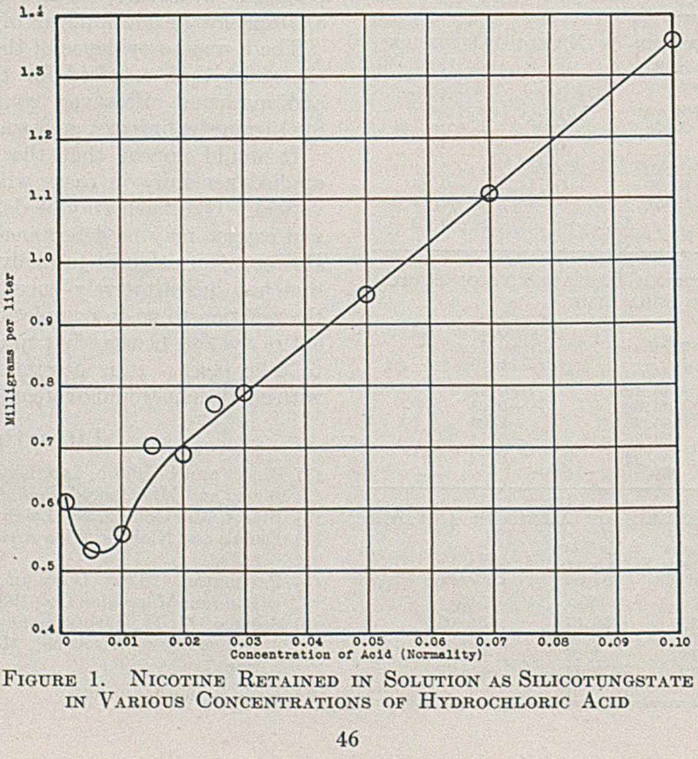

FIGURE 1. NICOTINE RETAINED IN SOLUTION AS SILICOTUNGSTATE IN VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID

The temperature of ignition is important, particularly with small quantities of nicotine silicotungstate, since nicotine is calculated from the weight of the residue, which is regarded as $SiO_2 \cdot 12WO_3$. Three factors are to be considered in the ignition: the complete burning off of the combined nicotine, the dehydration of silicic acid, and the prevention of volatilization of tungstic oxide. Hillebrand and Lundell (*4*) state:

> If both [Si and W] are to be determined in mixed oxides the analyst must therefore choose between getting high results for silica or low results for tungsten. Ordinarily the first choice is taken and causes less trouble, for when the two occur together the percentage of silicon is usually relatively small.

These authors recommend that the ignition be carried out below 850° C. in these cases. The present writer's experiments are in agreement with these conclusions, and in the case of nicotine silicotungstate one molecule of water represents only 0.63 per cent of the total weight of the residue. Pizer (*6*) recently reported 1000° C. as the desirable temperature of ignition of nicotine silicotungstate, but he used considerably larger quantities of nicotine silicotungstate, and 5 mg. was the smallest quantity of nicotine determined. In this work ignition has been carried out in an electric muffle at 650° C. for 30 minutes. Full dehydration of the silica does not occur, but burning of nicotine is complete and loss of tungstic oxide is prevented.

The foregoing conclusions are supported by the following experiment, which demonstrates that the residue can be cooled in air without taking up prohibitive amounts of water, and also by the results given in Table II: Approximately 0.2-gram samples of pure nicotine silicotungstate (*7*) were ignited at 650° C. in platinum crucibles for 0.5 hour. The tare platinum crucibles were treated in exactly the same way. The samples and tares were cooled in a desiccator over phosphorus pentoxide. The crucibles were weighed as soon as possible after removal from the desiccator and at intervals thereafter.

The results are given in Table I. It is evident that the weight becomes constant within 10 minutes. The increase during the first 10 minutes may be attributed to the film of water that condenses on any dry surface when exposed to air. The residue is slightly heavier than calculated for nicotine silicotungstate on the basis of the formula $SiO_2 \cdot 12WO_3 \cdot 2H_2O \cdot 2C_{10}H_{14}N_2 \cdot 5H_2O$. This is accounted for in part by incomplete dehydration of silica, although Bertrand and Javillier (*1*) state that the water of crystallization is not definitely five molecules but may vary with the humidity.

Table I. Effect of Time of Exposure on Absorption of Water from Air by Residue Obtained When Nicotine Silicotungstate Was Ignited for 30 Minutes at 650° C.

Exposure to Air	Residue Found on Ignition of Samples of Nicotine Silicotungstate: Sample 1	Sample 2
Minutes	*Gram*	*Gram*
2	0.16308	0.17270
5	0.16319	0.17279
10	0.16326	0.17286
30	0.16327	0.17283
60	0.16323	0.17286
120	0.16325	0.17282
180	0.16324	0.17286
120[a]	...	0.17281
Calcd.[b]	0.16253	0.17209
Weight of original sample	0.18827	0.19934

[a] After second ignition at 650° C. for 2 hours.

[b] Calculated as $SiO_2 \cdot 12WO_3 \cdot 2H_2O \cdot 2C_{10}H_{14}N_2 \cdot 5H_2O$ to $SiO_2 \cdot 12WO_3$.

Table II shows the results of two series of determinations of solutions containing from 0.5 to 0.1 mg. of nicotine in 10 ml. of 0.05 *N* hydrochloric acid. In one series the nicotine silicotungstate was ignited over a flame and in the other an electric muffle at 650° C. was used.

Table II. Analyses of Standard Nicotine Solutions

Method of Ignition	No. of Determinations	Average Nicotine Found[a]: Uncorrected	Corrected[b]	Calcd. Nicotine	Average Error: Uncorrected	Corrected[b]
		Mg.	*Mg.*	*Mg.*	%	%
Over flame at moderate red heat for 10 minutes	8	0.089 ± 0.002	0.099 ± 0.002	0.101	−12.0	−2.0
	9	0.189 ± 0.002	0.199 ± 0.002	0.202	− 6.4	−1.5
	9	0.289 ± 0.002	0.299 ± 0.002	0.302	− 4.3	−1.0
	12	0.489 ± 0.004	0.499 ± 0.004	0.504	− 3.0	−1.0
At 650° C. for 30 minutes	12	0.089 ± 0.002	0.099 ± 0.002	0.099	−10.0	0.0
	8	0.188 ± 0.002	0.198 ± 0.002	0.198	− 5.0	0.0

[a] Residue × 0.114.

[b] Corrected for loss of nicotine due to solubility of the silicotungstate at the rate of 0.001 mg. per ml. of 0.05 *N* hydrochloric acid.

Since the crucibles are weighed on different days, it is essential to use tares of the same density to compensate for variations in pressure, temperature, and humidity. The use of the usual glass lead-shot tares for porcelain crucibles was found to introduce an appreciable error due to these causes. The writer has used broken chips of porcelain to make the final adjustment of tares. Ordinary porcelain crucibles can be used as tares for the filterstick-crucible combination.

Experimental

Reagents. A 12 per cent solution of silicotungstic acid ($4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 22H_2O$), standard solution of hydrochloric acid for dilution to obtain proper acid concentration (this will vary with the experimental conditions), and solution of 0.005 *N* hydrochloric acid for washing the precipitate.

Apparatus. Microchemical balance (in this work a Kuhlmann balance, the rider of which was checked against a Bureau of Standards calibrated 10-mg. weight, was used). Porcelain crucibles with darkened interior and filterstick similar to those used in the sulfur microdetermination (*3*). The burets and volumetric flasks were calibrated to an accuracy consistent with the use to which they were put. To obtain the results given in Table II, standard solutions containing weighed amounts of pure nicotine in 0.1 *N* hydrochloric acid were used. The nicotine ($n_D^{22} = 1.5241$) was purified by repeated crystallization of the zinc chloride addition product and subsequent distillation *in vacuo*, according to the method of Lowry and Lloyd (*5*).

In weighing the samples of nicotine, precautions were taken to prevent absorption of moisture.

General Procedure. New crucibles and filtersticks should be boiled with dilute nitric acid and washed with distilled water before being used. The crucibles and filtersticks are then ignited to constant weight and the filtersticks removed and placed upright in a covered holder (*3*). In a crucible is placed an accurately measured aliquot containing the nicotine hydrochloride in 0.1 *N* hydrochloric acid, and the required amount of 0.05 *N* hydrochloric acid and water is then added to give a total volume of 10 ml. of 0.05 *N* acid. The solution is stirred with a short 2-mm. glass stirring rod while 0.1 ml. of the silicotungstic acid solution is being added (0.2 ml. of silicotungstic acid was used in precipitating 0.5 mg. of nicotine). The stirring rod is then removed and washed with a few drops of 0.005 *N* acid. The stirring rod should be cleaned with warm chromic acid each day before use, as otherwise particles tend to adhere to it. The crucibles are then covered and allowed to stand until the next day to ensure crystallization of the originally amorphous salt.

The liquid is filtered from the precipitate by means of the filterstick, and the walls of the crucible and filterstick are washed three times with approximately 1 to 2 ml. of cold 0.005 *N* hydrochloric acid. Before ignition the crucibles and filterstick are dried at 95° to 100° C. to remove excess water, which might cause spattering on ignition. For ignition the crucibles are placed within larger porcelain crucibles in an electric muffle at 650° C. for 30 minutes. Upon removal from the furnace the crucibles are cooled for 2 hours in a desiccator (no drying agent) and are then allowed to stand for 1 hour on a metal block within the outer balance case before weighing. The crucibles are weighed 5 minutes after they have been placed on the balance pan and the door has been closed. After weighing, the crucibles are ready for another run. It is unnecessary to remove the residue from the previous run, but great care must be taken to knock off all loosely adhering particles from the filterstick against the crucible wall before the filterstick is removed. In all operations the crucibles are never touched with the hands, platinum-tipped forceps being used. During filtration the crucible is placed on a watch glass which can be rotated to facilitate washing.

For general use it is convenient to scratch a mark on the inner wall of the crucible to indicate a volume of 10 ml. Precipitations have been made in concentrations up to 0.1 *N*, the appropriate correction being applied.

Summary

A micromethod for the determination of nicotine based on the precipitation of the silicotungstate is described. On the basis of eight to twelve runs each, solutions containing 0.1 to 0.5 mg. of nicotine were analyzed with an average accuracy of ±0.002 mg. It is necessary to correct the results for loss of nicotine due to the solubility of nicotine silicotungstate. The correction depends on the volume and acid concentration of the solution from which precipitation is made. The temperature of the ignition of the silicotungstate must be controlled; 650° C. has been found suitable for the micromethod. A concentration of 0.005 *N* hydrochloric acid is recommended for washing the precipitated nicotine silicotungstate, since its solubility is at a minimum at this concentration.

Acknowledgment

The author desires to thank Nathan L. Drake for his continued interest in this work.

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An Improved Semi-Micro and Micro-Carius Determination

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THE familiar method originated by L. Carius three-quarters of a century ago and still commonly employed for the elementary analysis of halogen in organic compounds suffers from several well-known disadvantages. A comparatively large sample is needed, proper sealing of the large bomb tube is difficult, and the apparatus is subject to explosion and inherently dangerous to handle because of the high pressures generated. On cracking off the end of the tube, glass chips often fall into the precipitate. Transfer and rinsing of the halide from the bomb tube and small specimen tube are inconvenient, and a second transfer to the Gooch crucible involves a further chance of loss.

Some of these difficulties have been mitigated by improvements which have been suggested from time to time. Adaptation to the micro scale is described by Pregl (*4*), the sample being weighed in small glass capillaries open at both ends. After cracking off the end of the bomb tube as usual, the contents are rinsed into a dish or the capillary is lifted out by means of a bent platinum wire, rinsed, and the halide siphoned directly from the bomb tube onto a micro filter tube. To obtain the same advantage of direct transfer of precipitate, H. Roth (*5*) introduces the unprotected sample by means of a long-stemmed funnel when dealing with substances unaffected by cold nitric acid. A semi-micromethod has been recently described by Clark (*1*), employing samples of approximately 25 mg. weighed to 0.02 mg. on a special semi-microbalance. After rinsing out the halide into a small beaker it is siphoned onto the filter tube. He has designed a small electric bomb furnace now on the market (The American Instrument Co., Inc., 774 Girard St., N. W., Washington, D. C.).

The procedure described below was developed 4 years ago, and sufficient results have now accumulated to show that the method is simple and reliable even in the hands of undergraduates. The weighings are done on an ordinary good analytical balance, adjusting the sensitivity and calibrating the weights to obtain an accuracy of 0.05 mg. Samples usually run from 25 to 35 mg., but have been varied from 20 to 100 mg. without change in the accuracy of the results.

The samples are weighed in small capsules of pure silver foil (fine silver foil, dead soft, about 0.0006 inch thick, obtainable inexpensively from the Peerless Roll Leaf Co., Inc., 911–17 New York Ave., Union City, N. J.) which effectively protects the substance from the nitric acid while the tube is being sealed, but dissolves on heating and supplies the necessary silver nitrate. No sample tube remains for removal, and the halide is siphoned directly from the bomb tube into the micro filter tube.

To obviate any chance of glass splinters contaminating the precipitate, the top is melted from the bomb tube in a flame. The procedure used here is somewhat similar to that recently described by Unterzaucher (*5*), but seems more reliable and convenient.

Procedure

SEMI-MICRO SCALE. A capsule is made by winding a strip of silver foil about 2 × 3 cm. around a 4-mm. glass rod, folding in the edges several times to make a tight seam, and pressing the end down firmly to form a cup. This is weighed to 0.05 mg. and contains about 90 mg. of silver. A 25- to 35-mg. sample is placed in the cup, which is closed by pressing the sides together and folding down the top edge, and finally is rolled into a tight coil and weighed again.

The bomb tube is made by sealing and rounding one end of a piece of ordinary Pyrex tubing 30 cm. long by 15 mm. outside diameter, not too thin-walled. After cleaning with acid and drying, 2 cc. of concentrated nitric acid (sp. gr. 1.42) free from halogen are introduced through a long-stemmed funnel. The capsule containing the sample is dropped in and the tube sealed in the oxygen flame, the action of the acid on the silver at room temperature being so slow that the sample is completely protected. Instead of the usual long capillary seal, it is easier to let the tube taper gradually to a point over 3 to 5 cm., and this facilitates rinsing down the walls after opening.

The heating can be carried out in any bomb furnace, making sure that the tube is inclined at a sufficient angle to keep the materials in the bottom. Here an ordinary electric bomb furnace is employed. The tube is wrapped in a sheet of paper and a wire looped around for convenience in drawing it from the iron jacket. The temperature rises gradually to 250° C. over about 3 hours and is held at that point for approximately the same time, and the tube is then allowed to cool in the furnace, conveniently overnight.

By means of the wire, the end of the tube is drawn slightly out of the iron sleeve and the tip of the seal is heated in an ordinary Bunsen flame till the very moderate pressure blows out an opening. The tube is then removed from the sleeve and the opening fire-polished. After cooling, a stream of water is directed into the tube to wash down any particles of halide, though as a matter of fact none are ever observed near the seal if the tube has been kept inclined. A piece of glass tubing about the same diameter as the bomb tube is inserted over the tapered end and sealed on roughly (Figure 1). The bomb tube is then heated at the shoulder and blown out into a thin-walled bulb; this can be blown in stages and may be very irregular. A hole is blown while the flame is playing on the thin side of the bulb and the flame then quickly worked around the bulb, drawing the glass apart. In this way the end of the tube can be quickly and easily cut off without danger of glass chips, leaving a flared edge around the opening.

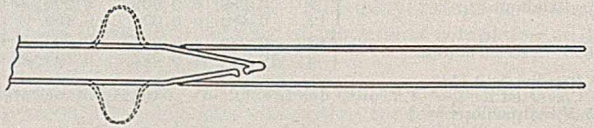

FIGURE 1. FLAME OPENING OF BOMB TUBE

Enough water is added to fill the bomb tube about one-third full and the contents are mixed by careful shaking. The halide can be filtered at once, but it is better practice to stand the tube for an hour in a beaker of hot water to coagulate the precipitate. After cooling, the halide is drawn directly from the bomb tube into a micro filter tube by the siphon method of Pregl (*4*). Any lumps should be broken up with the end of the siphon tube. The precipitate is rinsed several times with nitric acid (1 to 100) and then allowed to draw over through the siphon. The walls are rinsed several times alternately with dilute nitric acid and with 95 per cent alcohol until all the halide has been transferred to the filter. On completing the filtration, the siphon is removed from the filter tube, and that portion projecting into the tube is rinsed with water into the filter tube. The halide is finally washed with four half-filter-tube portions of distilled water.

The filter tube is then wiped with a damp cloth, placed in a wire holder for convenience in weighing, and slid into an ordinary glass adapter open at both ends. (The stems of the filter tubes were cut to 4 cm. to facilitate drying.) It is heated in the oven at 125° C. for an hour and allowed to cool for a half hour in the balance room. After removal from the adapter it is weighed to 0.05 mg. in the wire holder, which prevents rolling on the balance pan. By keeping the tube in the stoppered adapter, the final weight of one analysis can be used as the initial weight of the next. The bomb tube can be used for two more analyses before becoming inconveniently short.

MICRO SCALE. A series of analyses was made using samples of 6 to 10 mg., weighed in a slightly smaller silver capsule on the microbalance. After rolling between the fingers, the capsule is left on the balance pan for 10 minutes to reach constant weight. The bomb tubes are constructed of 10-mm. tubing and the amount of nitric acid is reduced to 1 cc. They are charged, heated, and opened, and the precipitate is transferred to the filter as before. Before the first weighing of any day the filter tube is wiped with a damp cloth, placed in the adapter, and heated in the oven at 125° C. The adapter is closed with cork stoppers and allowed to cool, and the filter tube wiped again with the damp cloth and left for a half hour on the pan of the microbalance before weighing. After filtration the identical procedure is followed, and this weight can be used as the first weight of any succeeding analysis on the same day. Obviously the drying block technic of Pregl could be employed if desired.

Table I. Results by Semi-Micromethod

Sample Mg.	Halide Mg.	Calcd. %	Found %	Difference %
p-Bromoacetanilide, $BrC_6H_4NHCOCH_3$				
22.30	19.80	37.34	37.79	+0.45
23.25	20.30		37.17	−0.17
48.50	42.30		37.12	−0.22
46.20	40.25		37.08	−0.26
26.55	23.30		37.36	+0.02
58.25	50.65		37.01	−0.33
23.70	20.80		37.36	+0.02
p-Chloroacetanilide, $ClC_6H_4NHCOCH_3$				
39.45	33.20	20.92	20.82	−0.10
58.25	49.10		20.85	−0.07
26.45	22.40		20.95	+0.03
43.10	36.00		20.66	−0.26
p-Nitrochlorobenzene, $ClC_6H_4NO_2$				
41.75	37.90	22.51	22.46	−0.05
29.85	27.00		22.38	−0.13
101.20	92.20		22.54	+0.03
61.05	54.75		22.18	−0.33
45.75	41.95		22.68	+0.17
20.75	19.15		22.82	+0.31
N-(γ-bromopropyl) phthalimide, $C_8H_4O_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2Br$				
31.45	22.00	29.82	29.77	−0.05
35.05	24.50		29.75	−0.07
37.15	25.95		29.73	−0.09
21.85	15.30		29.80	−0.02
63.00	44.05		29.76	−0.06
82.30	57.50		29.74	−0.08
Methyl-α-phenyl-β-bromo-β-benzoyl propionate (*2*), $C_{17}H_{15}O_3Br$				
37.25	19.90	23.03	22.74	−0.29
21.55	11.70		23.11	+0.08
19.65	10.60		22.96	−0.07
21.55	11.60		22.92	−0.11
Methyl-α,γ-diphenyl-α,β-dihydroxy-γ-chlorobutyrate (*3*), $C_{17}H_{17}O_4Cl$				
12.75	5.70	11.06	11.06	0
22.15	9.95		11.11	+0.05
20.80	9.25		11.00	−0.06

Table II. Results by Micromethod

Sample Mg.	Halide Mg.	Calcd. %	Found %	Difference %
p-Bromoacetanilide				
11.660	10.280	37.34	37.52	+0.18
10.710	9.395		37.34	0
10.666	9.370		37.39	+0.05
12.807	11.240		37.36	+0.02
p-Chloroacetanilide				
11.161	9.430	20.92	20.91	−0.01
7.156	6.095		21.07	+0.15
6.226	5.315		21.11	+0.19

The accuracy seems to be of the same order as the semi-microdeterminations. Slightly more time is required, so that economy of material is the only advantage of the micromethod.

Analytical Results

The data given in Tables I and II, obtained by undergraduate students, indicate that the degree of accuracy is about that normally expected. It is worthy of note that the use of a larger sample brings no corresponding increase in accuracy, showing that the errors in weighing are well within those inherent in the method itself. Of the few failures encountered, only two were not traced to faulty manipulation.

Summary

A simplified Carius method is described for the semi-micro- and microdetermination of chlorine and bromine in organic compounds. The sample is weighed on an ordinary analytical balance in a capsule of silver foil which dissolves and allows the halide to be siphoned directly from the bomb tube onto a micro filter tube. The bomb tube is opened with a flame which eliminates the danger of glass chips falling into the precipitate. The method is reliable and convenient and the results are of the usual order of accuracy.

Literature Cited

(1) Clark, *J. Assoc. Official Agr. Chem.*, 17, 483 (1934).
(2) Kohler and Goodwin, *J. Am. Chem. Soc.*, 49, 226 (1927); Kohler and Kimball, *Ibid.*, 56, 730 (1934).
(3) *Ibid.*, 55, 4637 (1933).
(4) Pregl, "Quantitative Organic Microanalysis," 2nd English ed., tr. by Fyleman, p. 149, Philadelphia, P. Blakiston's Son & Co., 1930.
(5) *Ibid.*, 4th German ed., p. 129, Berlin, Julius Springer, 1935.

Received August 20, 1936.

Preparation of Vehicle Films Free of Supporting Foundation

E. H. BAYOR and L. KAMPF
Division of Analyzing and Testing, Borough of Queens,
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IN THE analysis of paints, etc., useful information concerning their physical characteristics can be obtained by examination of a film of the vehicle. The following is a method of preparing such films: The vehicle must first be separated from the pigment by settling, centrifuging, or filtering with or without the aid of solvents or solvent mixtures. If a solvent is used, the solvent must subsequently evaporate so as not to change the nature of the vehicle. The separated vehicle is poured on a thin aluminum sheet and allowed to harden, and the aluminum is dissolved with dilute (1 to 10) hydrochloric acid to which a drop of platinum chloride solution has been added. The film is then washed and dried.

To avoid wrinkling of the film during preparation or afterwards, the authors found it practical to dip the four edges of the film in molten paraffin, after it dried on the aluminum sheet. This protects the aluminum underneath from the action of the acid bath and leaves a metal frame around the film.

Received November 3, 1936.

A Simplified Micro-Kjeldahl Apparatus

JOSEPH E. SCOTT AND EDWARD S. WEST
University of Oregon Medical School, Portland, Ore.

THE apparatus for the micro-Kjeldahl determination of nitrogen devised by Parnas and Wagner (*4*) is complicated and fragile as well as cumbersome to set up and manipulate: Recently Kirk (*3*) and Fife (*1*) have described different types of apparatus for the same purpose, which seem to represent improvements over that of Parnas and Wagner. For some time the writers have used an apparatus which may be of interest because of its relative simplicity, compactness, strength, and accuracy. Figure 1 shows the details of construction.

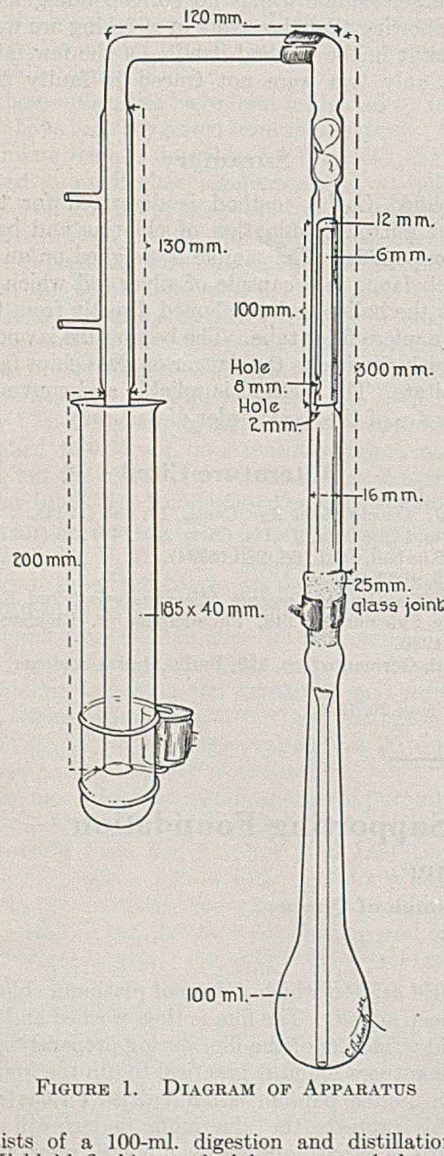

FIGURE 1. DIAGRAM OF APPARATUS

It consists of a 100-ml. digestion and distillation flask (a 100-ml. Kjeldahl flask) attached by a ground-glass joint to a distilling head composed of a West distilling trap (*6*) and a West condenser (*5*). The only part of the construction which may give trouble to the amateur glass blower is making the trap. As can be seen from the diagram, the trap consists essentially of a small sealed-in tube (about 6 mm.) with open end over which a small test tube, with a hole near the bottom, is inverted. There is a small water-return hole (about 2 mm.) in the bottom of the 6-mm. tube. The rim of the inverted test tube should have a few indentations in it (not shown) to facilitate return of water to the distilling flask. As can be seen, the vapor makes two 180° turns in passing through the trap. Two Pyrex bulbs are placed above the inverted tube to hold it in place and also to serve as additional baffles. The water condenser may be omitted if desired, though the writers have experienced less trouble with sucking back when the condenser is used. The distillation may also be carried out more rapidly with the condenser.

The sample to be analyzed is digested in the distilling flask according to the procedure of Harte (*2*).

After cooling, 25 ml. of water are added and the alkali tube is placed in the flask. The contents of the flask are further cooled if necessary and then 15 ml. of 65 per cent sodium hydroxide are carefully added from a pipet through the tube, forming a layer under the acid solution. The glass joint is moistened with water and the distilling head firmly set in place with the tip from the condenser just under the standard acid (10 ml. of 0.0143 *N* hydrochloric and 10 cc. of water) in the receiving tube. A vessel of cold water is placed around the distilling flask, which is then gradually shaken to mix the alkali and acid. The clamps (rubber-covered) holding the apparatus should be well tightened to hold the glass joint in place. The condensing water is turned on slowly and the flask is heated with a microburner. The alkali tube remaining in the flask serves as a boiling tube. A small U-shaped boiling tube may also be advantageously used, in addition.

Distillation is continued until solid sodium sulfate crystallizes out and the volume in the distilling flask has been reduced to about one-half. During the distillation the receiving tube should be moved down at intervals, so that the condenser tip never extends much below the surface of the acid. The last part of the distillation is carried out with the condenser tip just above the receiving acid. There is generally some bumping as the sodium sulfate separates, but with care this causes no trouble. After the distillation is complete, the tip of the condenser is washed down with a few milliliters of water and the excess acid in the receiving tube is titrated with 0.0143 *N* sodium hydroxide, using four drops of Tashiro's indicator (2 ml. of 1.0 per cent aqueous methylene blue mixed with 100 ml. of 0.04 per cent methyl red in 50 per cent alcohol). Blank determinations on the reagents gave about 0.07 ml. titration, correction for which was made in the calculations.

The titration is most efficiently carried out with the aid of a mechanical stirrer and buret which have been previously described (*7*). The stirring can be satisfactorily done, however, with a loop stirrer having a right-angle bend to serve as a handle.

TABLE I. ANALYSIS OF NITROGEN-CONTAINING SOLUTIONS

Substance	Nitrogen Present	Nitrogen Found	Error
	Mg.	*Mg.*	%
$(NH_4)_2SO_4$	0.997	0.987	−1.0
		0.993	−0.4
		0.993	−0.4
		0.991	−0.6
Urea	0.991	0.992	+0.1
		0.985	−0.6
		0.989	−0.2
Tyrosine	0.595	0.599	+0.7
		0.595	0.0
		0.591	−0.7
Creatinine	0.955	0.948	−0.7
	0.961	0.957	−0.4

Table I gives a series of unselected results obtained on ammonium sulfate, urea, tyrosine, and creatinine.

Literature Cited

(1) Fife, IND. ENG. CHEM., Anal. Ed., 8, 316 (1936).
(2) Harte, *Ibid.*, 7, 432 (1935).
(3) Kirk, *Ibid.*, 8, 223 (1936).
(4) Parnas and Wagner, *Biochem. Z.*, **125**, 253 (1921).
(5) West, IND. ENG. CHEM., Anal. Ed., 2, 199 (1930).
(6) *Ibid.*, 4, 445 (1932).
(7) *Ibid.*, 8, 62 (1936).

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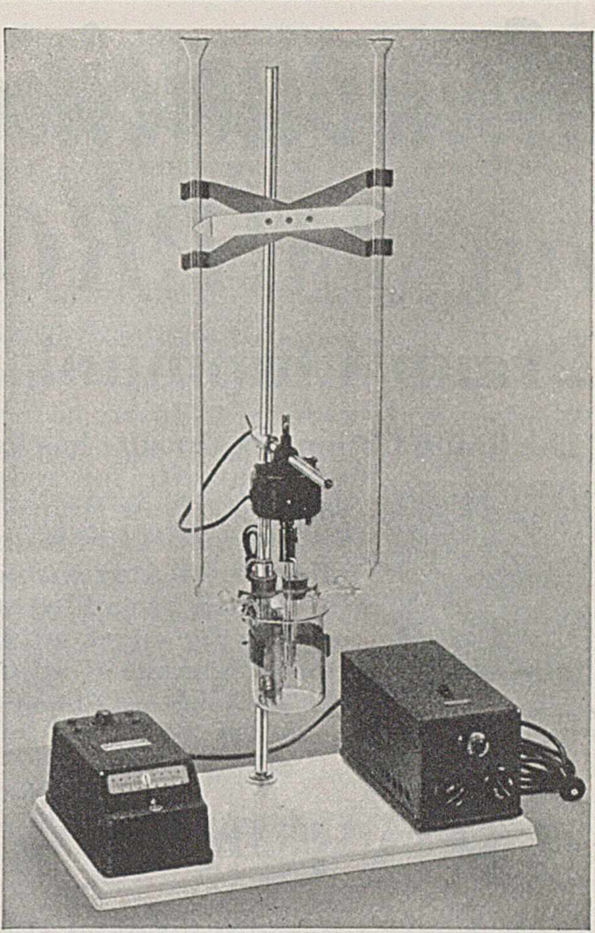

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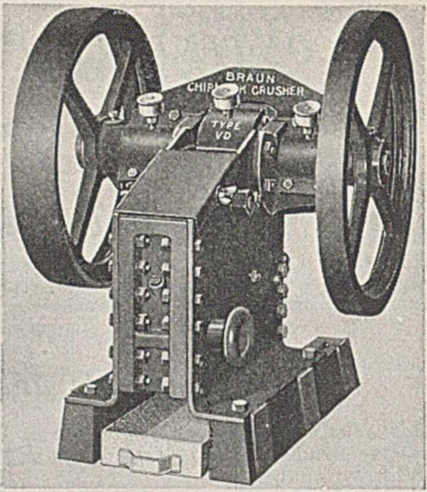

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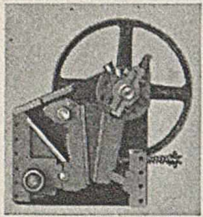

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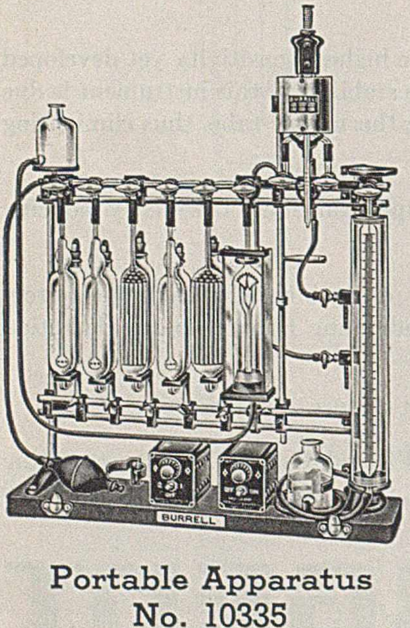

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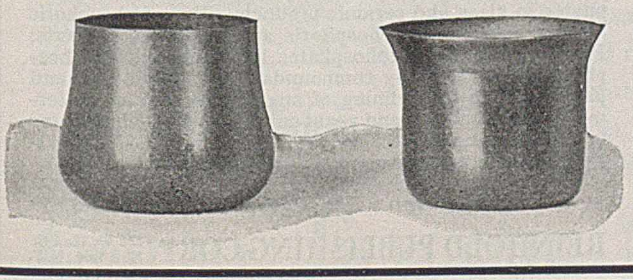

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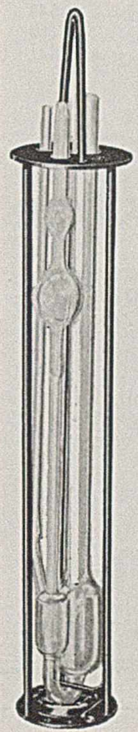

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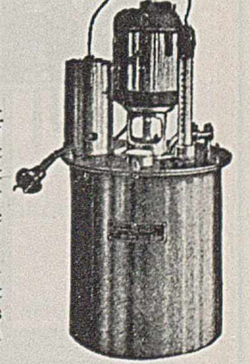

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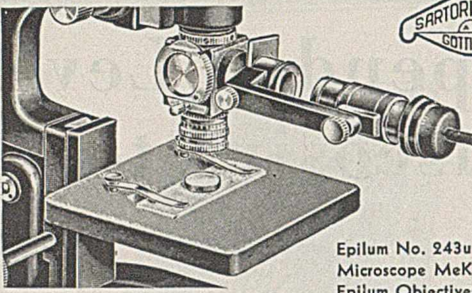

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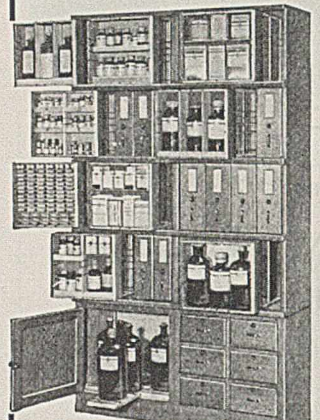

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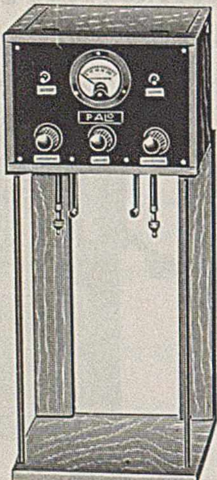

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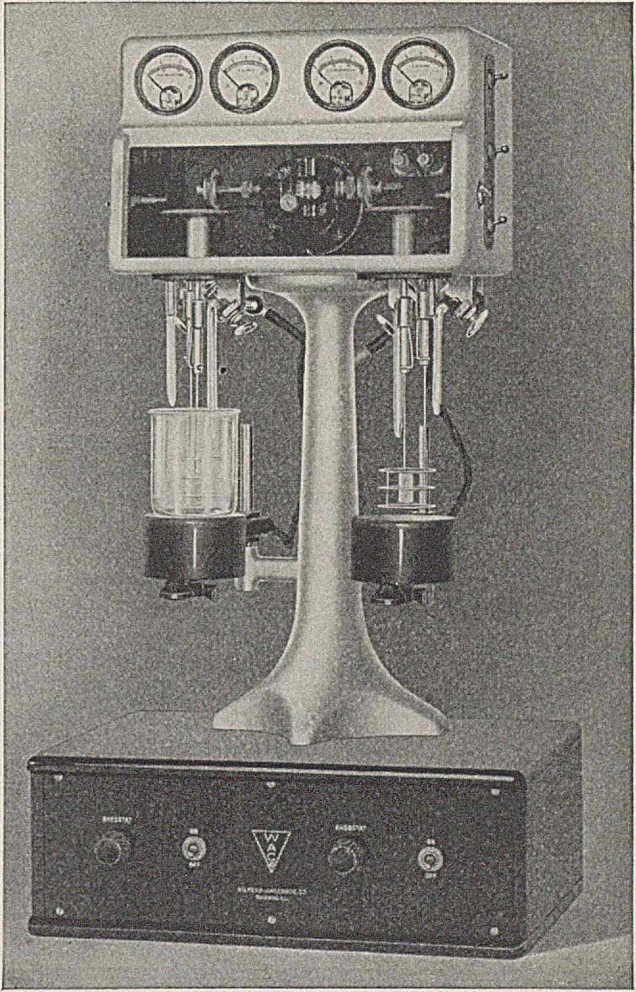

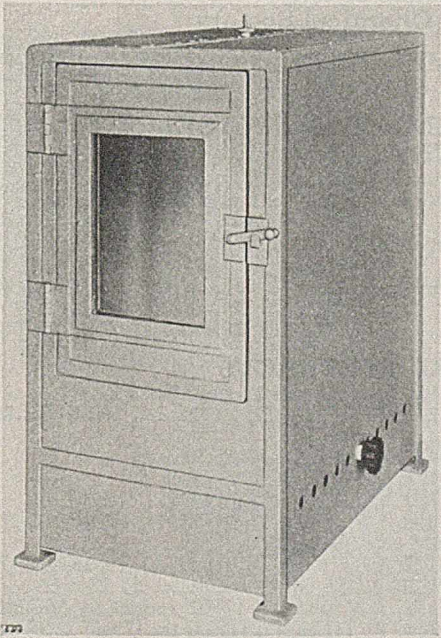

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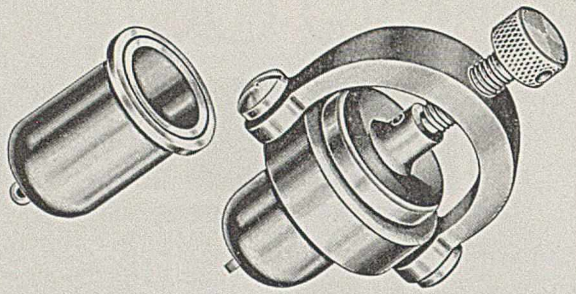

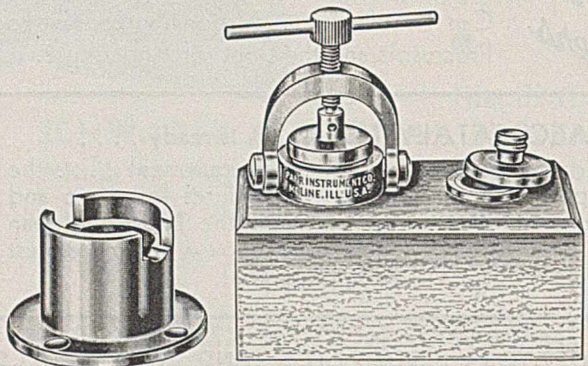
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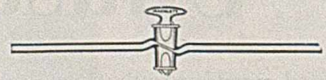


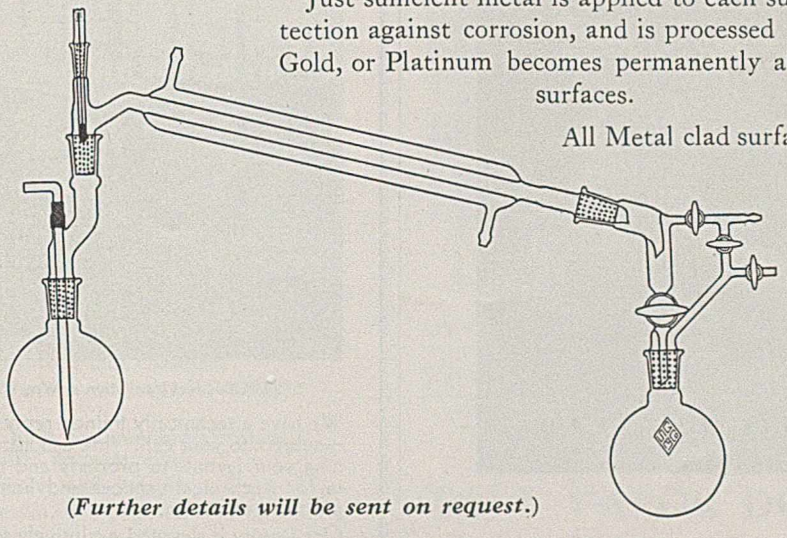
METAL CLAD JOINTED APPARATUS

(PATENT PENDING)

Interchangeable ground glass joints that will not stick or freeze are now available on every piece of equipment having ground connections. These are made possible by our new process of applying protective coatings of Silver, Gold or Platinum to glass.

Vacuum Distilling apparatus No. 1447 as illustrated is now being constructed with metal clad joints, thus reducing breakage due to sticking joints.

Stationary metal clad parts such as connections and stoppers may be used without lubricants.



Just sufficient metal is applied to each surface to assure protection against corrosion, and is processed so that the Silver, Gold, or Platinum becomes permanently attached to the glass surfaces.

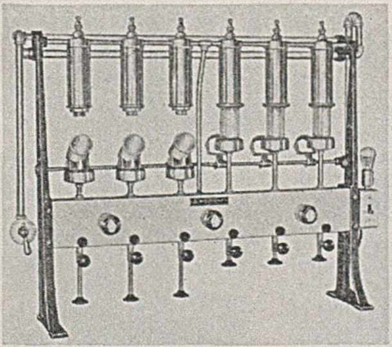
All Metal clad surfaces are finished to a bright polish and fit perfectly, forming smooth, ductile, metal to metal bearing surfaces.

(Further details will be sent on request.)

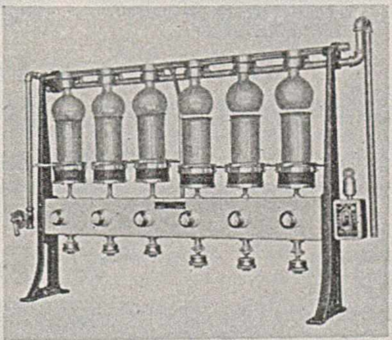
SCIENTIFIC GLASS APPARATUS COMPANY

49 ACKERMAN STREET BLOOMFIELD, NEW JERSEY

NEW ITEMS OF MODERN APPARATUS



Goldfisch Extraction Apparatus



Crude Fiber Apparatus

[*Complete Details on Request*]

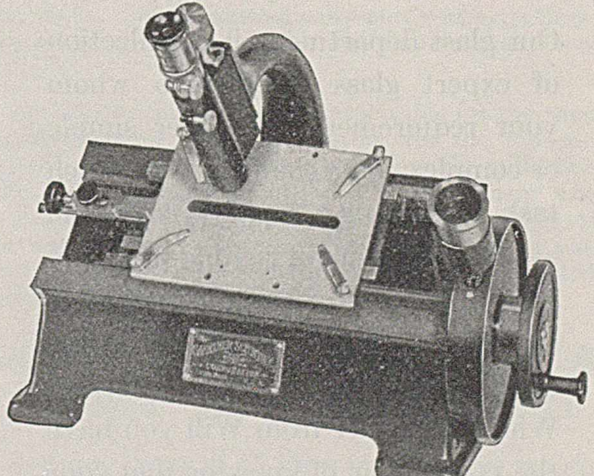
LABORATORY CONSTRUCTION COMPANY

Mfgrs. of Modern Kjeldahl Nitrogen Apparatus

1113-1115 Holmes St. Kansas City, Mo., U.S.A.

M1201—30 COMPARATOR

100 mm Range



This Comparator is especially designed for measuring spectrograms, but may also be used to advantage in calibrating scales and measuring linear distances on any object which may be conveniently placed on the stage.

This instrument, typical of our precision instruments, is of thoroughly modern design throughout, embodying many new features which add materially to its accuracy, convenience and permanency.

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SKILL THAT MATCHES YOUR EVERY NEED

Our glass department is a collection of expert glass blowers to whom your requirements, whether simple or complex, are a challenge. To each task they bring a rapid, precise skill—based on years of rigid apprenticeship under the exacting tutelage of craftsmen—that is reflected in the superb quality of their output. When you order from Will you have the satisfaction of knowing that your specifications will be met exactly at prices that are most reasonable.

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TABLES ~ FUME HOODS ~ CASES
in
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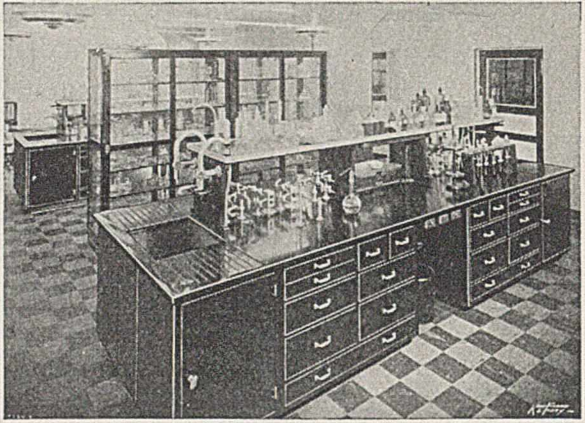
hundreds of standard designs or
special creations for special needs



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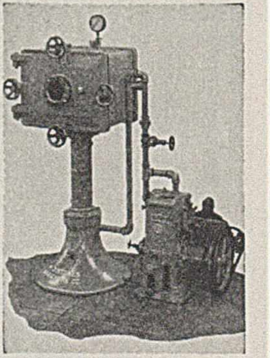
E. H. SHELDON & CO., Muskegon, Mich.

STOKES LABORATORY EQUIPMENT

Vacuum Shelf Dryers

Illustration shows small practical self-contained Vacuum Shelf Dryer for laboratory and experimental use. Compact, of neat appearance with vertical surface condenser and receiver forming the base. Chamber contains two 18″ x 12″ shelves with 4″ clearance. May be heated with hot water, hot oil or steam. Full line of commercial dryers available. Illustration also shows Stokes High Vacuum pump connected to dryer.



High Vacuum Pumps

Rugged, simple, compact, dependable. For all laboratory purposes. Vacuum within .01 mm. Five stock sizes, 10 to 225 cu. ft. capacity.

Autoclaves

Construction and design to suit requirements. Made of standard or special metals. Heated by steam, gas or electricity.

Water Stills

Produce highest quality distillate. 22 stock sizes from ½ to 100 gal. per hr.

FJSTOKES MACHINE COMPANY
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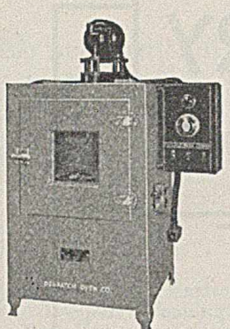
DESPATCH TEST OVENS
ROTARY TYPE
for
A. S. T. M.
Standard D6-33
and
A. S. S. H. O.
T-47 Test Specifications



Designed primarily for determination of loss on Heating of Oil and Asphaltic compounds according to above procedures.

Ready removal of perforated rotary shelf (9.75" dia.) allows oven to be used for general purposes.

Equipped with DeKhotinsky thermoregulator sensitive to ¼°C. changes, temperatures are maintained ±1°C. at 163°C.

Radically new type baffle plate guarantees positive natural circulation of air, insuring uniformity of heat distribution throughout chamber.

Many other new features and refinements have been incorporated.

Two sizes; each built for maximum temperatures of 180° or 260°C respectively.

Oven finish, attractive and durable.

Write for Bulletin No. C-3 page 7.

DESPATCH OVEN COMPANY
630 Ninth Street, S. E. Minneapolis, Minn., U. S. A.
Pioneer Builders of Laboratory Ovens Since 1902

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SUPERPRESSURE
EQUIPMENT

AMINCO SUPERPRESSURE

. . . includes a complete line of apparatus for the investigation of high-pressure catalytic reactions on a laboratory and semi-works scale.

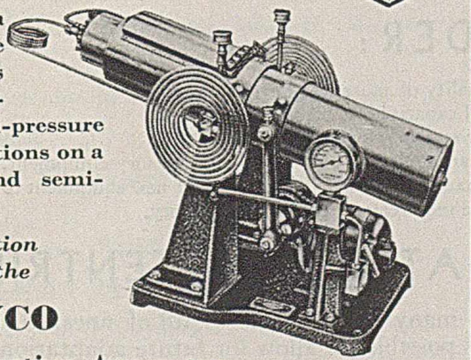

Illustration Shows the
AMINCO
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The American Instrument Company maintains a design department thoroughly familiar with the problems of super-pressure design and a special shop department for working up these designs in modern high-strength materials.

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AMERICAN INSTRUMENT CO., Inc.
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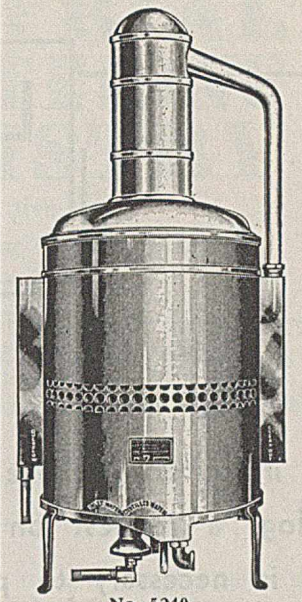

No. 5240
ABOVE—Gas heated "Precision" Automatic Water Still built in sizes of 1, 2 or 3 gals. per hour. Body is Monel metal; special evaporator insures gas combustion efficiency.

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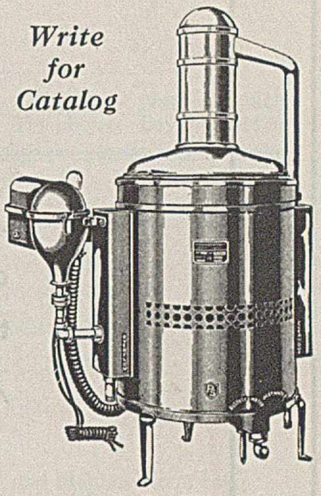

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TALL VAPOR DOMES
NOW STANDARD
—AT NO EXTRA COST

Thousands of installations in every conceivable kind of laboratory, in every field of industry and research, testify to the satisfactory performance of "Precision" Automatic Water Stills. Year in and year out these dependable Stills deliver distilled water that is chemically, physically, and bacteriologically pure—at extremely low operating cost and with practically no manual attention required.

Among the many features responsible for the superior performance of "Precision" stills are the following—tube-free non-clog condenser built into the still; removable cover for quick accessibility to evaporator interior to facilitate cleaning; each still equipped with evaporator communication nipple for flush and bleed valves; entire evaporator surface contacting vapors or distilled water coated with pure block tin.

Every "Precision" Automatic Water Still
Is Now a "HARD" WATER MODEL

And now added to all these vital features mentioned above, is the tall dome with gas vent at the top and containing a series of baffles to strip the ascending vapors of every vestige of solids and moisture before condensation takes place. This notable improvement promotes the purity of the distillate to an appreciable degree and offers another reason why it will pay you to install a "Precision" still in preference to any other.

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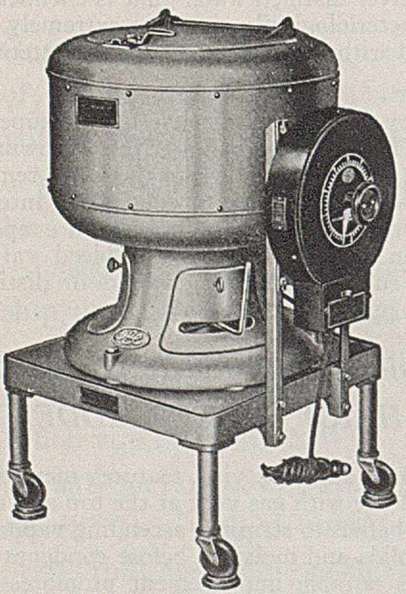

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