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CONTENTS

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| | | | | | |
|--|---|--|--|---|----|
| Composition of Fatty Acid Mixtures. II . Robert N. Wenzel | 1 | Iodine Value of Rubber and Gutta-Percha Hydrocarbons | A. R. Kemp and G. S. Mueller | 52 | |
| Examination of the Phenols of a Low-Temperature Coal Tar | S. Caplan, J. Ross, M. G. Sevag, and T. M. Switz | 7 | Testing Reclaimed Rubber | Henry F. Palmer | 56 |
| Short-Cut Method of Hydrocarbon Analysis. II | R. Rosen and A. E. Robertson | 12 | New Type of Antimony Electrode for pH Measurements | T. R. Ball, Webster B. Schmidt, and Karl S. Bergstresser | 60 |
| New Volumetric Method for Determination of Sulfate | V. R. Damerell and H. H. Strater | 19 | Colorimetric Determination of Fluorine | O. M. Smith and Harris A. Dutcher | 61 |
| Chemical Examination of Trichloroethylene for Anesthesia | Herman L. Tschentke | 21 | Determination of Potash in Fertilizers | F. B. Carpenter and R. O. Powell | 62 |
| Optical Density Color Measurement for Petroleum Oils | S. W. Ferris and J. M. McIlwain | 23 | Use of A' ration in Kjeldahl Distillations | W. B. Meldrum, R. Melampy, and W. D. Myers | 63 |
| Inverted Fractional-Distillation Analysis. | R. A. J. Bosschart | 29 | Determination of Lead as Dilead Hydrogen Arsenate. | C. L. Dunn and H. V. Tartar | 64 |
| Qualitative Method for Selenium in Organic Compounds | M. J. Horn | 34 | Purification of Substances by Electrodialysis | Albert L. Elder, Russell P. Easton, Harold E. Pletcher, and Floyd C. Peterson | 65 |
| Platinized Silica Gel as a Catalyst in Gas Analysis. II | Kenneth A. Kobe and E. Bruce Brookbank | 35 | New Apparatus for Determination of Size Distribution of Particles in Fine Powders | Robert T. Knapp | 66 |
| Volume of Sugar-Beet Marc and Its Adsorptive Effect | S. J. Osborn | 37 | Unitized Gas-Analysis Apparatus | Maryan P. Matuszak | 72 |
| Comparison of Extraction Formulas . Carroll W. Griffin | | 40 | Extraction of Triethanolamine Oleate from Aqueous Solution | Frank M. Biffen and Foster Dee Snell | 78 |
| Determination of Small Quantities of Nitrobenzene in Oils | C. E. Anding, Jr., B. Zieber, and W. M. Malisoff | 41 | Glass and Other Electrodes for Measuring pH Values of Very Dilute Buffers and of Distilled Water | John O. Burton, Harry Matheson, and S. F. Acree | 79 |
| Separation of Gold from Tellurium | Victor Lenher, G. B. L. Smith, and D. C. Knowles, Jr. | 43 | An Automatic, Modified Falling-Sphere Viscometer | B. A. Jones | 80 |
| Determination of Borate Ion in Ores of Borax . H. L. Payne | | 45 | Cleaning Platinum Wire for Flame Tests | Wesley G. Leighlon | 84 |
| Determination of Iron . Gladys Leavell and N. R. Ellis | | 46 | | | |
| Direct Determination of Chromium and of Vanadium in Steel | Hobart H. Willard and Philena Young | 48 | | | |

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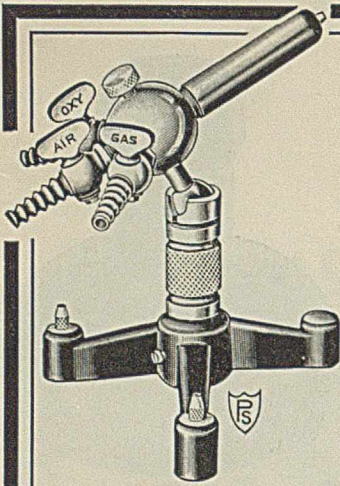
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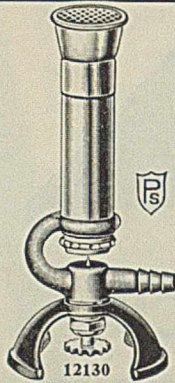
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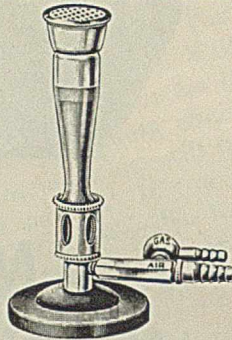
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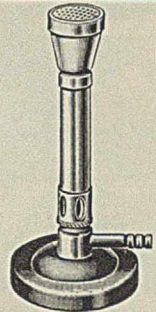
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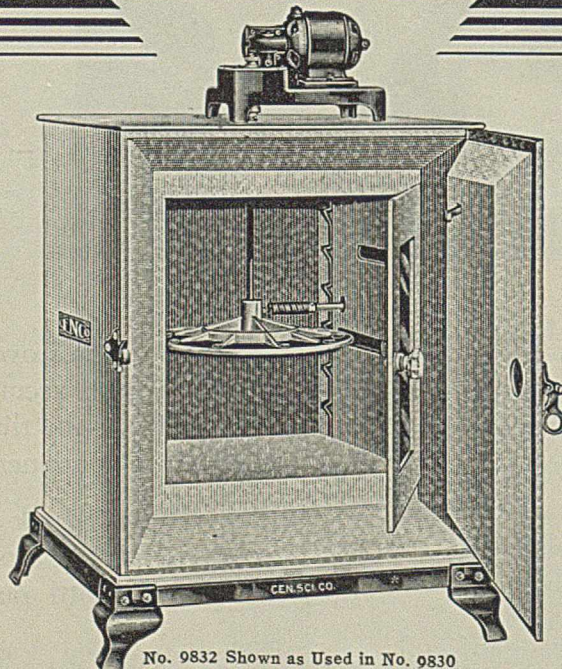


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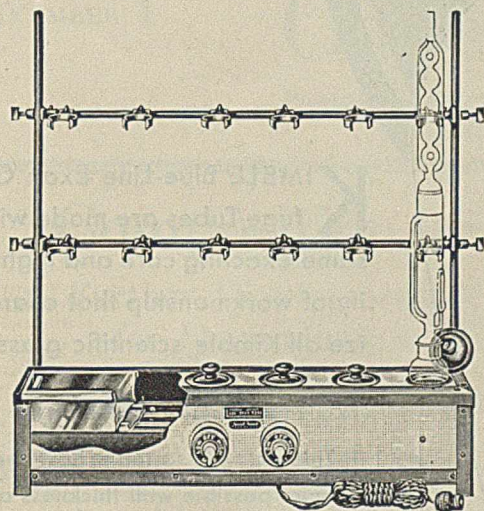
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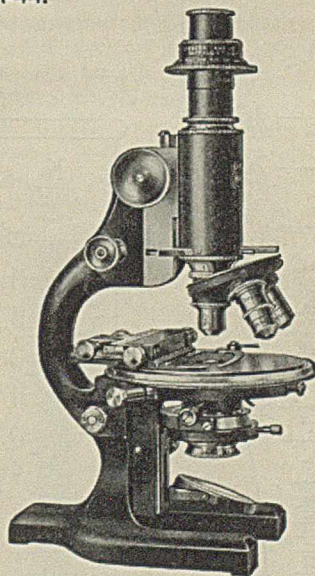
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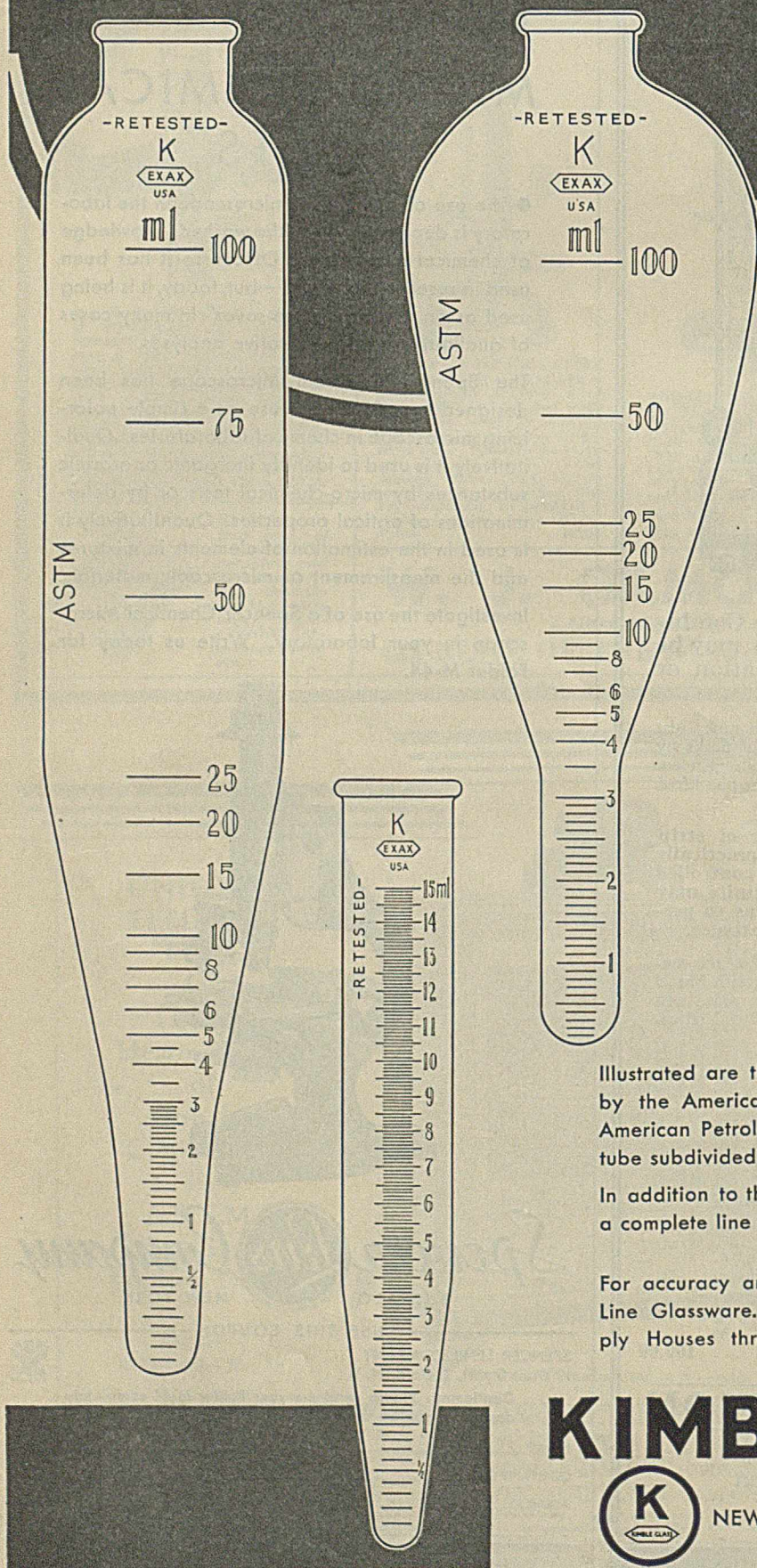
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Composition of Fatty Acid Mixtures

II. A Further Development of the Twitchell Mixed-Melting-Point Method for Determination of Individual Saturated Fatty Acids

ROBERT N. WENZEL, Mellon Institute of Industrial Research, Pittsburgh, Pa.

THE analytical methods usually applied to the testing of commercial fats and fatty acid mixtures leave the question of their composition, in terms of constituent fatty acids, largely undetermined. Where control of composition is an important factor in the success of commercial processes, as in the growth of crystals in molten fatty acid mixtures, reliance must therefore be placed largely on empirical formulas for the blending of fats of different grades and different sources. Blending formulas are not always dependable, however, because the raw materials themselves are usually subject to considerable variation. Again, in industrial research, analyses of fatty acid mixtures are frequently of service only in so far as they can be interpreted in terms of composition. Such interpretation, based solely on resultant properties of the mixture—total unsaturation, acid value, titer, etc.—is at best uncertain and often quite misleading. There is need therefore for methods that determine, specifically, the percentages of individual fatty acids present.

THE MIXED-MELTING-POINT METHOD

In view of this situation, the mixed-melting-point method devised by Twitchell (11) has certainly not received the attention that its possibilities would seem to merit.

The method is based on the fact that if a sample consisting of a mixture of fatty acids is added to a single pure fatty acid only those acids in the mixture that are not identical with the pure acid solvent will be effective in lowering its melting point. Twitchell reasoned that, because of their uniformly high molecular weights, all the fatty acids should have approximately equal effect in depressing the melting point of any solvent. Thus, if the solvent acid is stearic, the depression of the melting point gives a measure of all acids other than stearic acid in the mixture. From this the percentage of stearic acid in the sample is readily calculated.

As used by Twitchell, the method was subject to serious limitations, mainly because the melting-point determination itself was not sufficiently precise to permit the establishment of accurate, specific depression constants for the different individual acids. In addition, Twitchell measured all depressions at 20 per cent of total solute acids. This not only necessitated a preliminary trial, in each analysis, before

weighing out the final mixture, but it placed the measurements beyond the straight-line portion of the melting-point curve and therefore outside the range in which melting-point data can properly be applied.

The method was later used by McGregor and Beal (8), in their study of the fatty acids of menhaden oil, in essentially the form in which it was left by Twitchell.

A distinct improvement in the results obtainable by the mixed-melting-point method is made possible by an improved melting-point technic here described. Specific depression constants have been determined by measurements on binary mixtures of pure acids, including stearic, palmitic, myristic, and oleic. It has been found that depressions in palmitic acid and in stearic acid are apparently controlled, as might be expected, by definite molar depression constants characteristic of the solvent acid and independent of the solute. Reliable specific depression constants for the individual solute acids can thus be based on the molar constant for the solvent and the molecular weight of the solute. For solutions in myristic acid, the behavior of dissolved stearic acid is apparently anomalous, giving a molar depression constant higher than that obtained when the solute acid is palmitic or oleic. This departure from the theoretical has not been explained. For stearic acid in myristic, therefore, the specific depression constant directly determined must be accepted. The proper depression constant to use in any particular analysis is readily calculated from the specific constants here established.

The method gives results only reliable to within a few per cent, but, in spite of its limited accuracy, is an extremely valuable tool. As here worked out, it has proved very useful in the investigation of problems encountered in the manufacture of commercial fatty acids, particularly in defining the limits of toleration of the crystallizing process to variations in the composition of the stock.

THE MELTING-POINT DETERMINATION

Even in the case of pure compounds, melting points depend largely on apparatus and technic. Thus widely differing values for the melting point of any of the pure fatty acids will be found in the literature. With fatty acid mixtures there is the further difficulty that here we are dealing with a case of solid solutions. The composition-melting-point

diagram for mixtures of two fatty acids is not a single line, but two lines, the so-called liquidus and solidus curves. Even with the maintenance of ideal equilibrium conditions, melting will start at one temperature and continue over a considerable range of values; and at any temperature within this range

the mixture exists as a perfectly stable, two-phase system.

Theoretically, both the initial and final temperatures of this melting range are characteristic properties of the mixture. Practically, it is only the final point that can be determined with any accuracy. The point usually recorded in melting-point determinations—i. e., the temperature at which clear liquid first appears in the sample—comes at neither the beginning nor the end of the melting range, but depends upon the rate at which the solid settles through the liquid

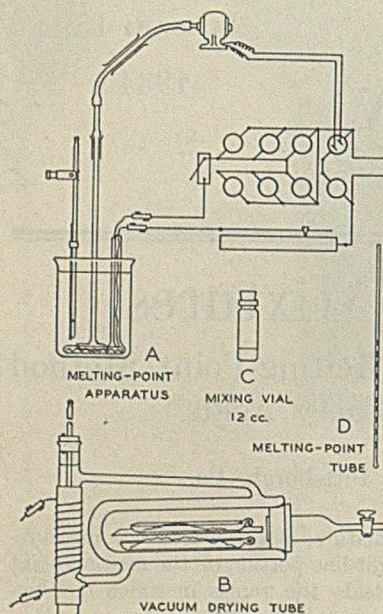


FIGURE 1. APPARATUS

first formed. In the present work, final temperatures were therefore used throughout.

McGregor and Beal, as well as Twitchell, allowed the material in the melting-point tube to stand for at least 12 hours to remove strain before the melting point was taken. The necessity for this precaution in the case of fats has been pointed out by Lewkowitsch (?), Bloor (?), and others. Burks (3) found, however, that the double melting points exhibited by recently melted glycerides are not encountered in the case of the free fatty acids.

Burks' observations are confirmed by the following series of melting-point readings taken on the same sample after exposing the tube to the various treatments indicated. The two readings recorded in each case were taken at the first appearance of clear liquid and at the disappearance of the last of the solid.

| | ° C. |
|---|----------------|
| Initial melting point | 60.76 to 61.08 |
| After solidifying and standing 43 hours at room temperature | 60.88 to 60.98 |
| After solidifying and again standing 52 hours at room temperature | 60.90 to 61.10 |
| After keeping melted in an oven at 65° to 70° C. for 17 hours and standing at room temperature 45 minutes | 60.94 to 61.14 |
| After cooling to, and holding at 55.5° to 57.5° C. for 4 hours | 60.97 to 61.14 |
| After plunging into ice water, holding there 5 minutes, and repeating the melting-point determination at once | 60.73 to 61.15 |

It will be seen that the melting point is not appreciably affected by repeated melting, long standing at room temperature, long continued heating just above the melting point, slow solidification just below the melting point, or rapid solidification in an ice bath. We may therefore conclude that there is no decomposition at the melting point to necessitate a rapid melting-point determination and that there is nothing to be gained by aging the sample in the melting-point tube.

Burks recommended an extremely slow rate of heating designed to simulate immersion of the sample tube for two minutes in each of a succession of constant-temperature baths differing by only 0.1° C. This procedure was adopted in the

present work because it makes possible a high degree of precision in the melting-point determination. The apparatus used is, in all its essential features, identical with that employed by Burks.

In order to obtain the sharp temperature control required, it is essential to use a closed melting-point tube immersed directly in the temperature bath. Twitchell's ingenious method of loading an open tube from the melted mixture, to insure a true sample, and then giving it a sharp jar, so that the sample solidifies as a string of short segments, has been retained, but the tube is then sealed in the Bunsen flame. With proper precautions this can be done without injuring the sample.

APPARATUS

Figure 1A is a diagram of the apparatus used for the melting-point determinations. A 600-cc. Pyrex beaker containing water or a light, colorless mineral oil serves as the heating bath. The immersion heater consists of a spiral coil of resistance wire sheathed in a loop of Pyrex glass tubing. The lamp bank and rheostat connections are indicated. The beaker is not insulated, as accurate temperature control depends upon a nice balancing of heat input against radiation, but it must be protected from fitful air drafts. Two melting-point tubes are fastened to the thermometer by means of a rubber band. In addition, a fork made of glass tubing, with two prongs extending into the bath parallel to the thermometer, makes it possible to introduce six tubes at a time. The slow rate of heating allows ample time for observing and recording the behavior of each sample.

The melting-point thermometers used are of ranges 20° to 60° C. and 40° to 80° C., graduated in 0.1° units and calibrated by comparison with thermometers certified by the United States Bureau of Standards. A magnifying attachment permits readings to 0.01° C. Emergent stem temperatures are also recorded.

The exact size of the melting-point tube is not critical. Tubes of inside diameter such as to accept a No. 22 B & S gage wire but not a No. 20 wire were selected. A small hand lens is used to observe the behavior of samples during melting.

It is of course essential that the fatty acids be dry. A convenient device for thorough and rapid drying of small samples, also suggested by Burks, is the vacuum drying tube shown in Figure 1B. The drying chamber is divided into upper and lower compartments by a screen of heavy wire gauze. Samples are placed in the upper compartment, phosphorus pentoxide in the lower. Water circulated through the jacket is heated in the upright tube, either electrically or by means of a small gas flame, and the temperature maintained at a point only a few degrees below the melting point of the sample. The tube is evacuated by means of an oil pump. Thorough drying is accomplished within 15 or 20 minutes in this apparatus.

PROCEDURE

Each analysis is run in duplicate, two mixtures with definitely different proportions of sample and pure acid being prepared. The mixture, weighing usually about 2 grams, is weighed out in a small square-shouldered vial of 12 cc. capacity (Figure 1C) and melted down in an oven at 100° C. Mixing is effected by tilting the vial until the liquid reaches the shoulder, rotating it in this position and shaking.

Two open melting-point tubes are then dipped into the mixture. Following Twitchell's technic, the sample in each tube is broken into a string of small uniform segments and, by proper manipulation above the flame, the last segment is spaced about 7 mm. from the end of the tube. By

TABLE I. MELTING-POINT DEPRESSIONS IN PALMITIC AND STEARIC ACIDS

| MIXTURE | PERCENTAGE COMPOSITION OF MIXTURE Palmitic acid | Stearic acid | Oleic acid | MOLE PER CENT TOTAL SOLUTE | MELTING POINT ° C. | MELTING-POINT DEPRESSION, L | 10 L + Wt. PER CENT SOLUTE, K _w | 10 L + MOLE PER CENT SOLUTE, K _m |
|---------|--|--------------|------------|-------------------------------|-----------------------|-----------------------------------|---|--|
| 1 | 100 | ... | ... | ... | 62.30 | .. | .. | .. |
| 2 | 95.00 | 5.00 | ... | 4.52 | 61.50 | 0.80 | 1.60 | 1.77 |
| 3 | 90.00 | 10.00 | ... | 9.10 | 60.62 | 1.68 | 1.68 | 1.84 |
| 4 | 85.00 | 15.00 | ... | 13.72 | 59.78 | 2.52 | 1.68 | 1.84 |
| 5 | 80.00 | 20.00 | ... | 18.38 | 58.62 | 3.68 | 1.84 | 2.00 |
| 6 | 94.51 | ... | 5.49 | 4.85 | 61.44 | 0.86 | 1.56 | 1.77 |
| 7 | 89.99 | ... | 10.01 | 9.17 | 60.63 | 1.67 | 1.67 | 1.82 |
| 8 | 84.95 | ... | 15.05 | 13.84 | 59.79 | 2.51 | 1.67 | 1.81 |
| 9 | 79.74 | ... | 20.26 | 18.76 | 58.79 | 3.51 | 1.73 | 1.87 |
| 10 | 89.67 | 4.98 | 5.35 | 9.44 | 60.63 | 1.67 | 1.62 | 1.77 |
| 11 | 84.81 | 4.99 | 10.20 | 13.95 | 59.74 | 2.56 | 1.68 | 1.83 |
| 12 | 84.99 | 10.00 | 5.01 | 13.77 | 59.79 | 2.51 | 1.67 | 1.82 |
| 13 | ... | 100 | ... | ... | 69.10 | .. | .. | .. |
| 14 | 5.00 | 95.00 | ... | 5.52 | 68.22 | 0.88 | 1.76 | 1.59 |
| 15 | 10.00 | 90.00 | ... | 10.98 | 67.39 | 1.71 | 1.71 | 1.56 |
| 16 | 15.00 | 85.00 | ... | 16.39 | 66.44 | 2.66 | 1.77 | 1.62 |
| 17 | 20.00 | 80.00 | ... | 21.74 | 65.47 | 3.63 | 1.82 | 1.67 |
| 18 | ... | 94.91 | 5.09 | 5.13 | 68.26 | 0.84 | 1.65 | 1.64 |
| 19 | ... | 89.58 | 10.42 | 10.52 | 67.41 | 1.69 | 1.62 | 1.61 |
| 20 | ... | 84.96 | 15.04 | 15.18 | 66.62 | 2.48 | 1.65 | 1.64 |
| 21 | ... | 80.01 | 19.99 | 20.16 | 65.72 | 3.38 | 1.69 | 1.68 |
| 22 | 4.99 | 89.78 | 5.23 | 10.74 | 67.40 | 1.70 | 1.66 | 1.58 |
| 23 | 9.99 | 84.74 | 5.27 | 16.20 | 66.49 | 2.61 | 1.71 | 1.61 |
| 24 | 4.99 | 84.83 | 10.18 | 15.70 | 66.58 | 2.52 | 1.66 | 1.61 |
| 25 | 30.00 | 70.00 | ... | ... | 63.20 | .. | .. | .. |
| 26 | 40.00 | 60.00 | ... | ... | 60.33 | .. | .. | .. |
| 27 | 50.00 | 50.00 | ... | ... | 56.71 | .. | .. | .. |
| 28 | 60.00 | 40.00 | ... | ... | 56.20 | .. | .. | .. |
| 29 | 70.00 | 30.00 | ... | ... | 55.50 | .. | .. | .. |

careful warming, the walls of the end section are now drained completely into the last segment. The tube is then sealed. Sometimes sealing the tube affects the melting point of the last segment, but it can have no effect, of course, on the others. All the segments in both tubes, melting simultaneously, give assurance that a homogeneous mixture has been obtained and that there is no irregularity in the melting point due to accidental factors. The loaded tube is shown in Figure 1D.

In melting the sample, it is heated rapidly to within 1° of the anticipated melting point. If this is not known approximately it is determined by a rapid preliminary melting. From there on the procedure is to hold the temperature constant, within a few hundredths of a degree, for 2 minutes and then allow it to rise 0.1° during the next minute, when it is again held constant for 2 minutes, and so on. The temperature at which the last speck of solid material in each separate portion of the sample disappears is taken as the melting point. Duplicate determinations should agree within 0.05° C.

PREPARATION OF PURE FATTY ACIDS

In order to establish specific depression constants, it was necessary to have samples of the pure fatty acids. In addition, the pure saturated acids are required as reagents in the mixed-melting-point method. The acids used were prepared as follows:

STEARIC ACID. The methyl esters obtained from commercial double-distilled oleic acid were distilled at low pressure through a fractionating column. The first half of the distillate, containing large amounts of methyl palmitate, was rejected. The second portion, boiling at practically constant temperature (174° to 178° C. at 3 mm.) and containing only C₁₈ acids, was hydrogenated in 25-gm quantities in alcoholic solution, using platinum oxide as catalyst (1). The combined alcoholic solutions were then refluxed 4 hours with 2 M equivalents of potassium hydroxide to saponify the esters and the soaps split with hydrochloric acid. The recovered acids, washed free of chlorides, were recrystallized once from petroleum ether and repeatedly from acetone until no further increase in melting point resulted. The product thus obtained consists of beautifully white, crystalline flakes. Samples of melting point 69.0° C. or higher are accepted for use in the mixed-melting-point method.

PALMITIC ACID. Fatty acids recovered from bayberry wax were converted to their methyl esters and distilled at low pressure

through an efficient fractionating column. The first 40 per cent of the distillate was rejected. The remainder, coming over at constant temperature, was treated for recovery of the acids which were then recrystallized from acetone. Preparations having melting points of 62.0° C. or higher are accepted.

MYRISTIC ACID. Nutmeg butter, obtained from ground nutmegs by extraction with ether after a preliminary alcohol extraction had removed most of the color and the volatile oil, was saponified and the soap solution acidified to liberate myristic acid. Recrystallized three times from acetone, the acid melted at 53.32° C. This product was distilled under reduced pressure and the first and last fractions were rejected. The remainder, again recrystallized from acetone, was recovered in two fractions melting at 54.17° and 53.88° C., respectively.

OLEIC ACID. Preparation of oleic acid of a high degree of purity is a matter of considerable difficulty. It was required here for the determination of melting-point depression constants, but is not required as a reagent in the mixed-melting-point method.

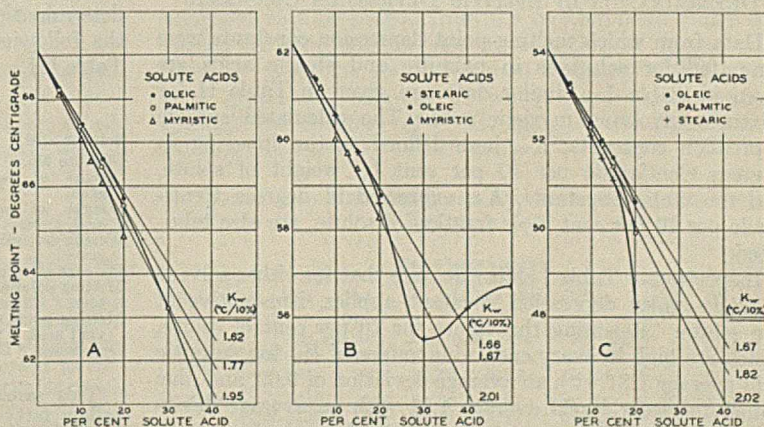


FIGURE 2. MELTING-POINT DEPRESSIONS

A, in stearic acid B, in palmitic acid C, in myristic acid

Olive oil fatty acids were used as the source of oleic acid. Most of the saturated acids were removed by Twitchell's lead soap-alcohol method (10, 12). Removal of most of the linoleic acid was effected by refluxing the unsaturated acids in alcohol, with enough finely ground solid barium hydroxide to convert 80 per cent of the acids to their barium soaps, thus leaving the linoleic acid, together with some oleic, in solution. This is a modification of the procedures of Farnsteiner (5) and of Lapworth and Pearson (6). For the final purification from small amounts of palmitic acid and linoleic acid, fractional crystallization of the lithium soaps according to Scheffers (9) was adopted. This method was found more effective in removing linoleic acid, however, than in concentrating palmitic acid in the first fractions.

TABLE II. MELTING-POINT DEPRESSIONS IN MIXTURES INVOLVING MYRISTIC ACID

| MIXTURE | WEIGHT OF ACIDS IN MIXTURE | | | | WEIGHT PER CENT SOLUTE | MOLE PER CENT SOLUTE | MELTING POINT ° C. | MELTING-POINT DEPRESSION, L | 10 L + WEIGHT PER CENT SOLUTE, K_w | 10 L + MOLE PER CENT SOLUTE, K_m |
|---------|----------------------------|---------------------|--------------------|------------------|------------------------|----------------------|--------------------|-----------------------------|--------------------------------------|------------------------------------|
| | Myristic acid Grams | Palmitic acid Grams | Stearic acid Grams | Oleic acid Grams | | | | | | |
| 30 | | 1.0000 | | | 0.00 | | 62.45 | | | |
| 31 | 0.1152 | 1.9286 | | | 5.64 | 6.28 | 61.39 | 1.06 | 1.88 | 1.69 |
| 32 | 0.2026 | 1.8089 | | | 10.07 | 11.17 | 60.53 | 1.92 | 1.91 | 1.72 |
| 33 | 0.2804 | 1.7523 | | | 12.94 | 14.30 | 59.88 | 2.57 | 1.99 | 1.80 |
| 34 | 0.3016 | 1.7062 | | | 15.02 | 16.56 | 59.53 | 2.92 | 1.94 | 1.76 |
| 35 | 0.4040 | 1.6008 | | | 20.05 | 22.08 | 58.42 | 4.03 | 2.01 | 1.82 |
| 36 | | | 1.0000 | | 0.00 | | 69.21 | | | |
| 37 | 0.1003 | | 1.9045 | | 5.00 | 6.16 | 68.20 | 1.01 | 2.02 | 1.64 |
| 38 | 0.2034 | | 1.8003 | | 10.15 | 12.34 | 67.19 | 2.02 | 1.99 | 1.64 |
| 39 | 0.2514 | | 1.7500 | | 12.53 | 15.17 | 66.68 | 2.53 | 2.02 | 1.67 |
| 40 | 0.3011 | | 1.7012 | | 15.04 | 18.05 | 66.18 | 3.03 | 2.01 | 1.68 |
| 41 | 0.4005 | | 1.6005 | | 20.01 | 23.75 | 64.97 | 4.24 | 2.12 | 1.79 |
| 42 | 1.0000 | | | | 0.00 | | 54.17 | | | |
| 43 | 1.9015 | 0.1007 | | | 5.03 | 4.50 | 53.26 | 0.91 | 1.81 | 2.02 |
| 44 | 1.8029 | 0.2000 | | | 9.99 | 8.99 | 52.35 | 1.82 | 1.82 | 2.02 |
| 45 | 1.7519 | 0.2506 | | | 12.51 | 11.30 | 51.95 | 2.22 | 1.77 | 1.96 |
| 46 | 1.7029 | 0.3026 | | | 15.09 | 13.66 | 51.45 | 2.72 | 1.80 | 1.99 |
| 47 | 1.6019 | 0.4019 | | | 20.06 | 18.26 | 49.93 | 4.24 | 2.11 | 2.32 |
| 48 | 1.9002 | | 0.1018 | | 5.08 | 4.12 | 53.16 | 1.01 | 1.99 | 2.45 |
| 49 | 1.8057 | | 0.2014 | | 10.03 | 8.22 | 52.15 | 2.02 | 2.01 | 2.46 |
| 50 | 1.7498 | | 0.2500 | | 12.50 | 10.29 | 51.65 | 2.52 | 2.02 | 2.44 |
| 51 | 1.6998 | | 0.2995 | | 14.98 | 12.39 | 51.14 | 3.03 | 2.02 | 2.44 |
| 52 | 1.6008 | | 0.4024 | | 20.09 | 16.79 | 48.24 | 5.93 | 2.95 | 3.53 |
| 53 | 1.9044 | | | 0.1024 | 5.10 | 4.17 | 53.36 | 0.81 | 1.75 | 1.94 |
| 54 | 1.8009 | | | 0.2023 | 10.10 | 8.33 | 52.46 | 1.71 | 1.69 | 2.08 |
| 55 | 1.7581 | | | 0.2510 | 12.49 | 10.35 | 52.05 | 2.12 | 1.70 | 2.04 |
| 56 | 1.7026 | | | 0.3019 | 15.06 | 12.54 | 51.65 | 2.52 | 1.67 | 2.01 |
| 57 | 1.6038 | | | 0.4021 | 20.05 | 16.86 | 50.64 | 3.53 | 1.76 | 2.10 |

Fractional distillation of the free acid, under reduced pressure and in an atmosphere of nitrogen, with rejection of a considerable first fraction, was finally resorted to and should preferably precede the lithium soap recrystallizations.

In the Scheffers lithium soap procedure, the successive recrystallizations are made after combining fractions of like iodine value. For this purpose Scheffers withdraws samples from which he liberates and recovers the free acids for analysis. The lithium soaps, however, can be dried at 110° C. without change and they are freely soluble in glacial acetic acid. Iodine values can therefore be taken directly on the lithium soaps, and much time and labor are thus saved.

The only satisfactory criterion of purity in the final oleic acid is to separate it by distillation through an efficient column into a number of fractions, all of which agree in iodine value with the theoretical. The product eventually obtained was a sparkling liquid, perfectly colorless and odorless, with an iodine value of 89.6.

DETERMINATION OF SPECIFIC DEPRESSION CONSTANTS

Data from which melting-point depression constants were computed for solutions in palmitic and stearic acids are given in Table I. Similar data are given in Table II for mixtures involving myristic acid. The calculated specific depression constants, K_w , here defined as the lowering in degrees Centigrade per 10 per cent by weight of solute, and the molar constants, K_m , expressed in degrees Centigrade per 10 per cent mole fraction of solute, are also tabulated.

Inspection of Table I shows at once that for either solvent a single molar depression constant applies, irrespective of the solute. Rejecting the values for 20 per cent of solute, which are high in every case, nine values of K_m for palmitic acid average 1.81 with an average deviation of 0.02, and nine values for stearic acid average 1.61 with an average deviation also 0.02. Discounting the results for only 5 per cent of solute, since these involve a higher experimental error, the accepted values are 1.82 and 1.61, respectively.

Using these molar constants and the molecular weights of the solute acids, we arrive at the numerical values shown in Figures 2A and 2B for the respective specific depression constants. The data points and curves show how well and how far the measured depressions follow these constant slopes.

Since the molar depression constants 1.82 and 1.61 for palmitic and stearic acids, respectively, are almost exactly in the inverse ratio of their molecular weights, it might seem reasonable to expect that the value of K_m for myristic acid would be found at about 2.02:

$$\begin{aligned}
 &K_m \quad \text{MOL. WT.} \\
 &1.82 \times 256 = 466 \\
 &1.61 \times 284 = 457 \\
 &\quad \text{Av.} \quad 461.5 \\
 &461.5/228 = 2.02
 \end{aligned}$$

This value is approximated very closely by solutions of palmitic acid and oleic acid in myristic, but solutions of stearic acid in myristic give a higher value—namely, 2.45. The specific depression constants shown in Figure 2C for palmitic acid and oleic acid were derived from the molar constant 2.02 for myristic acid and the molecular weights of the solute acids. For stearic acid in myristic, the value of K_w directly measured—namely, 2.02—is shown.

SAMPLE ANALYSIS

The manner of applying these depression constants in the determination of individual saturated acids is illustrated in the following example. The analytical data are given in Table III.

TABLE III. DATA, SAMPLE ANALYSIS

| Solvent acid Mixture No. | PALMITIC | | STEARIC | | MYRISTIC | |
|-------------------------------------|----------|--------|---------|--------|----------|--------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Weight of sample, gram | 0.1404 | 0.1496 | 0.1412 | 0.1522 | 0.1457 | 0.1542 |
| Weight of solvent acid, gram | 0.8600 | 0.8590 | 0.8678 | 0.8603 | 0.8890 | 0.8837 |
| Weight of mixture, gram | 1.0004 | 1.0086 | 1.0090 | 1.0125 | 1.0347 | 1.0379 |
| Per cent sample (a) | 14.03 | 14.83 | 13.99 | 15.03 | 14.08 | 14.86 |
| Melting point of mixture, ° C. | 60.12 | 60.02 | 67.18 | 66.98 | 51.44 | 51.24 |
| Melting point of solvent acid, ° C. | 61.93 | 61.93 | 69.21 | 69.21 | 53.88 | 53.88 |
| Depression, ° C. (L) | 1.81 | 1.91 | 2.03 | 2.23 | 2.44 | 2.64 |

This sample was obtained in the commercial processing of tallow fatty acids. It is known therefore to be essentially a mixture of palmitic, stearic, and oleic acids, with, possibly, smaller amounts of linoleic and myristic whose net effect on the melting-point depression rates may be neglected. For solutions in palmitic acid, the specific depression constants for stearic and oleic are practically identical, the values found being 1.66 and 1.67. Using the average value 1.665, we arrive at the following results for palmitic acid:

| | MIXTURE 1 | MIXTURE 2 | AVERAGE |
|---|-----------|-----------|---------|
| Per cent not palmitic in mixture (10 L/1.665) | 10.87 | 11.47 | .. |
| Per cent sample in mixture (a) | 14.03 | 14.83 | .. |
| Per cent sample palmitic in mixture (b) | 3.16 | 3.36 | .. |
| Per cent palmitic acid in sample (b/a) | 22.5 | 23.2 | 22.8 |

In calculating the percentage of stearic acid in the sample, the value of K_w to be used will lie between 1.62 for oleic and 1.77 for palmitic at a figure depending upon the proportions of these

two acids in the sample. Since the palmitic acid content is now known and the total acids other than stearic can be approximately determined by the use of a trial value, say 1.7, for the depression rate, the proper value of K_w to use can be determined as follows:

| | MIXTURE 3 | MIXTURE 4 | AVERAGE |
|--|-----------|-----------|---------|
| Per cent acids other than stearic in sample (10 L/1.7 a) | 85.4 | 87.4 | 86.4 |
| Per cent palmitic acid in sample | .. | .. | 22.8 |

$$K_w = 1.62 + (22.8/86.4)(1.77 - 1.62) = 1.62 + 0.04 = 1.66$$

The results of the analysis for stearic acid are then as follows:

| | MIXTURE 3 | MIXTURE 4 | AVERAGE |
|---|-----------|-----------|---------|
| Per cent not stearic in mixture (10 L/1.66) | 12.23 | 13.42 | .. |
| Per cent sample in mixture (a) | 13.99 | 15.03 | .. |
| Per cent sample stearic in mixture (b) | 1.76 | 1.61 | .. |
| Per cent stearic acid in sample (b/a) | 12.6 | 10.7 | 11.6 |

For myristic acid the procedure is the same except that here three acids must be considered: palmitic, stearic, and oleic, for which the specific depression constants in myristic acid are respectively 1.82, 2.02, and 1.67. The approximate proportions of these three acids in the sample will determine the value of K_w to be used. Making use here of the figures 22.8 per cent palmitic, 11.6 per cent stearic and the free fatty acid value which was found by titration to be 99.3 per cent as oleic acid—i. e., 99.3 per cent expressed on the basis of an average molecular weight of 282—the proper value of K_w is found as follows:

| | |
|---|---------------------|
| Per cent palmitic, as oleic (22.8 × 282/256) | 25.1 |
| Per cent stearic, as oleic (11.6 × 282/284) | 11.5 |
| Sum | 36.6 |
| Per cent total free fatty acids, as oleic | 99.3 |
| Per cent remaining acids, largely oleic, as oleic | 62.7 |
| | % K_w |
| Palmitic acid | 22.8 × 1.82 = 41.5 |
| Stearic acid | 11.6 × 2.02 = 23.4 |
| Oleic acid | 62.7 × 1.67 = 104.6 |
| | 97.1 |
| | 169.5/97.1 = 1.75 |

The results for myristic acid are then as follows:

| | MIXTURE 5 | MIXTURE 6 | AVERAGE |
|--|-----------|-----------|---------|
| Per cent not myristic in mixture (10 L/1.75) | 13.93 | 15.10 | .. |
| Per cent sample in mixture (a) | 14.08 | 14.86 | .. |
| Per cent sample myristic in mixture (b) | 0.15 | -0.24 | .. |
| Per cent myristic acid in sample (b/a) | 1.1 | -1.6 | -0.2 |

While very close checks are often obtained, the mixed-melting-point results are not accurate to more than a few per cent. Especially in determining small amounts of acid, duplicate analyses may fail to agree within 5 per cent or even more. The values here found for myristic acid are totally without significance except to show that myristic acid is probably absent from this sample.

It might at first appear that these low results for myristic acid must necessarily follow from the fact that there has been no allowance for myristic acid in determining the value of K_w employed. On the contrary, however, one might allow for a considerable percentage of myristic acid, say 15 per cent, without greatly affecting either the value of K_w that would be chosen or the final analytical results. Thus, if the acids determined above, by difference, as 62.7 per cent oleic are assumed to consist of only 47.7 per cent oleic and 15 per cent myristic (as oleic), the total percentage of acids other than myristic becomes 82.1 instead of 97.1, their total per cent × K_w product becomes 144.6, the resulting value of K_w becomes 1.76, and the calculated percentages of myristic acid in the sample are 1.6 and -0.95, averaging 0.3 per cent. Of course, should the sample prove to contain a considerable percentage of myristic acid, this must also be taken into account when estimating K_w values to be used in determining the other saturated acids.

IMPORTANCE OF PROPER SELECTION OF K_w VALUES

The results obtained by this method are dependent, in part, upon the proper selection of the K_w value to be used in each case and the determination of this value, which is based on the specific depression constants for the pure acids, as indicated above, requires also some preliminary knowledge of the chief constituent fatty acids present and their ap-

proximate proportions. The analyst will usually have sufficient information of this sort about his samples to lead him to the proper constants. If not, however, the approximate composition is readily obtained by a preliminary examination of the melting-point data, using trial constants.

It is not likely, therefore, that any considerable error in the assignment of K_w values will be made. Nevertheless, it is of interest to note the magnitude of the errors that can be introduced into the final results by the use of wrong constants.

Let us assume that the sample being analyzed consists entirely of palmitic and stearic acids and that, after mixing with pure stearic acid, the composition of the mixture is 85 per cent stearic and 15 per cent palmitic. The melting-point depression is 2.66 degrees. The proper K_w value to use is 1.77. Suppose, however, that the value 1.70 is used instead. The calculation would then indicate 10 × 2.66/1.70 or 15.65 per cent of acids other than stearic and therefore 84.35 per cent of stearic acid in the mixture. Expressed as a percentage of the original sample, the error would be considerably magnified, depending upon the ratio of sample to pure acid used in making up the melting-point mixture or, in other words, upon the percentage of stearic acid in the sample. The proportions it might thus reach are shown in Table IV, where five different cases are assumed.

TABLE IV. EFFECT OF ERROR OF 0.07 IN VALUE OF K_w

| STEARIC ACID IN SAMPLE | COMPOSITION OF MIXTURE | | STEARIC ACID IN MIXTURE | FOUND IN MIXTURE | CALCULATED IN SAMPLE (c-a)/b | ERROR IN PER CENT OF SAMPLE |
|------------------------|------------------------|----------|-------------------------|------------------|------------------------------|-----------------------------|
| | Pure stearic a | Sample b | | | | |
| % | % | % | % | % | % | % |
| 5 | 84.21 | 15.79 | 85 | 84.35 | 0.9 | 4.1 |
| 10 | 83.33 | 16.67 | 85 | 84.35 | 6.1 | 3.9 |
| 20 | 81.25 | 18.75 | 85 | 84.35 | 16.5 | 3.5 |
| 50 | 70 | 30 | 85 | 84.35 | 47.8 | 2.2 |
| 80 | 25 | 75 | 85 | 84.35 | 79.1 | 0.9 |

Large errors such as these are therefore possible, particularly where low percentages of the acid being determined are present in the sample. They are, however, greatly reduced by more careful selection of the constant used.

EFFECT OF NEUTRAL FAT IN SAMPLE

The effect of the presence of neutral fat in the sample analyzed may be judged from the melting-point depressions caused by pure triglycerides in palmitic and stearic acids. Table V gives the results of such measurements for three pure glycerides, samples of which were made available through the courtesy of C. G. King of the University of Pittsburgh Chemistry Department.

TABLE V. MELTING-POINT DEPRESSIONS CAUSED BY NEUTRAL FAT

| FAT (SOLUTE) | WEIGHT | | PER CENT SOLUTE | | MELTING POINT ° C. | DEPRESSION ° C. | DEPRESSION PER 10 PER CENT K_w | DEPRESSION PER 10 PER CENT K_m |
|---|--------|--------|-----------------|---------------|--------------------|-----------------|----------------------------------|----------------------------------|
| | Acid | Fat | Weight per cent | Mole per cent | | | | |
| IN PALMITIC ACID (MELTING POINT 61.95°) | | | | | | | | |
| Trimyristin | 0.8332 | 0.1445 | 14.79 | 5.80 | 60.93 | 1.00 | 0.68 | 1.72 |
| | 0.8577 | 0.1601 | 15.73 | 6.22 | 60.78 | 1.15 | 0.73 | 1.85 |
| Tristearin | 0.8616 | 0.1515 | 14.95 | 4.81 | 60.96 | 0.97 | 0.65 | 2.01 |
| | 0.9139 | 0.1466 | 13.81 | 4.41 | 61.08 | 0.85 | 0.61 | 1.93 |
| Palmito-dimyristin | 0.8496 | 0.1384 | 14.00 | 5.26 | 60.93 | 1.00 | 0.71 | 1.90 |
| | 0.6368 | 0.0945 | 12.92 | 4.83 | 61.03 | 0.90 | 0.70 | 1.86 |
| Average 1.88 | | | | | | | | |
| IN STEARIC ACID (MELTING POINT 69.21°) | | | | | | | | |
| Trimyristin | 0.8623 | 0.1402 | 13.98 | 6.00 | 68.29 | 0.92 | 0.66 | 1.53 |
| | 0.8838 | 0.1506 | 14.53 | 6.26 | 68.19 | 1.02 | 0.70 | 1.63 |
| Tristearin | 0.8807 | 0.1384 | 13.59 | 4.78 | 68.49 | 0.72 | 0.53 | 1.51 |
| | 0.8585 | 0.1537 | 15.17 | 5.40 | 68.33 | 0.88 | 0.58 | 1.63 |
| Palmito-dimyristin | 0.8313 | 0.1099 | 11.69 | 4.77 | 68.39 | 0.82 | 0.70 | 1.72 |
| | 0.8655 | 0.1536 | 15.08 | 6.31 | 68.19 | 1.02 | 0.68 | 1.62 |
| Average 1.61 | | | | | | | | |

The molar depression constants here obtained for palmitic and stearic acids are approximately the same as those found when using fatty acids as solutes. Agreement among the present results is less close because the molar percentages of

solute present in the mixtures made up, and consequently the total depressions observed, were in all cases small. It is apparent, however, that, as compared with the effect of an equal weight of free fatty acids, neutral fat causes only three- or four-tenths as much depression of the melting point,

the total free fatty acid, as oleic, determined by titration. The three components are then expressed as percentages of their total. For the present samples, these conversions are indicated in Table VIII, the last three columns giving the coordinates of the points laid down in Figure 3.

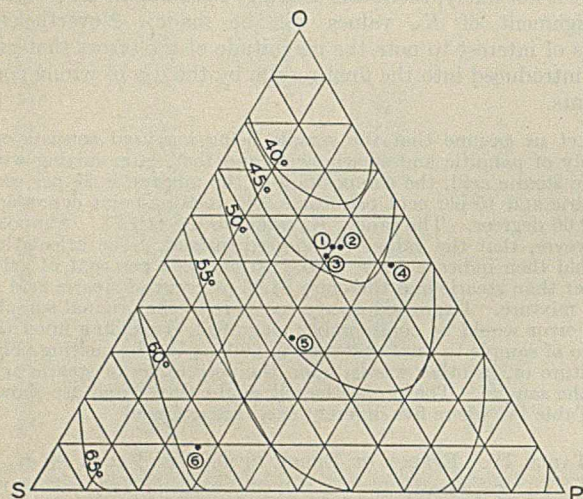


FIGURE 3. FATTY ACID COMPOSITION OF TYPICAL STOCK GREASES

In terms of palmitic acid, stearic acid, and oleic acid (plus others) by difference

depending upon the nature of the glyceride or glycerides present. The effect is thus to cause the mixed-melting-point method to give results that are high by a fraction of the amount of the neutral fat present.

APPLICATION TO STUDY OF TECHNICAL MIXTURES

As an example of the application of the mixed-melting-point method to technical fatty acid mixtures, we may consider the results of analyses for palmitic and stearic acids made on samples of the following six raw greases which enter the manufacture of commercial fatty acids: (1) hard grease (tallows), (2) brown grease, (3) garbage grease, (4) palm oil, (5) oleostearin, and (6) hydrogenated cottonseed stearin.

The fatty acids from these stocks were obtained by Twitchell saponification of the fats in 200-pound batches following the regular commercial procedure. They were not distilled.

Titer, free fatty acid, iodine, and thiocyanogen iodine values are given in Table VI, together with the percentages of oleic and linoleic acids calculated from the two latter determinations. The mixed-melting-point data and results are tabulated in Table VII.

The triangular diagram shown in Figure 3 affords a convenient method for recording and comparing the fatty acid compositions of different samples. The total free fatty acids are here expressed in terms of the three components, palmitic acid, stearic acid, and oleic acid (plus others) by difference. The latter value is obtained by converting the percentages of palmitic acid and stearic acid to their equivalent percentages as oleic and subtracting their sum from

TABLE VI. ANALYSES OF FATTY ACID MIXTURES FROM TYPICAL STOCK GREASES

| | HARD GREASE | BROWN GREASE | GARBAGE GREASE | PALM OIL | OLEO-STEARIN | COTTON-SEED STEARIN |
|--------------------------------|-------------|--------------|----------------|----------|--------------|---------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Titer, ° C. | 42.80 | 40.10 | 37.10 | 43.60 | 50.30 | 60.00 |
| Free fatty acids (as oleic), % | 97.79 | 96.16 | 93.48 | 99.46 | 97.88 | 99.74 |
| Iodine value | 47.10 | 57.10 | 63.66 | 53.74 | 24.64 | 6.54 |
| Thiocyanogen iodine value | 40.46 | 45.80 | 47.75 | 43.54 | 22.12 | 6.34 |
| Linoleic acid, % | 7.35 | 12.48 | 17.56 | 11.26 | 2.78 | 0.23 |
| Oleic acid, % | 37.56 | 38.36 | 35.40 | 37.07 | 21.80 | 6.81 |

TABLE VII. MIXED-MELTING-POINT RESULTS, FATTY ACIDS FROM STOCK GREASES

| STOCK | MIXTURES WITH PALMITIC ACID | | | | MIXTURES WITH STEARIC ACID | | | |
|-------|-----------------------------|--------------------|-----------------|------------|----------------------------|--------------------|-----------------|-----------|
| | Sample % | Melting point ° C. | Depression ° C. | Palmitic % | Sample % | Melting point ° C. | Depression ° C. | Stearic % |
| 1 | 16.03 | 60.52 | 1.88 | 29.7 | 16.01 | 67.09 | 2.23 | 16.6 |
| | 18.01 | 60.22 | 2.18 | 27.3 | 18.00 | 66.77 | 2.55 | 15.2 |
| | | | | 28.5 | | | | 15.9 |
| 2 | 16.01 | 60.51 | 1.89 | 29.1 | 15.99 | 67.03 | 2.29 | 14.3 |
| | 17.98 | 60.31 | 2.09 | 30.2 | 17.95 | 66.77 | 2.55 | 14.9 |
| | 13.96 | 60.72 | 1.68 | 27.7 | 19.97 | 66.47 | 2.85 | 14.5 |
| | | | 29.0 | | | | 14.6 | |
| 3 | 8.99 | 61.33 | 1.07 | 28.5 | 9.98 | 67.99 | 1.33 | 20.2 |
| | 10.99 | 61.06 | 1.34 | 26.8 | 11.06 | 67.79 | 1.53 | 17.2 |
| | 12.98 | 60.83 | 1.57 | 27.3 | 11.98 | 67.61 | 1.71 | 14.5 |
| | | | 27.5 | | | | 17.3 | |
| 4 | 17.98 | 60.63 | 1.77 | 40.9 | 15.01 | 66.98 | 2.34 | 7.4 |
| | 20.01 | 60.42 | 1.98 | 40.6 | 16.96 | 66.68 | 2.64 | 7.6 |
| | | | | 40.7 | | | | 7.5 |
| 5 | 17.95 | 60.34 | 2.06 | 31.1 | 20.00 | 67.09 | 2.23 | 33.9 |
| | 20.01 | 60.07 | 2.33 | 30.1 | 22.01 | 66.78 | 2.54 | 31.5 |
| | | | | 30.6 | | | | 32.7 |
| 6 | 19.97 | 59.99 | 2.41 | 27.5 | 22.04 | 67.88 | 1.44 | 62.0 |
| | 22.01 | 59.61 | 2.79 | 23.9 | 24.05 | 67.78 | 1.54 | 62.8 |
| | | | | 25.7 | | | | 62.4 |

In addition to the ruled coordinates the triangular diagram carries constant-temperature curves showing the solidifying points of ternary mixtures of palmitic, stearic, and oleic acids, drawn according to the data of Carlinfanti and Levi-Malvano (4). As pointed out by Lapworth and Pearson (6), the oleic acid used by these experimenters could not have been of high purity, so that the position of these curves can only be considered roughly approximate. However, if the samples analyzed and plotted on the triangular diagram actually contained, in addition to palmitic and stearic acids, only oleic acid, their positions with relation to the constant-temperature lines should agree at least approximately with their titers.

The close agreement, in solid acid content, between stocks 1, 2, and 3 is of particular interest. They are identical within the limits of measurement by the mixed-melting-point method, yet in general character and behavior in the plant these stocks are widely different. It will be seen that, if their titers and iodine values are compared with the values that would be expected according to Figure 3, stock 1 appears to be about properly placed, but stocks 2 and 3, having

TABLE VIII. COMPARISON OF FATTY-ACID CONSTITUENTS OF SIX STOCK GREASES

| No. | PER CENT PALMITIC | PER CENT STEARIC | EQUIVALENT PER CENT AS OLEIC | | PER CENT FREE FATTY ACID AS OLEIC | PER CENT OLEIC (+ OTHERS) BY DIFFERENCE | TOTAL FATTY ACIDS | PERCENTAGE COMPOSITION OF TOTAL FATTY ACIDS | | |
|-----|-------------------|------------------|------------------------------|------|-----------------------------------|---|-------------------|---|------|------|
| | P | S | p | s | f | $O = f - p - s$ | T | P/T | S/T | O/T |
| 1 | 28.5 | 15.9 | 31.4 | 15.8 | 97.8 | 50.6 | 95.0 | 30.0 | 16.7 | 53.3 |
| 2 | 29.0 | 14.6 | 31.9 | 14.5 | 96.2 | 49.8 | 93.4 | 31.1 | 15.6 | 53.3 |
| 3 | 27.5 | 17.3 | 29.2 | 17.2 | 93.5 | 47.1 | 91.9 | 29.9 | 18.8 | 51.3 |
| 4 | 40.7 | 7.5 | 44.9 | 7.4 | 99.5 | 47.2 | 95.4 | 42.7 | 7.8 | 49.5 |
| 5 | 30.6 | 32.7 | 33.7 | 32.5 | 97.9 | 31.7 | 95.0 | 32.2 | 34.4 | 33.4 |
| 6 | 25.7 | 62.4 | 28.3 | 62.0 | 99.7 | 9.4 | 97.5 | 26.4 | 64.0 | 9.6 |

higher iodine values and lower titers, call for positions nearer the vertex O. The explanation, of course, lies in the presence of a considerable percentage of linoleic acid in the liquid acids of these stocks. The effect of linoleic acid on the shape of the titer surface, of which the constant-temperature lines represent projected contours, has been discussed in Part I of this series (13). The position of stock 4 also reflects an appreciable linoleic acid content.

The composition of any mixture of these stocks can be determined graphically on the diagram. Differences in behavior among such mixtures can thus be considered in relation to specific differences in fatty acid composition.

The usefulness of this type of data in the study of plant processes in the fatty acid industries will be readily apparent.

ACKNOWLEDGMENTS

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rate stock greases. Important contributions to this study were made by George D. Beal, under whose supervision the investigations were conducted, and by H. H. R. Weber who assisted in carrying out the laboratory experimental work.

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Examination of the Phenols of a Low-Temperature Coal Tar

S. CAPLAN, J. ROSS, M. G. SEVAG, AND T. M. SWITZ, Combustion Utilities Corporation, Linden, N. J.

The commercial utilization of low-temperature tar would remove one of the chief obstacles to the establishment of low-temperature carbonization processes in this country. This primary tar is a unique source of high-boiling phenols, concerning whose chemical structure there has been considerable conjecture but little data.

More exact knowledge of the constitution of these phenols would serve to indicate those industrial

markets in which they might be utilized as a new raw material. It is now shown that the fraction of these tar acids boiling up to 260° C. consists of homologs of phenol in which the alkyl groups are largely in a meta position to the hydroxyl group. The methods used in separating individual phenols from groups of isomers are presented and two of the phenols are identified as mesitol and 3-methyl-5-ethylphenol.

THE large proportion of high-boiling constituents is a well-known characteristic of low-temperature tar, particularly of the phenolic portion of the distilled tars. Thus the outstanding point of difference between high-temperature or coke-oven tar phenols and the phenols of low-temperature tar is the relative proportion of low- and medium-boiling constituents, as shown in Table I.

TABLE I. COMPOSITION OF COKE-OVEN AND PRIMARY TAR PHENOLS

| | 180- 210° C. | 210- 225° C. | 225- 280° C. | 280- 320° C. | PITCH |
|-----------------------|-----------------|-----------------|-----------------|-----------------|-------|
| | % | % | % | % | % |
| Coke-oven tar phenols | 60 | 15 | 10 | 7 | 8 |
| Primary tar phenols | 9 | 24 | 22 | 15 | 30 |

Although the phenols above the xylenol range form approximately 66 per cent of the tar acids of low-temperature tar, no exact knowledge of their constitution or structure is available. The phenols up to and including the xylenol range have been studied by many investigators, but fractions above 225° C. have received little attention.

Glud and Breuer (3) made cresoxyacetic acid derivatives of a fraction boiling from 237° to 241° C. and from the analyses showed that the phenol approximated the formula $C_9H_{12}O$ which they considered indicated trimethylphenol. Avenarius (1), however, from consideration of analyses of allophanic acid deriva-

tives concluded that the low hydrogen content indicated presence of unsaturated side chains in this series, as did Weindel (11) who made analyses of the acetyl esters. Steinkopf and Höpner (8) stated that some of the phenols above the cresols evidently contained side chains longer than the methyl.

Morgan and Soule (6) carefully fractionated the whole range of phenols from both a low-temperature tar and a coke-oven tar and plotted curves of specific gravities versus the mean boiling points of the respective fractions. These curves (Figure 1) show a well-defined minimum point and also indicate that the Carbo-coal tar phenols are lower in density than the corresponding fractions of coke-oven tar over almost the entire range. Regarding these curves, Morgan and Soule state: "The decrease in specific gravity of the phenols as the boiling point increases indicates the presence of aliphatic side chains of lower density attached to the phenol nucleus—e. g., cresols and xylenols. In the higher homologs a sharp rise in density and a notable increase in the viscosity of the fractions mark the appearance of α - and β -naphthols in the high-temperature phenols, and bicyclic compounds at least in the low-temperature phenols."

PREPARATION OF FRACTIONS

In the present investigation the phenols boiling from 220° to 260° C. have been examined, particularly to determine the changes in composition responsible for the shape of the specific gravity-boiling point curve as noted by Morgan and Soule (6)—i. e., the inflection point—and the appreciable differences in density of corresponding fractions of the

phenols of high- and low-temperature tar. The tar acids studied were obtained from a low-temperature tar produced during some large-scale tests on the Doherty complete gasification process at Toledo, Ohio, May to November, 1925. This tar is usually known as Hydrogas tar.

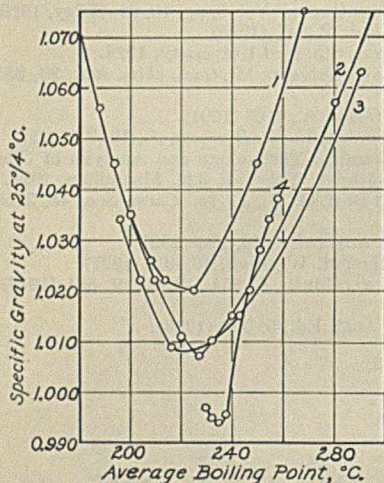


FIGURE 1. BOILING POINT VS. SPECIFIC GRAVITY OF FRACTIONS OF PHENOLS FROM VARIOUS TARS

1. Coke-oven tar phenols (Morgan and Soule)
2. Carbocoal tar phenols (Morgan and Soule)
3. Hydrogas tar phenols (Morgan and Meighan)
4. Low-temperature tar phenols (present investigation)

using a 50-gallon (189-liter) iron still with a fractionating column, 6 feet (180 cm.) long and 6 inches (15 cm.) in diameter, filled with 1-inch (2.5-cm.) Raschig rings. During the distillation the pressure averaged 53 mm.

TABLE II. ANALYSIS OF TAR

| | |
|--|---------|
| Sp. gr. at 25/25° C. | 1.03 |
| "Free carbon" | 0.71% |
| Distillation end point at 50 per cent off by volume | 330° C. |
| Pitch melting point (cube-in-water) at 50 per cent off by volume | 40° C. |
| Sp. gr. of distillate at 25/25° C. | 0.96 |
| Tar acid content of distillate | 21.6% |
| Nitrogen bases in distillate | 3.0% |
| Sp. gr. of neutral oil at 25/25° C. | 0.91 |
| Sulfonation residue, per cent of neutral oil | 30.0 |

Great attention was paid to efficient fractionation, without which the separation by distillation of even fairly simple mixtures is valueless and misleading. After several tests a fractionating column was finally designed that gave excellent results. This was a modification of the column described by Peters and Baker (7). Using this column at atmospheric pressure, several of the cuts obtained in the large-scale distillation *in vacuo* were subjected to repeated fractionations. In the first fractionation, two 15° cuts were separated. The first, boiling at 225° to 240° C., was selected because it contained the phenol corresponding to the minimum point of the specific gravity-boiling point curve, while the fraction boiling at 240° to 255° C. was taken as being well up on the rising part of this curve and hence in the range in which clues might be found to account for the difference in density of corresponding fractions of high- and low-temperature tar phenols. During the succeeding fractionations the cuts were made narrower and narrower, until in the sixth and final distillation of the original 225° to 240° C. cut 0.5° cuts were taken, as was also the case in the fifth and last fractionation of the 240° to 255° C. portion. The largest fraction

obtained boiled at 234° to 234.5° C., which coincides with the point of minimum density, so that this fraction was used for the attempt to isolate individual compounds and to study their chemical structures.

That the fractionation of the tar acids used in this work was fairly efficient is evidenced by the fact that the specific gravity-boiling point curve (Figure 2) shows to a slight extent the irregularities obtainable by splitting a complete set of isomers into its constituents or into several groups of constituents.

During each fractionation of the two 15° cuts, "spot cuts," consisting of a few drops each, were taken at close intervals for the determination of refractive indices. The curves obtained by plotting these data assisted in following the progress in separation made by each fractionation, and the curves for the final fractionations are shown in Figure 2 together with a curve of specific gravities of the individual cuts. It will be observed that both the refractive index and the specific gravity curves show distinct minima, as in the curve of Morgan and Soule. This point of inflection was considered by Curtis and Beekhuis (2) to indicate the appearance above that point of dihydric phenols in appreciable quantity.

CHARACTERISTICS STUDIED

DEHYDROGENATION AND DEOXYGENATION. Partial hydrogenation of the nucleus is one of the possible differences of structure that might account for the observation of Morgan and Soule that phenols of low-temperature tar have lower densities than phenols of the same boiling point from high-temperature tar. In order to test this point, several fractions between 250° and 260° C. were passed over a nickel-thoria catalyst at 350° C. The gas liberated was negligible, whereas with tetrahydronaphthol and tetrahydronaphthalene almost theoretical yields of hydrogen were obtained, together with naphthol in one case and naphthalene in the other. This excludes the possibility of the presence of polynuclear phenols, since the naphthols themselves boil above 280° C., whereas the failure to liberate hydrogen rules out the hydrogenated naphthols.

By deoxygenation the parent hydrocarbon can be obtained. An active carbon catalyst in the presence of hydrogen was found to give better results and at a lower temperature than the classical zinc-dust method of Baeyer. In each case only small yields of hydrocarbons were obtained and these were mixtures of a number of compounds as indicated by the wide boiling range, so that no definite conclusions could be drawn from these tests.

SOLID DERIVATIVES. Attempts were then made to prepare various solid derivatives in order to characterize the phenols more definitely and to aid in the separation of isomers by fractional crystallization. The phenoxyacetic acids, by reaction of the phenols with chloroacetic acid, had been employed by Glud and Breuer (3) in the identification of the lower-boiling phenols of low-temperature tar and had later been applied by Steinkopf and Höpner (8) to the xylenols. However, when this method was used with the higher-boiling liquid fractions of tar acids being studied in the present investigation, the reactions were violent and the products consisted largely of noncrystallizable oils. Much more satisfactory results were had with the preparation of the phenylurethans and naphthylurethans, which were also employed by Steinkopf and Höpner. Molecular weight determinations and ultimate analyses of the urethans indicated that the fraction boiling at 234° C. could be represented by the formula $C_9H_{12}O$. Bromo derivatives of the 234° C. fraction were obtained in crystalline form and on analysis confirmed the formula $C_9H_{12}O$ for this cut.

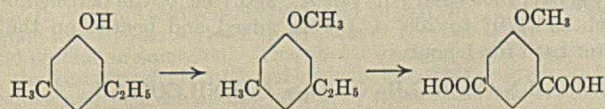
MOLECULAR WEIGHTS OF FRACTIONS. The molecular weights of the phenol fractions were determined indirectly by the cryoscopic method using the methyl ether of the phenol in benzene solution. This method was found to be more reliable and accurate than the hydrogen equivalent method, using sodium and the toluene solution of the free phenol (5). After the third distillation the molecular weights of all of the 5° C. fractions were determined. Unusually high values obtained for the fraction 220° to 225° C., which is in the xylol range, showed that a large percentage of phenols of molecular weight higher than 122 must be present in this fraction. This fraction was therefore examined more thoroughly and the trimethylphenol, mesitol, separated from the xylenols by the method given below.

SEPARATION BY FRACTIONAL LIBERATION AND EXTRACTION. The degree of hydrolysis of the sodium salt of a phenol in aqueous solution, and the partition of the phenol itself between two solvents, such as ether and water, are known to be functions of the chemical constitution of the phenol considered. Fractional precipitation by successive addition of small portions of acid to the sodium phenolates has been applied to the separation of phenols, cresols, and xylenols by previous workers. Vavon and Zaharia (9) examined various synthetic phenols and found that all phenols could be extracted by ether from the aqueous solution of their sodium salts. The percentage of phenol that was extracted by the ether varied greatly according to the constitution of the phenol. Notably many ortho and diortho compounds were almost completely extracted by the ether in one extraction, demonstrating the high degree of hydrolysis of their sodium salts. A more recent paper on the use of this method presents quantitative data for a number of phenols and indicates commercial possibilities (4).

A method of separation combining fractional precipitation and extraction by ether of the phenols from their sodium salts was used in the examination of the phenols boiling over the range 220° to 225° C., proving them to consist of a mixture of mesitol and xylenols. The mesitol was identified by preparation of the dibromide, and by mixed melting point of this with a synthetic specimen of mesitol dibromide.

OXIDATION OF SIDE CHAINS. Although the fractions examined evidently consisted of homologs of phenol, the number, position, and length of the alkyl side chains were yet to be determined, with the evidence strongly in favor of a single long side chain for the 234° C. fraction, since it occurred at the inflection point of the specific gravity and refractive index curves. For this determination, recourse was had to conversion of the alkyl groups into carboxyl groups.

The fraction boiling at 234° C. was in this way converted to a dicarboxymethoxy derivative whose identity with 1-methoxy-3,5-dicarboxybenzene was proved by a mixed-melting-point determination with a sample of this acid obtained synthetically from another source. Since the original tar acid has been shown by several different methods to consist largely of a phenol having the formula $C_9H_{12}O$, the latter must be *m*-methylethylphenol.



The fractions above the 234° C. cut were found to be much more resistant to oxidation with alkaline permanganate, which observation would cast doubt on the existence of either long side chains or unsaturated side chains on the nucleus of these higher boiling phenols.

PROBABLE COMPOSITION OF TAR ACIDS 235° TO 260° C.

Every test that has been applied to the fractions of these low-temperature tar acids up to 260° C. has failed to show any structural differentiation between them and the corresponding fractions of tar acids from high-temperature tar. A series of cuts of the high-temperature tar phenols were prepared for this comparison from a 10-gallon (37.85-liter) sample of "carbolic tar"—the still residue of coke-oven tar phenols after removal of the cresols and xylenols—which was obtained through the courtesy of the Barrett Company. But nevertheless there remain to be explained the marked differences in physical properties, in the density and refractive index.

A rather simple explanation to account for the relatively low density of the primary tar phenols occurs to the authors. This consists, in brief, in the supposition that in each group of phenol homologs the isomers which predominate in the low-temperature tar acids are those having the alkyl side chains meta or para to each other, while in the high-temperature tar acids an ortho grouping of the same alkyl chains predominates. Examination in the literature of the only group of aromatic homologs for which fairly complete density figures are available, the polymethylated benzenes, reveals rather strikingly the effect of the ortho grouping of side chains in elevating the densities, as shown in Table III, taken from International Critical Tables, and in Figure 3.

TABLE III. DENSITY FIGURES

| HYDROCARBON | BOILING POINT ° C. | d_4^{20} | n_D^{20} |
|----------------------------|-----------------------|------------|------------|
| Benzene | 80 | 0.878 | 1.5014 |
| Toluene | 110 | 0.866 | 1.4962 |
| <i>o</i> -Xylene | 144 | 0.879 | 1.5058 |
| <i>m</i> -Xylene | 139 | 0.865 | 1.4973 |
| <i>p</i> -Xylene | 138 | 0.861 | 1.4956 |
| 1,2,3-trimethylbenzene | 176.5 | 0.895 | 1.5132 |
| 1,2,4-trimethylbenzene | 170 | 0.870 | 1.5051 |
| 1,3,5-trimethylbenzene | 165 | 0.863 | 1.4967 |
| 1,2,3,4-tetramethylbenzene | 204 | 0.901 | 1.5187 |
| 1,2,3,5-tetramethylbenzene | 197 | 0.894 | |
| 1,2,4,5-tetramethylbenzene | 193 | 0.888 | |

It is worthy of note in this connection that the largest 0.5° fraction that was obtained in the fractionation of the low-temperature tar phenols, that boiling from 234° to 234.5° C., was found to consist largely of 3-methyl-5-ethylphenol—i. e., the alkyl groups were in a meta position to one another, while the phenol of $C_9H_{12}O$ formula which was isolated from the 218° to 220° C. fraction was mesitol, in which the three methyl groups are again in a meta grouping.

Of course, the above evidence is entirely too fragmentary to make the proposition anything more than mere conjecture, nor are there sufficient data on the pyrolytic behavior of these phenols to enable one to predict whether the homologs with the alkyl side chains in ortho position to each other would be more stable and hence would be likely to remain in high-temperature tar, whereas the others would be, to a greater extent, destroyed. It is hoped, however, that future workers in this field may devote further attention to this question, and it is suggested that the fractional liberation of the phenols from their phenolate solutions, together with the oxidation of their ethers, offers a convenient method of separating and identifying the isomers.

FRACTIONATION OF TAR ACIDS

The fractionating column used was 1.65 meters long, 12 mm. internal diameter, and packed with 5×5 mm. glass Raschig rings. It was connected to the flask by a ground-glass joint and the whole apparatus was made of Pyrex glass. An air condenser or dephlegmator at the top of the column maintained an adequate reflux ratio (approximately 15 to 1). To prevent heat loss the column was surrounded by a close-

fitting concentric glass tube wound with nichrome ribbon which was heated electrically, and the whole assembly was jacketed to avoid drafts.

From the tar acids which had been distilled on a larger scale under reduced pressure, two large fractions were collected over the ranges 225° to 240° C. and 240° to 255° C. These were each separately fractionated at atmospheric pressure, cuts being taken at progressively smaller intervals. The results for the sixth fractionation of acids boiling 225° to

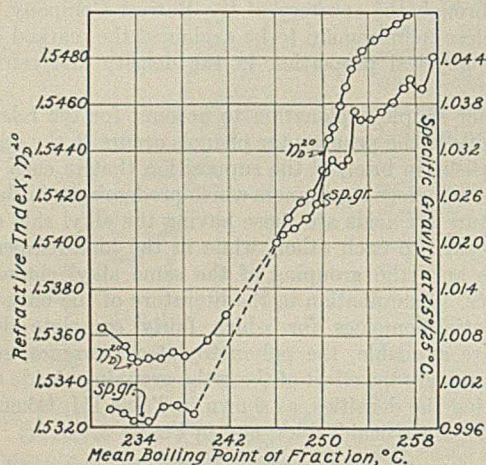


FIGURE 2. REFRACTIVE INDEX AND SPECIFIC GRAVITY OF FRACTIONS AFTER LAST FRACTIONATION

240° C. are shown in Figure 2. The largest fraction, boiling at 234° C., was selected for particular examination. The fractionation of acids of boiling range 240° to 255° C. was not carried beyond the fifth distillation (Figure 2).

FRACTION 220° TO 225° C.

METHYLATION. Samples of the 5° C. cuts obtained after the third distillation of the xylenol range of tar acids were dissolved in an excess of 10 per cent sodium hydroxide solution and converted to their methyl ethers by treatment with dimethyl sulfate. Molecular weights of the ethers were then obtained by the cryoscopic method in benzene.

TABLE IV. MOLECULAR WEIGHTS

| FRACTION ° C. | MOLECULAR WEIGHT OF PHENOL |
|------------------|-------------------------------|
| 205-215 | 126 |
| 215-220 | 131 |
| 220-225 | 130 |
| 225-230 | 141 |
| 230-235 | 143 |
| 235-240 | 149 |

SEPARATION BY FRACTIONAL LIBERATION FROM PHENOLATES. A sample of 185 grams of phenols boiling from 220° to 225° C. was dissolved in the equivalent amount, 500 cc., of 10 per cent caustic soda solution. This alkaline solution was twice treated with 50 cc. of ether, shaking thoroughly in a separatory funnel for each extraction (extract 1). Then 65 cc. of 2.5 *N* hydrochloric acid were added, 15 cc. at a time, shaking after each addition. The precipitated phenol was extracted with 100 cc. of ether. Another 65-cc. portion of the acid was similarly added, followed by shaking with ether, etc. In all, 500 cc. of acid were added, making 8 extractions. The ethereal extracts were washed with dilute acid, then with water, and after drying over anhydrous sodium sulfate the ether was removed on the water bath. The phenol portions were distilled at 15 mm. pressure.

Table V shows the degree of separation of compounds that was obtained.

The molecular weights were determined by the cryoscopic method, using the methyl ether of the phenol with benzene as solvent. Of known phenols of molecular weight 136 boiling within the range 215° to 225° C. the following are

described: mesitol (2,4,6-trimethylphenol), boiling point 220° C.; 2-methyl-5-ethylphenol, boiling point 220° C.; and 2-ethyl-5-methylphenol, boiling point 226° C.

Mesitol, being substituted in both ortho positions to the hydroxyl group, would be less acid than the xylenols present and therefore would be expected in the first fractions. Fraction 1 was therefore redistilled at atmospheric pressure and that part boiling between 218° and 220° C. was taken for examination.

BROMIDES. A portion (5 grams) of the phenols boiling at 218° to 220° C. was brominated in the cold, in chloroform solution, by addition of one molecular equivalent of bromine. The monobromide was distilled under reduced pressure after removal of the solvent. Since no solid product could be obtained, a second molecule of bromine was added. On cooling, a crystalline solid (4 grams) separated from the chloroform solution. After recrystallization it had a melting point of 159° to 160° C. Analysis showed this to be a dibromide, $C_9H_{10}OBr_2$.

Calculated for $C_9H_{10}OBr_2$: Br, 54.33. Found: Br, 54.2.

Dibromomesitol is described as having a melting point of 159° to 160° C. The melting point of a mixture of the above dibromide with an authentic specimen of 3,5-dibromomesitol was unchanged. In this way the identity of the above dibromide was established and the presence of mesitol in the tar acids boiling at 220° C. confirmed. The residual liquid bromide was not examined further.

TABLE V. SEPARATION OF COMPOUNDS

| FRACTION | WEIGHT Grams | n_D^{20} | MOLECULAR WEIGHT |
|----------|-----------------|------------|---------------------|
| 1 | 35 | 1.5335 | 133.5 |
| 2 | 25 | 1.5350 | 132 |
| 3 | 25 | 1.5350 | 134 |
| 4 | 25 | 1.5360 | 129 |
| 5 | 25 | 1.5360 | 127 |
| 6 | 20 | 1.5360 | 127 |
| 7 | 20 | 1.5380 | 126 |
| 8 | 10 | 1.5380 | 125 |

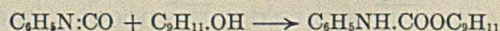
METHYL ETHER. The methyl ether of the phenol boiling at 218° to 220° C. was prepared by treatment at 30° C. of an alkaline solution of the phenol with dimethyl sulfate. This ether had a boiling point of 203° C., and molecular weight of 147 by the cryoscopic method in benzene. $C_9H_{11}OCH_3$ requires a molecular weight of 150.

FRACTION 234.0° TO 234.5° C.

This was the largest 0.5° cut obtained after the sixth fractionation of the original fraction, 225° to 240° C.

Calculated for $C_9H_{12}O$: C, 79.4; H, 8.82. Found: C, 79.98; H, 9.00.

PHENYLURETHAN. The method found to be best applicable for the preparation of the phenylurethan of this phenol fraction was that described by Wehuizen (10), who recommended carrying out the reaction in petroleum naphtha (boiling point, 170° to 200° C.) solution, obtained for this work by the fractional distillation of some commercial kerosene. Three grams of the tar acid, 3 grams of phenyl isocyanate (a slight excess over molecular equivalent), and 7 cc. of the petroleum naphtha (170° to 200° C.) were mixed and heated on the water bath for 1 hour.



After the mixture had been standing at room temperature overnight, the phenylurethan crystallized out. The yield of crude urethan was 2.1 grams, or 36 per cent of the theoretical yield. It was purified by several crystallizations from carbon tetrachloride followed by one from ligroin (80° to 100° C.). The melting point was 145° C.

Calculated for $C_{10}H_{17}O_2N$: C, 75.29; H, 6.65; N, 5.49. Found: C, 75.26; H, 6.79; N, 5.63.

Molecular weight, calculated: 255. Found (Rast's camphor method): 249.

NAPHTHYLEURETHAN. This was prepared in the same manner as the phenylurethan except that α -naphthyl isocyanate was used. This reagent had the disadvantage of producing dinaphthyl urea which was insoluble in the petroleum ether and had to be separated by fractional crystallization. The melting point of the naphthylurethan was $140^\circ C$.

Calculated for $C_{20}H_{19}O_2N$: C, 78.68; H, 6.22; N, 4.59. Found: C, 78.89; H, 6.47; N, 4.59.

Molecular weight, calculated: 305. Found (in camphor): 297.

BROMIDES. Bromides of the phenol fraction were prepared by the slow addition of a chloroform solution of bromine to the phenol, also in chloroform, while cooling with ice water. After standing until the solution was only slightly colored with bromine, the chloroform was removed by a vacuum pump and the liquid residue distilled. The distillate thus obtained crystallized on cooling. By fractional crystallization from petroleum ether (40° to $60^\circ C$.) two solid bromides were obtained. A dibromide, which was the more soluble in the petroleum ether, was secured in the form of stout needles and boiled at $160^\circ C$. at 5 mm. The melting point was $150^\circ C$. A tribromide was obtained (from petroleum ether) as fine needles, melting point $91^\circ C$.

Calculated for $C_9H_5OBr_3$: Br, 64.31. Found: Br, 64.00.

A liquid, apparently a monobromide, was also obtained. On treatment with more bromine it yielded a mixture of the above two bromides.

METHYL ETHER. This was prepared by treating the sodium salt of the phenol fraction in alkaline solution with dimethyl sulfate at 40° to $50^\circ C$. The yield was almost theoretical. In benzene solution it gave excellent results for the determination of molecular weight by the cryoscopic method, unlike the phenols themselves which are highly associated in benzene.

This ether was a colorless liquid of pleasant odor and did not darken on standing. It had a boiling point of 83° to $85^\circ C$. at 12 mm.

Molecular weight, calculated for $C_9H_{12}O + CH_2$: 150. Found: 150.

OXIDATION OF ETHER. The ether was suspended in a small amount of 5 per cent sodium hydroxide solution, and boiling 5 per cent potassium permanganate solution was run in dropwise with vigorous stirring, while the reaction liquid was kept boiling. Sufficient permanganate was added to oxidize all side chains to carboxyl groups, but apparently because of side reactions, much more than theoretical was required to get a fair yield of acid. The methoxy acids when formed were quite stable. Addition of 1 liter of the potassium permanganate solution usually required 2 to 3 hours. The supernatant liquid was then generally colorless. Unchanged ether was removed by steam distillation and the solution then separated from the manganese dioxide by filtration. The manganese dioxide was twice treated with 5 per cent sodium hydroxide solution and the washings were added to the main filtrate which was then evaporated to small bulk on the water bath. On acidifying the cold concentrated aqueous solution, the organic acid was liberated and filtered off. The aqueous liquor was shaken with ether to recover the last traces of the acid product of oxidation. This gave a total yield of 43 per cent of the theoretical of crude acid which was recrystallized from acetone and benzene as flat prisms, or from water as very fine needles, melting point $275^\circ C$.

Calculated for $C_9H_8(OCH_3)(COOH)_2$: C, 55.09; H, 4.11; OCH_3 , 15.81. Found: C, 55.39, 55.27; H, 4.12, 4.20; OCH_3 , 15.85, 15.73.

A smaller amount of an acid, melting point $238^\circ C$., was also isolated in this oxidation and was shown to be identical

with the acid obtained on the oxidation of the ether of tar acid fraction 250° to $251^\circ C$. No other acids were isolated. A small amount of sirupy residue on further oxidation gave the acid of melting point $275^\circ C$.

SYNTHESIS OF 5-METHOXY-1,3-DICARBOXYBENZENE. The starting material for this synthesis was a sample of 150 grams of 4-amino-1,3-dimethylbenzene obtained from the Eastman Kodak Company. In brief, the steps consisted of a nitration of the acetylated amine for introduction of the nitro group into the 5-position, diazotization of the amino group and replacement with H, reduction of the nitro group to the amino, diazotization of the

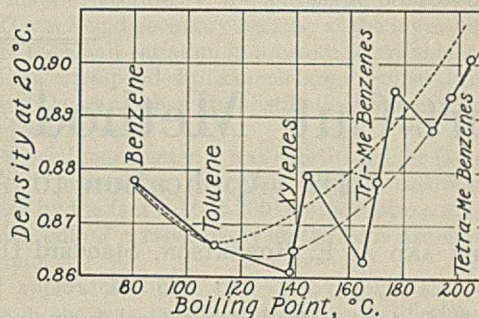


FIGURE 3. DENSITIES OF BENZENE HOMOLOGS, WITH TWO HYPOTHETICAL CURVES

Upper curve, mixture rich in ortho homologs
Lower curve, mixture poor in ortho homologs

latter, and conversion to the hydroxyl. (Since the completion of this work, the 5-amino-1,3-dimethylbenzene has been made available by the Eastman Kodak Company, greatly simplifying the above operations.) The yield of the 5-hydroxy-1,3-dimethylbenzene was only 5 grams, or 3.3 per cent of the theoretical after all these operations. This product was then methylated and oxidized with alkaline permanganate as described above. After several crystallizations from 15 per cent alcohol, the dicarboxy acid was obtained as fine needles with a melting point of $275^\circ C$. The melting point of the methoxydicarboxybenzene obtained from the tar acid fraction boiling at $234.5^\circ C$. had a melting point of $275^\circ C$. and a mixed melting point of the two was $274^\circ C$.

FRACTION 250.5° TO $251^\circ C$.

This was the largest 0.5° cut obtained after the fifth distillation of the original fraction 240° to $255^\circ C$. The analyses for carbon and hydrogen content of the phenol as well as of the phenylurethan suggested a mixture of phenols, $C_9H_{12}O$ and $C_{10}H_{14}O$. No solid bromides could be obtained from this fraction of phenols.

METHYL ETHER. This was prepared as described above and gave a liquid boiling at 96° to $98^\circ C$. at 12 mm., with a pleasant odor and slightly yellow color which did not darken on standing. The molecular weight, calculated for $C_{10}H_{14}O + CH_2$ was 164; found (in benzene), 158. This suggests that this fraction is probably a mixture of phenols $C_9H_{12}O$ and $C_{10}H_{14}O$.

SUMMARY

Low-temperature tar phenols over the range 220° to $260^\circ C$. have been carefully fractionated and examined, and the fraction boiling around $220^\circ C$. shown to contain mesitol. The fraction of minimum density, boiling at $234^\circ C$., has been shown to consist mainly of 3-methyl-5-ethylphenol.

Crystalline derivatives, bromides, and phenylurethans of mesitol and methylethylphenol are described.

Examination of the fractions of tar acids up to $260^\circ C$. has indicated that they consist of mixtures of the simple alkylated homologs of phenol.

A tentative explanation for the uniformly lower densities of fractions of low-temperature tar acids as compared with

corresponding fractions of high-temperature tar acids is offered.

ACKNOWLEDGMENT

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Short-Cut Method of Hydrocarbon Analysis

II. Application to Analysis of Stabilizer Bottoms

R. ROSEN AND A. E. ROBERTSON, Standard Oil Development Company, P. O. Box 485, Elizabeth, N. J.

A short-cut method of hydrocarbon analysis applicable to certain types of routine samples has been developed to reduce the time and expense of such analyses. Its application to the analysis of stabilizer gas and reflux has previously been described, and its further application to stabilizer bottoms is described in this paper.

Synthetic samples, covering the range of compositions normally found for stabilizer bottoms, have been made up and run by the short-cut method employing the changes in apparatus and procedure necessary for samples of this type. From the resulting distillation curves, graphs have been prepared by the use of which routine samples of

stabilizer bottoms may be analyzed. In the use of these graphs, corrections must be applied for the presence in such samples of certain constituents not present in the synthetic samples, and correction charts for this purpose have been prepared by calculating the effect of these components on the distillation curves.

This method, applied to stabilizer bottoms, checks microfractionation analysis within 0.5 per cent on the propane, 1 per cent on the butane, and 2 per cent on the pentane and hexane plus heavier hydrocarbon fractions. It offers distinct advantages from the standpoint of ease of operation and economy in time and materials.

IN VIEW of the fact that control of refinery equipment requires frequent analyses of samples of similar composition, it was felt that a rapid, economical, and accurate method of analysis would be of great value. Such a method, based on a distillation analogous to the Engler distillation for naphthas, was described by Rosen and Robertson (7) and is now being used by several laboratories for analyzing stabilizer gas and reflux. In the present paper its application to the analysis of stabilizer bottoms is described.

So-called graphic methods of analysis are limited in application because they are based on physical characteristics of the mixture to be analyzed, and the number of components which can be determined is only one more than the number of determinable physical characteristics. In the short-cut method the analysis is obtained by considering temperatures at different per cents-off on a distillation curve. Thus, for three-component mixtures or mixtures which can be reduced to three components, such as stabilizer gas and reflux, it is necessary to consider temperatures at two different per cents-off, while for four-component systems, or mixtures which can be so treated, such as stabilizer bottoms, it is necessary to employ temperatures at three different per cents-off.

Several graphical methods for the analysis of hydrocarbons and similar mixtures have been described in the literature. Colman and Yoeman (4) supplied this principle to the analysis of mixtures of benzene, toluene, and xylene.

Methods for the graphical analysis of gasolines and natural gasolines from the A. S. T. M. distillation curve have been described by Smith (8), Pocock and Blair (6), and Blair and Alden (1), and appear to have considerable application for such hydrocarbon mixtures.

Stabilizer bottoms or similar light naphthas consist of propane, butane, pentane, and hexane plus heavier hydrocarbons having compositions varying between the two following extreme type analyses:

TABLE I. WEIGHT PER CENT OF STABILIZER BOTTOMS

| SAMPLE | PROPANE | BUTANE | PENTANE | HEXANE PLUS HEAVIER HYDROCARBONS |
|--------|---------|--------|---------|--|
| | | | | |
| 1 | 3 | 42 | 45 | 10 |
| 2 | 0 | 22 | 24 | 54 |

The analysis of samples of this type by the short-cut method necessitated changes in apparatus, changes in procedure, and preparation of curves applicable to the analysis of four-component mixtures covering the above composition range. The method of attack was to develop an apparatus and procedure applicable to this type of sample, to make up synthetic mixtures representing various concentrations of the different components, to run these mixtures by the apparatus, and to prepare the graphical analysis curves from the distillation curves thus obtained.

The propane and butane used in this investigation were the same purified hydrocarbons used in the investigations by

Rosen and Robertson (?). The pentane and hexane were obtained from the fractionation of natural gasoline. Micro-fractionation analyses showed that these hydrocarbons were not pure, but in making up synthetic mixtures allowance was made for the impurities. The pentane and hexane contained iso-compounds, but no unsaturates.

APPARATUS

The apparatus used in this work is shown in Figure 1.

The graduated buret *B* and the leveling bulb *A* are for measuring the gases to be used in the preparation of the synthetic mixtures, the gas containers being attached at *Q*. The distillation bulb *C* is surrounded by test tube *D*, while the thermocouple leads *E* connect the thermocouple resting on the bottom of bulb *C* to the potentiometer. The open-end manometer *F* shows the

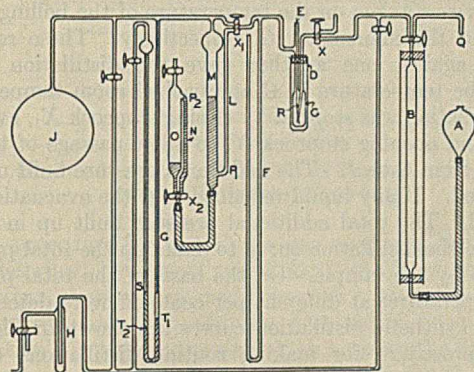


FIGURE 1. APPARATUS FOR DISTILLING LIQUID SAMPLES

pressures on the distillation bulb *C*. The tube *L*, the bubbler *M*, and the reservoir *O* are so arranged that any desired pressure may be automatically maintained on the bulb *C*. The closed-end manometer *G* is so constructed that the readings are greatly magnified for accurate reading. It is made of 2-mm. tubing with about 12 inches (30 cm.) of the bottom made of 6-mm. tubing, and partly filled with mercury. Above the mercury (point T_2) on the closed side is a light hydrocarbon oil having substantially zero vapor pressure. The manometer is evacuated on the closed side above the oil. In Figure 1 the manometer is represented as it would be if the receiving bulb *J* were evacuated, the oil in the closed side just reaching up into the small part of the manometer to the point *S*. Now as pressure builds up in *J*, as gas is admitted into this receiver, the level T_1 will drop, pushing the oil level up on the other side much more than the drop at T_1 . The oil level at *S* is used as the indication of pressure, and it will move about 4 mm. for each mm. of pressure built up in *J*, if the manometer is constructed as described.

It is necessary to calibrate the manometer *G* and since, in the apparatus shown in Figure 1, the volume of *J* plus the additional volume of lines and free space above the mercury level in *M* is different at different pressures, owing to the drop in the mercury level in *M*, this was taken into account in calibrating *G*, so that at any pressure one division corresponded to a definite volume of gas entering *J* and was equal to the amount which would build up 1 mm. pressure when the mercury level in *M* was even with P_2 .

The receiving bulb *J* is of 3-liter capacity. The mercury trap *H* is placed in the vacuum line.

The arrangement shown at *L*, *M*, *O* is for the purpose of maintaining a constant pressure on *J*. At the beginning of the run, *J*, *M*, and *O* are evacuated and as the sample in distillation bulb *C* (Figure 1) gradually builds up pressure (with stopcock X_1 open to *L*), the mercury in *L*, which, if there were no pressure in *C*, would stand even with point P_2 , is pushed down toward P_1 . Now when, with stopcock X_2 open to *N*, the pressure in *C* in mm. of mercury equals the vertical distance between P_1 and P_2 , gas will bubble up through the mercury in *M* and escape into receiver *J*. As vapor collects in *J* the pressure therein gradually builds up so that the mercury level in *M* drops, the excess mercury flowing over at P_2 into reservoir *O*. Meanwhile the pressure at P_1 does not change, always remaining the vertical distance between P_1 and P_2 . At the end of a determination when *J* is evacuated, stopcock X_2 is opened to *O* directly and the reservoir raised so that the mercury therein flows back into *M*. The apparatus is then ready for another determination.

The inner tube *R* in the distillation bulb *C* is for the purpose of facilitating the boiling of the sample and was found necessary because of the tendency of the sample to superheat, thus destroying the smoothness of the distillation curve. This tendency was much more marked in the case of stabilizer bottoms than in that of the lighter stabilizer gas and reflux.

It was found necessary to distill stabilizer bottoms at 200 mm. pressure instead of at 760 mm., because at the latter pressure only a small percentage of the sample would distill over below room temperature, and room temperature cannot be exceeded in this type of apparatus without condensation in the lines. Accordingly, the automatic pressure regulator *L*, *M*, *O* was found necessary because at the lower distillation pressure the small variation in pressure, inevitable in manual regulation, corresponded to a much larger temperature change than was the case when the distillation was carried out at atmospheric pressure.

The special manometer *G* was substituted for the ordinary closed-end manometer to obtain greater accuracy, made necessary by the fact that at 200 mm. pressure a much larger expansion bulb *J* was necessary for the same size sample than at 760 mm.

This apparatus differs from the original short-cut apparatus in the way heat is supplied to distillation bulb *C*. Since, in the course of distilling stabilizer bottoms at 200 mm., it is necessary for distillation bulb *C* to be warmed to approximately room temperature, it was impractical to warm it by exposure to atmospheric temperature as was found satisfactory in the original short-cut procedure. The arrangement adopted was to enclose *C* in test tube *D* and surround this with a Dewar flask, filled with acetone cooled down with solid carbon dioxide, in which was inserted an immersion heater.

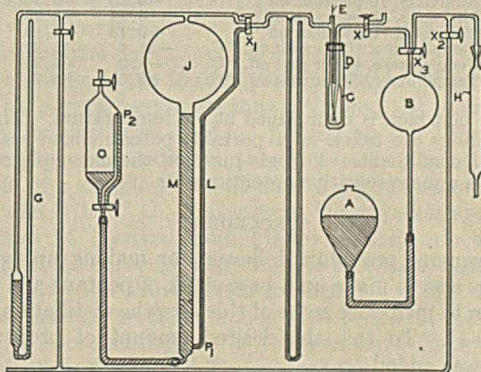


FIGURE 2. APPARATUS FOR DISTILLING EITHER LIQUID OR GASEOUS SAMPLES

It is entirely practical to construct a single apparatus capable of running stabilizer gas, reflux, or bottoms. Figure 2 is the diagram of the apparatus constructed in the laboratory for this purpose.

The measuring bulb *B* (500 cc. capacity) and drying tube *H* are provided for measuring and introducing gas samples. The other parts of Figure 2 serve the same purpose as the corresponding parts of Figure 1. For convenience *J* (3000 cc. capacity) is mounted on top of *M* (25 mm. inside diameter), while the latter is made more than 760 mm. long, so that with *J* evacuated the distillation may be carried on at atmospheric pressure, which is the pressure used in the analysis of stabilizer gas and reflux. However, it is not necessary that *M* be more than 300 or 400 mm. long, since the distillation of stabilizer gas can be started with sufficient pressure in *J*, which added to the length of *M* will equal 760 mm. The manometer *G* is of the closed-end reservoir type, since it was felt that such a manometer would be accurate enough for routine analysis. The volume of bulb *C* and lines from *X* to P_1 is about 11 cc.

At the bottom of distillation bulb *C* is a triple junction copper-constantan thermocouple made of No. 36 B & S wire, the cold

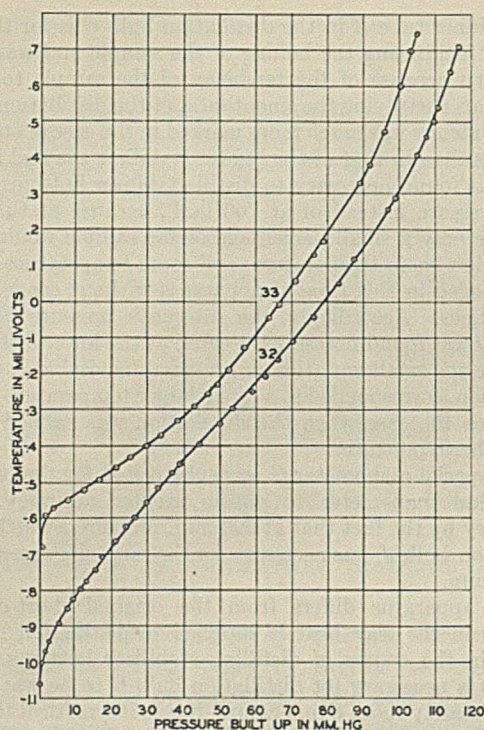


FIGURE 3. TYPICAL DISTILLATION CURVES FOR SYNTHETIC LIQUID SAMPLES

| | CURVE 32 | CURVE 33 |
|-----------------------------------|----------|----------|
| Propane, weight per cent | 5.0 | 0.0 |
| Butane, weight per cent | 30.0 | 30.0 |
| Pentane, weight per cent | 43.4 | 46.6 |
| Hexane, weight per cent | 21.6 | 23.4 |
| Total pressure, mm. | 126 | 112 |
| Millivolts, 10 per cent off | -0.80 | -0.50 |
| Millivolts, 40 per cent off | -0.34 | -0.26 |
| Millivolts, 70 per cent off | +0.13 | +0.18 |
| Temperature, 10 per cent off, °C. | -21.4 | -13.3 |
| Temperature, 40 per cent off, °C. | -9.0 | -6.3 |
| Temperature, 70 per cent off, °C. | +3.5 | +4.7 |

junction of which is maintained at ice temperature. The millivolt readings are taken on a portable potentiometer reading to tenths of a millivolt. A single-junction thermocouple could be used with a more sensitive potentiometer.

PROCEDURE

The general procedure followed for making up synthetic mixtures was to make up a base stock of pentane and hexane and then to introduce some of this into the distillation bulb *C* (Figure 1). To this the desired amount of propane and butane was added.

To make the base stocks a glass bulb fitted with a stopcock was evacuated and weighed. A measured amount of hexane was introduced into this bulb and the weight taken; pentane was then introduced and the bulb weighed again. From these weights and the analysis of the pentane and hexane, the exact composition of the base stock was calculated.

Some of this stock was then quantitatively introduced into the distillation bulb of the apparatus through stopcock *X*. This was done by cooling the bulb *C* with solid carbon dioxide, inverting the glass bulb containing the base stock, connecting it to stopcock *X* with rubber tubing, and after opening *X* (with the lines evacuated), opening the stopcock on the glass bulb slightly; thereby all the base stock coming from the bulb was collected in *C*, leaving the lines clear. Stopcock *X* was then closed and the bulb containing the base stock removed and weighed. The weight of the base stock introduced was thus obtained by difference, and from this weight the amount of propane and butane necessary for any desired composition was calculated, measured in *B*, and added to the sample.

In the course of the work this procedure was used to make up base stocks of various compositions ranging from a pentane-hexane ratio of 0.5 to 2.

After the synthetic mixture was prepared as described above, tube *D* was placed around *C* and the whole surrounded with a Dewar flask containing acetone cooled with solid carbon dioxide to below the boiling point of the sample. A 10-ohm heater was placed in the bottom of the Dewar flask, and for a 1-pint (0.473-liter) flask, one ampere of current passed through the heater. The amount of heat was regulated so that the actual distillation was completed in 30 to 40 minutes.

With *J*, *M*, and *L* evacuated, the height of the reservoir *O* was adjusted to maintain a pressure of 200 mm. on distillation bulb *C*. When the distillation was started, simultaneous readings were taken on the temperature of the boiling liquid in *C* and the manometer *G*, respectively. These readings plotted against one another gave the distillation curve. When the temperature in *C* approached room temperature, the distillation was stopped by closing stopcock *X*₁, evacuating *J*, and opening stopcock *X*₁ to allow passage of the gas directly from *C* to *J*. The additional pressure built up in *J* was noted. If any liquid remained in *C* the evacuation was repeated. The total additional pressure built up in *J* was added to the distillation curve to make up the total pressure built up by the sample. On the basis of the total pressure the temperatures at different per cents-off were determined. Typical synthetic distillation curves are shown in Figure 3.

The procedure for making routine distillations on the apparatus shown in Figure 2 is much the same as that just described.

To analyze a liquid sample, *O*, *J*, and *C* are evacuated and *C* is surrounded with solid carbon dioxide. The bomb containing the sample is connected with the valve on the underside by means of a short piece of rubber tubing to stopcock *X*, which is opened to allow evacuation of the line to the valve on the bomb. With *X*₁ closed the valve on the bomb is opened slightly until about 3 cc. of liquid sample collect in *C*. The stopcock *X* is now closed and the sample bomb removed. From this point, the procedure is the same as that described above.

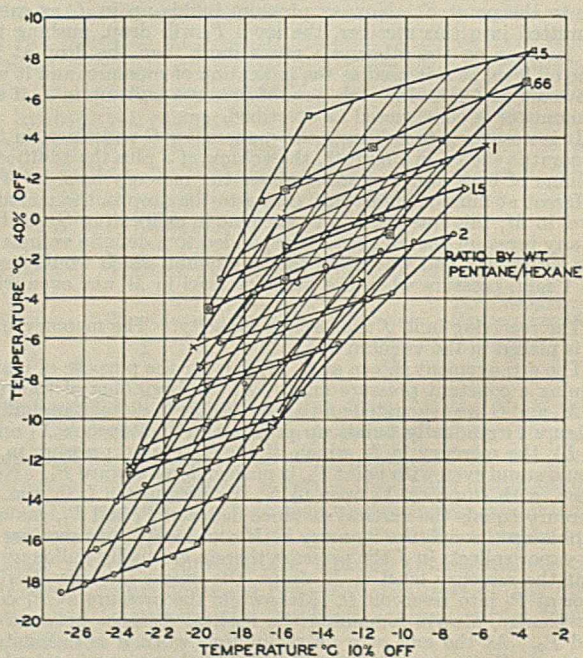


FIGURE 4. 10 AND 40 PER CENT TEMPERATURES FOR ALL SYNTHETIC SAMPLES

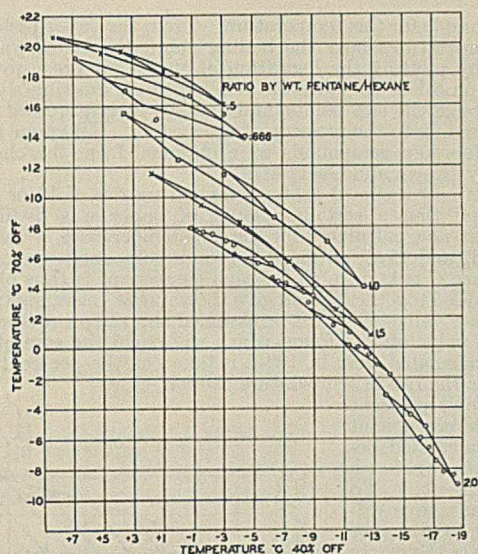


FIGURE 5. 40 AND 70 PER CENT TEMPERATURES FOR ALL SYNTHETIC SAMPLES

The procedure for distilling a gas sample is the same as that described by Rosen and Robertson (7) except that a few minor changes are made necessary by the automatic pressure regulator. In addition, just before beginning the distillation it is believed preferable to measure the fixed gases and methane over into *J* by opening *X*₁ directly to *J*, rather than to pump directly from *C* as described in the above paper.

PREPARING GRAPHS

As previously explained, it is necessary to consider temperatures at three different per cents-off in order to form a basis for the analysis of four-component mixtures. There still remains the problem of choosing the best three per cents-off and the best method of plotting these temperatures obtained from runs on synthetic mixtures.

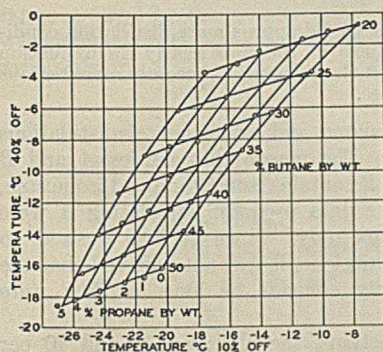


FIGURE 6. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 2

| Pentane-hexane | Correction | |
|----------------|------------|----------|
| | 10% ° C. | 40% ° C. |
| 1.8 | +0.3 | +0.8 |
| 1.9 | +0.2 | +0.4 |
| 2.0 | 0.0 | 0.0 |

In this work the temperatures at 10, 40, and 70 per cent have been chosen as being the most feasible. The 10 per cent point was chosen because it is as near the beginning of the distillation as it is safe to assume that the unevenness due to slight superheating and other irregularities incident to starting the distillation have been smoothed out. The 70 per cent point is as near the end of the curve as it is practical to take, since with heavy samples the 70 per cent point may be near or past the end of the curve. The 40 per cent point was chosen because it is approximately half-way between the other two and apparently gave as good graphs as any other point. In addition to the above considerations, these three per cents-off gave graphs which permitted the greatest accuracy in the determination of propane.

The method adopted was to prepare graphs representing plane sections of a solid figure, thus limiting each graph to temperatures at two per cents-off. Figure 4 shows all the 10 and 40 per cent temperatures plotted against each other for all the synthetic samples, while Figure 5 shows all the 40 and 70 per cent points similarly plotted. The lines in each system of curves on this figure represent constant concentration of propane and butane. Figures 6, 7, 8, 9, and 10 are the curves in Figure 4 plotted separately. Figure 5 could also be divided into several curves, but this was not considered necessary since such a series would not differ greatly.

It is to be noted that the graphs in Figures 6, 7, 8, 9, and 10 each have a corresponding graph in Figure 5 and that all points in each graph represent the samples made up with a base stock having the pentane-hexane ratio given with the graph.

These graphs are used to analyze unknown samples. The procedure is to plot the 40 and 70 per cent temperatures against one another on Figure 5. These temperatures are plotted first because the corresponding graphs do not intersect as do the 10 to 40 per cent graphs (Figures 4 and 5).

This gives a pentane-hexane ratio, and the 10 and 40 per cent-off temperatures are then plotted on the 10 to 40 per cent graph corresponding to this pentane-hexane ratio. For example, if a sample shows 40 and 70 per cent temperatures of -4 and +13.6° C., respectively, these values are plotted on Figure 14 (derived from Figure 5 as described below) and fall on the curve corresponding to a pentane-hexane ratio of 1. This value corresponds to Figure 8 of the 10 to 40 per cent graphs; so this graph is used to obtain the propane and butane concentrations of this sample. The procedure in cases where the 40 and 70 per cent temperatures fall on a curve in Figure 14, for which there is no corresponding 10 to 40 per cent graph, will be described below. The pentane and hexane concentration may be obtained from the following formula:

$$\% \text{ pentane} = \frac{R}{1 + R} (100 - P - B)$$

$$\% \text{ hexane} = \frac{1}{1 + R} (100 - P - B)$$

when *R* is the pentane hexane ratio, *P* is the per cent of propane, and *B* is the per cent of butane.

CORRECTIONS

In analyzing routine samples by the above procedure it was found necessary to correct for the effect of butylene and isobutane on the distillation curves, since only normal butane was used in making up the synthetic mixtures. Graphs giving the corrections for the 10 and 40 per cent points for this effect are shown in Figure 11.

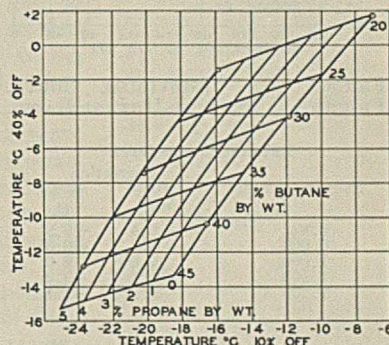


FIGURE 7. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 1.5

| Pentane-hexane | Correction | |
|----------------|------------|----------|
| | 10% ° C. | 40% ° C. |
| 1.3 | +0.2 | +0.4 |
| 1.4 | +0.1 | +0.2 |
| 1.5 | 0.0 | 0.0 |
| 1.6 | -0.2 | -0.4 |
| 1.7 | -0.3 | -0.8 |

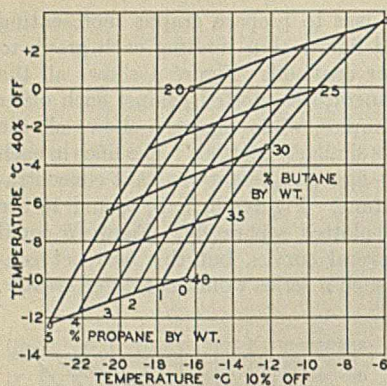


FIGURE 8. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 1

| Pentane-hexane | EXTRAPOLATION DATA | |
|----------------|---------------------|---------------------|
| | 10% Correction ° C. | 40% Correction ° C. |
| 0.832 | +0.4 | +0.9 |
| 0.909 | +0.2 | +0.5 |
| 1.000 | 0.0 | 0.0 |
| 1.100 | -0.1 | -0.2 |
| 1.200 | -0.2 | -0.4 |

the curves was undertaken to avoid making numerous synthetic runs.

These calculations were carried to the 40 per cent point, so that the correction at 10 and 40 per cent could be obtained. While it is realized that such a calculated curve might not be the same as an experimental one of the same composition, it is felt that, inasmuch as the curves being compared are calculated in the same manner, the butylene would have the same effect on the experimental curves as on those calculated.

The method employed for calculating the distillation curves is based on Murray's formula (5) for calculating equilibrium between liquid and vapor hydrocarbon mixtures:

$$C_1 = \frac{LC}{100 \frac{P_c}{P} + L \left(1 - \frac{P_c}{P}\right)}$$

where C_1 = liquid moles of any hydrocarbon
 L = sum of all liquid moles
 C = total moles of a component in the mixture
 P_c = vapor pressure of a pure component
 P = absolute pressure of the system

A graph for the rapid solution of Murray's formula was prepared by Cerini (2). This graph, however, was not accurate enough for the purpose desired, since it was designed to take care of all values

of L . Accordingly a simplified nomographic chart shown in Figure 15 has been constructed to cover only high values of L .

A distillation was considered as a series of small flash distillations. To calculate a distillation curve, the mole per cent of each component for the original mixture was first calculated, and from this the boiling point of the mixture was determined by assuming a boiling temperature and calculating the vapor pressure

of the sample for this temperature. From the vapor pressures at two temperatures near the boiling point, the latter was ascertained by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperatures, drawing a straight line through the two points, and noting where it crossed the line corresponding to the pressure of the system. All vapor pressure values for pure compounds were obtained from the chart prepared by Brown and Coats (3).

It was now assumed that a temperature rise of 1° or 2° took place and that a certain amount of vapor was distilled off. P_c/P was now calculated for the new temperature, a value of L assumed, and C_1/C obtained for each component from Figure 15. Since C is known, C_1 for each component is thus obtained. These added together should give the value of L assumed; otherwise a new value of L must be assumed and the process repeated. When a value of L is found which will equal the sum of the C_1 values calculated from it, 100- L is taken as the per cent evaporated for the rise in temperature chosen.

The mole per cent for each component is now calculated, being C_1/L for each component. To check the above calculation, the vapor pressure of the partly distilled sample may now be calculated at the new temperature and should equal P . Another rise in temperature is now assumed and the above calculation repeated. Each of these calculations gives a point on the distillation curve, the temperature being plotted against the total mole per cent weathered off.

In this work a temperature rise was chosen which would give an L value of about 95, since it was believed that such a value would approximate distillation conditions. The larger the value of L , the more nearly are distillation conditions approached, but the calculation becomes more tedious as the value of L increases.

A comparison of calculated and experimental distillations is shown in Figure 16. The reason that curves A and B diverge is probably that B contains isopentane and isohexane, while the vapor pressure data used for calculating A were for normal hydrocarbons only. Since it was desired to determine the effect of butylene, it was not believed that the curves should necessarily coincide as long as they were similar.

To apply these corrections, the observed 10 and 40 per cent temperatures are plotted on the proper graph and observed propane and butane percentages obtained. These are plotted on Figure 11 to obtain 10 and 40 per cent corrections, which are algebraically added to the original values and the correct propane and butane concentrations obtained from the 10 to 40 per cent graph.

In the example given above, if the 10 per cent temperature was -15° C. this would be plotted against the 40 per cent temperature of -4° C. on Figure 8, and propane and butane values of 1.8 and 29.5 per cent, respectively, obtained. These, however, are not the correct values for the sample, but have been obtained only for purposes of plotting on Figure 11 to obtain the 10 and 40 per cent corrections. When this is done the 10 and 40 per cent corrections of +2.7 and +0.7° C. are respectively obtained. These corrections applied to the above 10 and 40 per cent temperatures give corrected values of -12.3 and -3.3° C., respectively. These corrected values are then plotted on Figure 8 to obtain final correct values of 0.0 and 30.5 per cent for the propane and butane fractions.

It was also found necessary to apply a correction to the 70 per cent temperature in the case of samples high in hexane

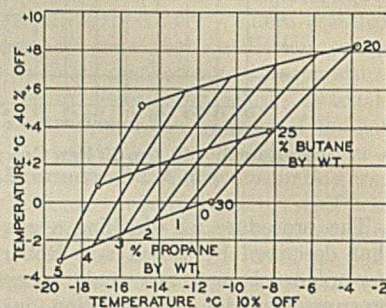


FIGURE 10. INDIVIDUAL CURVE, FIGURE 4. PENTANE-HEXANE RATIO, 0.5

| Pentane-hexane | EXTRAPOLATION DATA | |
|----------------|---------------------|---------------------|
| | 10% Correction ° C. | 40% Correction ° C. |
| 0.500 | 0.0 | 0.0 |
| 0.526 | +0.1 | +0.4 |
| 0.555 | +0.2 | +0.7 |

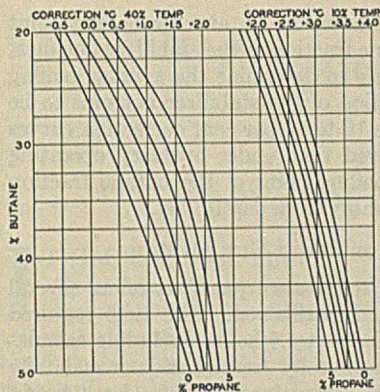


FIGURE 11. CHART FOR CORRECTING 10 AND 40 PER CENT TEMPERATURES FOR EFFECT OF ISOMERS AND UNSATURATES IN BUTANE FRACTION

making the synthetic mixtures had only 11 per cent heptane in the corresponding fraction.

Microfractionation and short-cut runs on several stabilizer bottoms samples established the 70 per cent correction curve shown in Figure 12. It is obvious that since the 70 per cent correction can be correlated with the temperature of the 70 per cent point, Figure 5 could be revised to apply the correction automatically. Such a revision is shown in Figure 13.

With Figure 13 as a basis, the working graph, Figure 14, used in actual analysis of routine samples was prepared by drawing the heavy lines to approximate the positions of the groups of curves on the former figure and dividing the intervening spaces into equal parts. The method of constructing Figure 14 involves the assumption that for a given pentane-hexane ratio, the 40 to 70 per cent points fall on a single curve, if the concentrations of propane and butane are within the range covered by the graphs. This is not strictly true, but was assumed for the sake of simplicity, and does not involve a serious error.

plus heavier hydrocarbons, because in such cases this fraction contains much more heptane than the corresponding fraction used in making the synthetic mixtures. One sample of stabilizer bottoms with a content of 42.6 per cent of hexane plus heavier hydrocarbons showed 32 per cent of heptane plus heavier hydrocarbons in this fraction, whereas the hexane plus heavier hydrocarbons used in

It will be observed that if the 40 to 70 per cent temperature of an unknown sample does not fall on a point corresponding to one of the 10 to 40 per cent curves, it will be necessary to extrapolate between the two curves between which this temperature falls. For this purpose extrapolation data are provided with each 10 to 40 per cent curve which correct the 10 and 40 per cent temperatures, so that the graph is applicable to the sample under consideration. These data were calculated by noting the average difference in temperature between corresponding points on consecutive 10 to 40 per cent graphs, and dividing the difference into five equal portions. As indicated in the extrapolation data, one or two of these portions are added to or subtracted from the experimental 10 to 40 per cent temperatures to make the curve nearest them applicable.

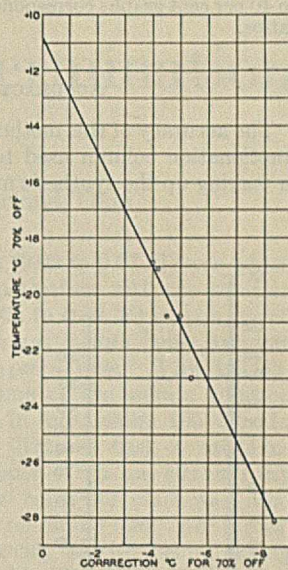


FIGURE 12. CURVE FOR CORRECTING 70 PER CENT TEMPERATURE FOR EFFECT OF HEPTANES AND HEAVIER IN HEXANE+ FRACTION

For example, if a sample had 40 and 70 per cent temperatures of +1 and +19.7° C., respectively, a pentane-hexane ratio of 0.769 would be obtained from Figure 14, since this line lies nearest the point. There is no 10 to 40 per cent graph corresponding to this value, but the graph nearest this value is Figure 9 with a pentane-hexane ratio of 0.666 and under "Extrapolation Data" with this graph will be found the ratio 0.769 together with 10 and 40 per cent temperature correction values which, when applied to the 10 and 40 per cent temperatures for the sample, make the graph applicable to its analysis. This procedure was adopted to avoid the necessity of making up 10

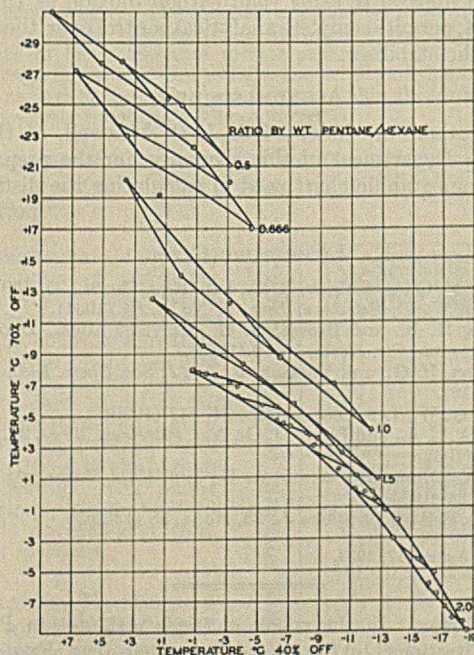


FIGURE 13. 40 AND 70 PER CENT TEMPERATURES AFTER APPLYING CORRECTIONS INDICATED IN FIGURE 12

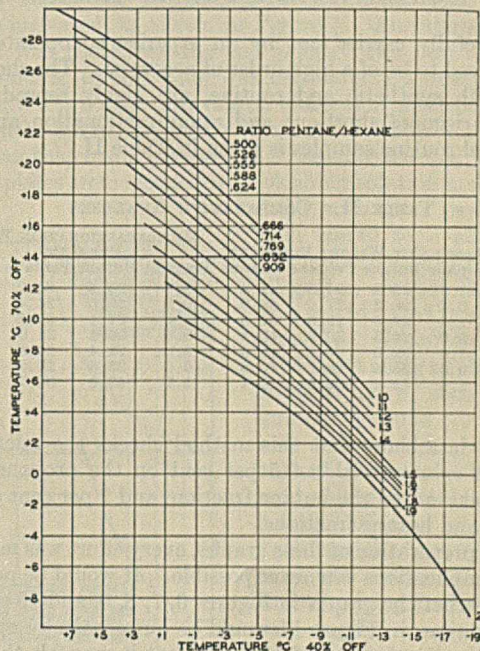


FIGURE 14. WORKING GRAPH FOR 40 TO 70 PER CENT TEMPERATURES, PREPARED ON BASIS OF FIGURE 13

to 40 per cent graphs corresponding to all possible pentane-hexane ratios.

ACCURACY OF METHOD

The accuracy of this method is limited by that of the microfractionation column used to analyze the materials required in making up the synthetic mixtures. However the analyses

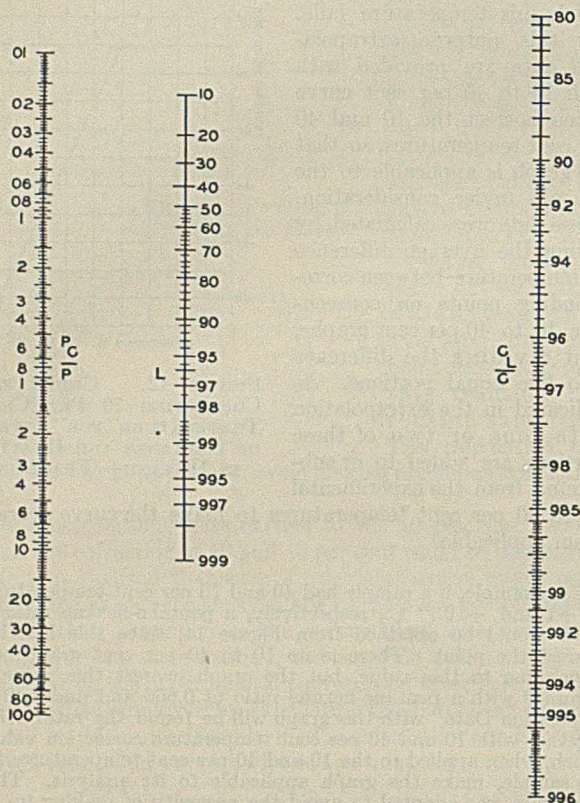


FIGURE 15. NOMOGRAPH FOR CALCULATING LIQUID-VAPOR EQUILIBRIA FOR SMALL AMOUNTS VAPORIZED

were carefully carried out by an experienced operator and are believed to be of a high order of accuracy. The short-cut runs, both synthetic and routine, are highly reproducible. A comparison of short-cut and microfractionation analyses on several routine samples is given in Table II.

TABLE II. COMPARATIVE ANALYSES

| SAMPLE | SHORT-CUT WEIGHT PER CENT | | | | MICROFRACTIONATION WEIGHT PER CENT | | | |
|--------|---------------------------|--------|---------|--------|------------------------------------|--------|---------|--------|
| | Propane | Butane | Pentane | Hexane | Propane | Butane | Pentane | Hexane |
| 1 | 1.0 | 25.8 | 31.8 | 41.4 | 0.9 | 25.4 | 31.2 | 42.5 |
| 2 | 0.7 | 26.3 | 27.0 | 46.0 | 0.9 | 26.3 | 26.4 | 46.4 |
| 3 | 1.4 | 27.5 | 29.6 | 41.5 | 1.1 | 27.1 | 29.5 | 42.3 |
| 4 | 0.0 | 26.3 | 30.6 | 43.1 | 0.0 | 26.6 | 31.0 | 42.4 |
| 5 | 3.6 | 22.0 | 25.6 | 48.8 | 3.2 | 22.4 | 24.5 | 49.9 |
| 6 | 0.0 | 25.5 | 28.7 | 45.8 | 0.0 | 25.6 | 29.2 | 45.2 |
| 7 | 1.9 | 44.4 | 33.6 | 20.1 | 1.7 | 43.6 | 34.7 | 20.0 |

These data show that this method checks the microfractionation column within 0.5 per cent on the propane fraction, 1 per cent on the butane fraction, and 2 per cent on the pentane and hexane fractions.

In the preparation of these graphs, every effort was made to avoid complications whenever possible. It would be possible to reconstruct the graphs in Figures 6, 7, 8, 9, and 10 so that the corrections in Figure 11 would be automatically applied, as was done in the case of Figure 5, but it was felt that the 70 per cent correction would probably be fairly constant for all sorts of samples whereas the 10 and 40 per cent corrections would probably not be constant. The 10 to 40 per cent

corrections presented are based on an average boiling point of -3.2°C . for the butane fraction of the stabilizer bottoms. Accordingly, it is desirable to determine the average boiling point of the butane fraction of the stabilizer bottoms to be analyzed and to alter the 10 to 40 per cent correction curves accordingly. It is believed that under ordinary operating conditions the average boiling point of the butane fraction would not change appreciably from day to day.

ADVANTAGES OF SHORT-CUT METHOD

The short-cut method for control purposes offers several advantages over fractional distillation. The time required for a short-cut analysis is about 1.5 hours, including calculations, while a similar analysis by fractionation would take about 3.5 hours for a gas sample and 6 hours for a liquid sample. The operation is simple and does not require as great expertness for good results as microfractionation; furthermore the operation, being largely automatic, is less subject to the human element, which often leads to widely divergent results in microfractionation, especially in routine analysis.

Rosen and Robertson (7) describe the analysis of stabilizer reflux by the short-cut method without the use of liquid nitrogen and it is known that such an analysis may be used to calculate the amount of butane in the stabilizer gas. Since the analysis of stabilizer bottoms by the short-cut method does not require liquid air, the short-cut apparatus, using solid carbon dioxide as the cooling agent, permits complete analytical control over the operation of the stabilizer.

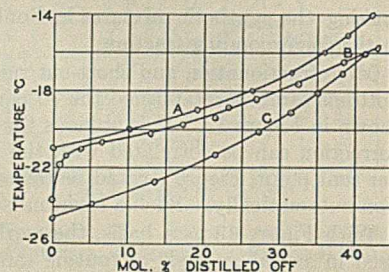


FIGURE 16. COMPARISON OF CALCULATED AND SYNTHETIC DISTILLATION CURVES

A and C calculated, B synthetic run

| | COMPOSITION WEIGHT PER CENT | | |
|----------|-----------------------------|------|------|
| | A | B | C |
| Butylene | .. | .. | 26.5 |
| Butane | 50 | 50 | 23.5 |
| Pentane | 33.3 | 33.3 | 33.3 |
| Hexane | 16.7 | .. | 16.7 |
| Hexane + | .. | 16.7 | .. |

ACKNOWLEDGMENT

The authors are indebted to J. B. Maxwell, of the Engineering Department of this company, for the preparation of the nomographic chart used in calculating the distillation curves.

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RECEIVED August 17, 1933.

CORRECTION. In the article entitled "Asbestos in Permanganate Titrations" by Curtis and Finkelstein [*IND. ENG. CHEM., Anal. Ed.*, 5, 318 (1933)] the second line in the second column on page 318 should read "in a typical limestone carrying 54 per cent of calcium as calcium oxide."

New Volumetric Method for Determination of Sulfate

V. R. DAMERELL AND H. H. STRATER, Western Reserve University, Cleveland, Ohio

IT HAS long been known that when sulfate solutions are added to mercuric nitrate solutions under the proper conditions a yellow colored, basic mercuric sulfate, known as "turpeth," precipitates (2). It occurred to one of the authors that this substance, because of its color, might serve as an indicator in a volumetric sulfate analysis. It could not be used successfully in the titration mixture, but when employed as an outside indicator the results were of such accuracy that the authors believe the method to be of value.

This paper describes the titration, together with experiments designed to determine favorable conditions under which it should be carried out.

EXPERIMENTAL

PREPARATION OF REAGENTS. Good grades of potassium sulfate and barium chloride dihydrate were further purified by recrystallization, and solutions of the two salts were made in distilled water.

Mercuric nitrate solution was prepared by dissolving mercuric oxide in nitric acid. After some experiments the following preparation was used:

Twenty grams of mercuric oxide were treated with 18 cc. of nitric acid, made by diluting 10 cc. of strong acid (specific gravity, 1.42) with water. The mixture was stirred with a glass rod, and the reaction allowed to take place until the solution became strongly turbid. It was then filtered, and to the filtrate were added 6 cc. of water. The solution was allowed to stand several hours before using. During this time a light-colored, crystalline precipitate of basic mercuric nitrate separated out. For best results it was found essential to have the acidity of this indicator solution as low as possible, and to insure this the presence of the basic nitrate precipitate was required.

A color standard was used in determining the end point, and after a number of experiments the following simple preparation was employed:

Potassium sulfate (4.3 grams) and 0.2 gram of potassium dichromate were dissolved in a liter of water. Eight grams of barium chloride dihydrate were dissolved in another liter of water. To make up the color standard 10 cc. of the sulfate-dichromate solution were pipetted into a small flask, and 10 cc. of the barium chloride solution were added with swirling. Fresh standard was made up each day from the stock solutions.

All flasks, pipets, and burets used in the work were calibrated at least twice.

TECHNIC USED IN TITRATION. Barium chloride solu-

A direct volumetric method is described. Standard barium chloride solution is added to the solution containing sulfate, using mercuric nitrate as an outside indicator. A technic is described in which a preliminary end point is reached several cubic centimeters in advance of the final end point, enabling the analyst to add the bulk of the barium chloride solution rapidly.

tion (0.02 to 0.07 M) was added to potassium sulfate solution (0.005 to 0.02 M) from a buret, both solutions being at room temperature. The initial volume of the sulfate solution was in most cases 100 cc. In the titration flask a medicine dropper with an extra-long glass tube (22 cm.) was used for obtaining test portions.

The titration mixture was vigorously swirled before taking out test portions. The barium chloride solution was added slowly (about 15 cc. per minute), and in the case of very dilute solutions the titration mixture was allowed to stand after each addition for at least a minute (Table II) before taking out test portions.

A drop of mercuric nitrate solution was put in each of the outer depressions of a clean spot plate with another dropper. In each of the two inside depressions were put 4 drops of well-mixed color standard from a third dropper. The color tests were made by allowing a drop of the titration mixture to fall into a drop of the mercuric nitrate solution on the spot plate. The time was then noted, by counting slowly, or with a watch, when the color of the mixture just exceeded that of the standard in intensity. When the tests were made in this manner the color exceeded that of the standard almost immediately up to within a few cubic centimeters of the end point. At this stage the amount of titration mixture was increased to 3 or more drops per test. Upon the addition of more barium chloride solution the time interval before the appearance of the proper yellow color rapidly increased, as shown in Figure 1. An interval of 30 seconds was chosen as the end point. The buret volume corresponding to this time was calculated by interpolation between the two time intervals on either side of the 30-second point, although a fair degree of accuracy could be obtained by calling that reading closest to 30 seconds the end point.

Spot plates were cleaned with cleaning solution and water, dried with filter paper, and then rinsed with ether. It was found helpful to remove all grease, so that the drops of liquid flattened out properly. Experiments were carried out using a spherically shaped drop, such as described by Pond (1) for the zinc ferrocyanide titration, but satisfactory results could not be obtained in the present determination.

A daylight-type electric lamp was used in the work. In determining the time intervals, a greater accuracy resulted if the spot plate was moved around so that the test mixture was always on the same side of the standard.

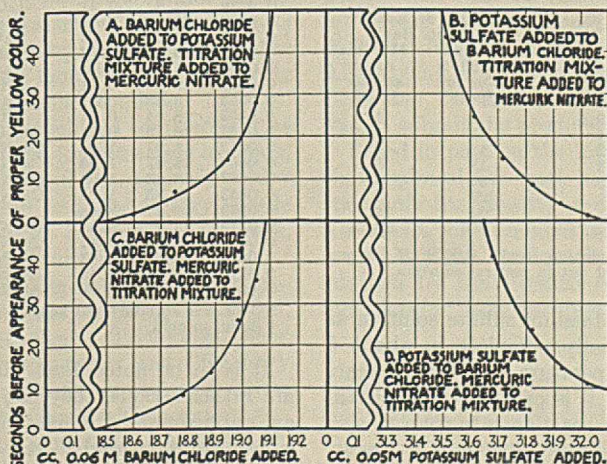


FIGURE 1. EFFECT OF ORDER OF ADDITION OF REAGENTS

ORDER OF ADDITION OF REAGENTS. Four experimental procedures were tried in determining the best order of addition of reagents. Barium chloride solution was added to potassium sulfate solution, and vice versa, and on the spot plate the titration mixture was added to mercuric nitrate solution, and the reverse. An experimental curve for each of these titrations is given in Figure 1.

TABLE I. EFFECT OF ORDER OF ADDITION OF REAGENTS UPON SENSITIVITY

| ORDER OF ADDITION | SENSITIVITY (Mean of several) |
|--|----------------------------------|
| 1. 0.0501 M potassium sulfate solution added to 100 cc. of 0.0155 M barium chloride solution. Mercuric nitrate solution added to titration mixture on spot plate | 90 |
| 2. 0.0501 M potassium sulfate solution added to 100 cc. of 0.0155 M barium chloride solution. Titration mixture added to mercuric nitrate solution on spot plate | 140 |
| 3. 0.0621 M barium chloride solution added to 100 cc. of 0.0125 M potassium sulfate solution. Titration mixture added to mercuric nitrate solution on spot plate | 200 |
| 4. 0.0621 M barium chloride solution added to 100 cc. of 0.0125 M potassium sulfate solution. Mercuric nitrate solution added to titration mixture on spot plate | 150 |

The sensitivity at the end point will be defined as the reciprocal of the number of milliequivalents of reagent being added from the buret necessary to cause the time interval (before the appearance of the proper yellow color) to change from 25 to 35, or from 35 to 25 seconds. Thus the larger the sensitivity the sharper the end point. The sensitivity for each of these procedures is given in Table I.

The average deviation from the mean for these sensitivities is about ± 30 . It was decided from the results in Table I that procedure 3 was the best, and this was used for all later work.

STRENGTH OF INDICATOR. Many concentrations of mercuric nitrate were tried. Among the higher concentrations very little difference in behavior was observed, but with dilute solutions a definite drop in sensitivity was apparent. Sensitivities obtained with three concentrations were as follows: 6 M, 210; 3 M, 220; 0.2 M, 130. Approximately 3 M mercuric nitrate solution was used for most of the later work.

REACTION TIME. The authors were uncertain as to the length of time necessary for the completion of the barium sulfate reaction at room temperature, since it is generally believed that precipitation takes place slowly, even in hot solution. The point was cleared up by mixing various quantities of barium chloride and potassium sulfate solutions, and then noting whether the time interval before the appearance of the proper yellow color (in test portions) changed with time. The results are given in Table II.

TABLE II. EFFECT OF CONCENTRATION UPON REACTION TIME

| 0.0152 M K ₂ SO ₄ 23.33 cc. BaCl ₂ | | 0.0050 M K ₂ SO ₄ 7.63 cc. BaCl ₂ | | 0.0025 M K ₂ SO ₄ 3.70 cc. BaCl ₂ | |
|--|---|---|---|---|---|
| Seconds for yellow color to appear | Minutes after adding BaCl ₂ | Seconds for yellow color to appear | Minutes after adding BaCl ₂ | Seconds for yellow color to appear | Minutes after adding BaCl ₂ |
| 33 | 1.5 | 4 | 0.5 | 0 | 1 |
| 37 | 3 | 9 | 1 | 3 | 1.5 |
| 37 | 6 | 27 | 2 | 12 | 2 |
| 34 | 14 | 27 | 3 | 18 | 3.5 |
| 40 | 15 | 26 | 5 | 32 | 5 |
| 35 | 21 | .. | .. | 27 | 7 |
| .. | .. | .. | .. | 25 | 12 |
| .. | .. | .. | .. | 30 | 23 |

100-cc. samples of potassium sulfate solution used. 0.0621 M barium chloride solution added. Titration carried out in neutral solution.

Even when using as dilute a potassium sulfate solution as 0.0025 M the reaction is essentially complete in about 5 minutes. Titration at room temperature therefore appears to be entirely feasible. However, it is probable that certain types of impurities cause a slower reaction rate than this.

RELATION OF END POINT TO STOICHIOMETRICAL POINT. The 30-second end point and the stoichiometrical point do not coincide under the (otherwise) most favorable conditions

so far worked out. Thus when 0.0621 M barium chloride solution was added to 100 cc. of 0.0125 M potassium sulfate solution (neutral), 19.16 cc. were required, while the stoichiometrical amount necessary was 20.13 cc.

The error may of course be overcome by standardizing the barium chloride solution with an easily purified sulfate, such as potassium sulfate. This procedure should be followed in any event, since both barium chloride dihydrate and anhydrous barium chloride are poor standards.

EFFECT OF ACIDITY. The acidity of the titration mixture was found to affect markedly the position, sensitivity, and reproducibility of the end point. Results of experiments on this phase of the work are given in Table III. A neutral or slightly acid solution appears to be the best in running the titration. Experiments carried out at higher acidities and alkalinities than those of Table III gave, in general, more erratic results and lower sensitivities.

TABLE III. EFFECT OF ACIDITY

| SOLUTION BEING TITRATED | | | 0.0621 M BaCl ₂ REQUIRED FROM BURET ^a | MEAN SENSITIVITY |
|---|--------------|-----------------------|--|---------------------|
| 0.0501 M K ₂ SO ₄ Cc. | Water Cc. | 0.1 N Acid or base | | |
| 25.00 | 73 | 2 cc. NaOH | 20.02 \pm 0.04 | 170 |
| 25.00 | 75 | None | 19.16 \pm 0.01 | 200 |
| 25.00 | 73 | 2 cc. HCl | 18.91 \pm 0.01 | 190 |
| 25.00 | 70 | 5 cc. HCl | 18.86 \pm 0.01 | 200 |
| 25.00 | 65 | 10 cc. HCl | 18.74 \pm 0.05 | 130 |

^a Average of four determinations in each case.

EFFECTS OF OTHER IONS. Titrations of potassium sulfate solutions were carried out in the presence of five times the amount (equivalents) of other salts, in neutral solution. The results are given in Table IV. The errors are seen to be smallest, on the whole, when the solutions were most dilute. Nitrates caused large errors in dilute solution, although in more concentrated solution the error due to calcium nitrate was smaller and different in sign. The results can be explained, for the most part, by assuming precipitation of complexes of the type (Ba, K)SO₄ when the results were low, and Ba(SO₄, NO₃) when the results were high.

TABLE IV. EFFECT OF IMPURITIES

| MOLALITY ^a OF BaCl ₂ SOLUTION | BaCl ₂ SOLU- TION | IM- PURITY | NATURE OF IMPURITY | SO ₄ PRESENT | SO ₄ FOUND | ERROR |
|---|------------------------------------|---------------|--|----------------------------|--------------------------|---------|
| | Cc. | Grams | | Gram | Gram | Gram |
| 0.0219 | 22.9 | None | None | 0.0482 | 0.0482 | |
| 0.0219 | 22.7 | 0.24 | MgCl ₂ | 0.0482 | 0.0478 | -0.0004 |
| 0.0219 | 22.9 | 0.24 | MgCl ₂ | 0.0482 | 0.0482 | 0.0000 |
| 0.0219 | 22.8 | 0.24 | MgCl ₂ | 0.0482 | 0.0480 | -0.0002 |
| 0.0219 | 22.6 | 0.29 | NaCl | 0.0482 | 0.0476 | -0.0006 |
| 0.0219 | 22.6 | 0.29 | NaCl | 0.0482 | 0.0476 | -0.0006 |
| 0.0219 | 22.9 | 0.41 | Na ₂ C ₂ H ₃ O ₂ | 0.0482 | 0.0482 | 0.0000 |
| 0.0219 | 22.6 | 0.41 | Na ₂ C ₂ H ₃ O ₂ | 0.0482 | 0.0476 | -0.0006 |
| 0.0219 | 22.7 | 0.83 | KI | 0.0482 | 0.0478 | -0.0004 |
| 0.0219 | 22.6 | 0.83 | KI | 0.0482 | 0.0476 | -0.0006 |
| 0.0219 | 22.4 | 0.21 | LiCl | 0.0482 | 0.0471 | -0.0011 |
| 0.0219 | 22.6 | 0.21 | LiCl | 0.0482 | 0.0476 | -0.0006 |
| 0.0600 | 20.86 | None | None | 0.1202 | 0.1202 | |
| 0.0600 | 20.30 | 0.73 | NaCl | 0.1202 | 0.1170 | -0.0032 |
| 0.0600 | 20.24 | 0.73 | NaCl | 0.1202 | 0.1166 | -0.0036 |
| 0.0653 | 19.16 | None | None | 0.1202 | 0.1202 | |
| 0.0653 | 18.70 | 0.51 | LiCl | 0.1202 | 0.1173 | -0.0029 |
| 0.0653 | 18.63 | 0.51 | LiCl | 0.1202 | 0.1169 | -0.0033 |
| 0.0653 | 18.64 | 0.51 | LiCl | 0.1202 | 0.1169 | -0.0033 |
| 0.0653 | 18.73 | 0.51 | LiCl | 0.1202 | 0.1175 | -0.0027 |
| 0.0653 | 18.97 | 1.03 | Ca(NO ₃) ₂ | 0.1202 | 0.1190 | -0.0112 |
| 0.0653 | 18.87 | 1.03 | Ca(NO ₃) ₂ | 0.1202 | 0.1184 | -0.0018 |
| 0.0653 | 18.83 | 1.03 | Ca(NO ₃) ₂ | 0.1202 | 0.1181 | -0.0021 |
| 0.0653 | 18.85 | 1.03 | Ca(NO ₃) ₂ | 0.1202 | 0.1182 | -0.0020 |
| 0.0219 | 22.9 | None | None | 0.0482 | 0.0482 | |
| 0.0219 | 23.3 | 0.41 | Ca(NO ₃) ₂ | 0.0482 | 0.0490 | +0.0008 |
| 0.0219 | 23.7 | 0.41 | Ca(NO ₃) ₂ | 0.0482 | 0.0499 | +0.0017 |
| 0.0219 | 24.5 | 0.43 | NaNO ₃ | 0.0482 | 0.0516 | +0.0034 |
| 0.0219 | 24.0 | 0.43 | NaNO ₃ | 0.0482 | 0.0505 | +0.0023 |
| 0.0219 | 26.6 ^b | 0.36 | Al(NO ₃) ₃ | 0.0482 | 0.0560 | +0.0078 |

^a Solutions standardized against potassium sulfate.

^b Solution acid.

It is to be noted that while some of the errors involved are rather serious, they can be largely corrected by having an approximately equal amount of the impurities in the sulfate solution used to standardize the barium chloride.

INTERFERING SUBSTANCES. The titration cannot be carried out in the presence of appreciable amounts of ammonium

compounds, as they prevent the formation of basic mercuric sulfate. The titration is also unsuccessful in the presence of ions that cause precipitates with mercuric nitrate, or with barium chloride, such as tartrates, phosphates, etc. Potassium iodide is an exception (Table IV). The insoluble mercuric iodide could be made to dissolve in excess mercuric nitrate solution by stirring the color test mixture with a glass rod, and the end point could then be determined as usual. Colored substances may also make the end point difficult or impossible to detect.

TABLE V. EFFECT OF SOLID BARIUM SULFATE UPON END POINT

| TITRATION MIXTURE PER DROP Hg(NO ₂) ₂ Drops | 0.0207 M BaCl ₂ SOLUTION NEEDED PER MILLIMOL BaSO ₄ , 100 cc. NEUTRAL K ₂ SO ₄ SOLUTION | | |
|--|---|--|--|
| | About 0.12 g. BaSO ₄ formed | About 0.24 g. BaSO ₄ formed | About 0.36 g. BaSO ₄ formed |
| 2 | Cc. 42.2 | Cc. 44.0 | Cc. 44.3 |
| 3 | 44.7 | 45.2 | 45.3 |
| 4 | 45.5 | 45.8 | 45.7 |
| 5 | 46.0 | 46.2 | 45.9 |

EFFECT OF BARIUM SULFATE CONCENTRATION ON END POINT. The effect of concentration of barium sulfate, and of the number of drops of titration mixture per drop of mercuric nitrate on the position of the end point was determined in neutral solution, using 0.02 M barium chloride solution. The results, given in Table V, indicate that the error due to difference in concentration of barium sulfate may be minimized by taking a sufficient number of drops of titration mixture near the end point. This is also recommended because the end point is then more sensitive and closer to the stoichiometric point. A small-sized drop of mercuric nitrate is also advantageous, since the same effect

can then be produced with a smaller amount of titration mixture.

DISCUSSION

The method is recommended for routine analysis, rather than for single determinations. All the solutions involved are of stable inorganic compounds, and can be made up in large quantities and kept for long periods of time.

The biggest advantage of the method is that it is time-saving. The authors are able to finish an ordinary titration, working individually and not knowing the sulfate content, in about 10 minutes. This is possible, in spite of the outside indicator, because the method is a direct one, and because a preliminary end point is reached (using one drop of titration mixture) several cubic centimeters in advance of the final end point (using several drops of titration mixture). Thus the barium chloride solution can be added 2 or 3 cc. at a time until the final end point is nearly reached. The apparatus necessary is also simple and inexpensive.

No attempt will be made here to give further procedure for the method other than that connected with the titration itself, because of the great variety of substances and solutions in which sulfate may be determined.

Aside from any analytical considerations, the method employed in obtaining Table II seems to be useful in measuring the rate of formation of barium sulfate under various conditions.

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RECEIVED August 12, 1933.

Chemical Examination of Trichloroethylene for Anesthesia

HERMAN L. TSCHENTKE, American Medical Association, Chemical Laboratory, Chicago, Ill.

AMONG the various chemical compounds recently used for local anesthesia is trichloroethylene, CHCl=CCl₂. This compound has been described in the literature since 1864; it is not, therefore, a new substance. During the World War, Plessner (2) found symptoms of poisoning in men using trichloroethylene for removing grease from metal parts of machinery, and noted that the poison had special affinity for the sensory fibers of the trigeminal nerve. Oppenheim (1) recognized the possibility of lessening sensitiveness of the diseased trigeminal nerve in cases of facial neuralgia by giving the patient small doses of this compound to inhale.

Trichloroethylene has also been developed commercially as a low-boiling, nonflammable solvent for extracting oils, fats, and waxes, for degreasing metals, and for purposes of dry cleaning. For these uses, a rather impure "factory" grade ordinarily has been sufficient. For therapeutic purposes, only a much more refined product is suitable.

Several firms have been supplying medicinal trichloroethylene under various brand names, such as Westrosol, Gemalgene, Chlorylen, and Trethylene. Trichloroethylene was presented to the Council on Pharmacy and Chemistry of the American Medical Association for inclusion in "New and Nonofficial Remedies" and the Chemical Laboratory was asked to make an examination of the product. Accordingly, examination was made of two brands of trichloroethylene preparations presented; a specimen of Eastman grade and

of a practical grade purchased from Eastman Kodak Co.; and another brand used medicinally, obtained on the open market. The results of this investigation are given in Table I, which includes qualitative and quantitative determinations.

The boiling point range of Chlorylen and of Trichloroethylene zu Chlorylen was determined after extraction of the preparation with an equal volume of water to remove any interfering substances such as alcohol, and subsequent drying of the trichloroethylene layer with anhydrous sodium sulfate. After being notified of the results of the investigation of Chlorylen, the firm indicated a desire to investigate further, and to submit the product again in the future.

Based in part on the information in the literature and on the results of the work reported herein, somewhat rigorous standards for identity and purity were elaborated. These were sent for comment to the firm which submitted the product; then in due time the following standards were adopted by the Council on Pharmacy and Chemistry for inclusion in "New and Nonofficial Remedies."

STANDARDS

TRICHLOROETHYLENE.¹ Trichloroethylenum, trichlorethylene, CHCl:CCl₂, 1-chloro-2-dichloroethylene.

¹ Solutions referred to in the descriptions of qualitative and quantitative tests are, unless otherwise stated, of the strength described in the current U. S. Pharmacopeia.

TABLE I. EXAMINATION OF TRICHLOROETHYLENE AND TRICHLOROETHYLENE PREPARATIONS

| | BEILSTEIN I, 4TH ED. | N. N. R. STANDARDS | CALCO BULK SAMPLE | CALCO AMPULES | TRETHYLENE ^a | EASTMAN | EASTMAN (PRACTICAL) | TRICHLORO- AETHYLEN ^b ZU CHLORYLEN | CHLORYLEN ^b (MARKET SPECIMEN) |
|---|-----------------------------|--------------------------------|--------------------------|---------------------|--------------------------|------------------------------|--|--|--|
| Boiling point range (U. S. P. X method, 760 mm.) | 87.15 | 86-88 | 86.1-88.0 | 85.4-87.4 | 83.8-88.0 | 85.4-87.9 | 85.6-88.2 | 85.7-88.2 | 85.7-89.6 |
| Specific gravity, 25° C./25° C. | 1.4598 (25.5/25.5) | 1.458-1.460 | 1.460 | 1.460 | 1.452 | 1.460 | 1.460 | 1.450 | 1.447 |
| Refractive index, 20° C. | | | | | | | | | |
| a. Original | 1.4777 (n_D^{20}) | 1.4770-1.4780 | 1.4777 | 1.4775 | | 1.4770 | 1.4774 | 1.4767 | 1.4755 |
| b. Distillate | | 1.4770-1.4780 | 1.4770 | 1.4776 | | 1.4774 | 1.4774 | 1.4774 | 1.4774 |
| Titration of aqueous extract, 0.01 N HCl or NaOH consumed | | Not more than 0.1 cc. 0.1 N | 0.05 cc. | 1.06 cc. | 0.40 cc. | Negligible | Negligible | Less than 0.1 cc. 0.1 N | Less than 0.1 cc. 0.1 N |
| Residue on evaporation, 100° C. | | Not weighable (25 cc.) | Less than 0.0001 gram | | Less than 0.0001 gram | 0.0001 gram | 0.0002 gram | | 0.0004 gram |
| QUALITATIVE TESTS | | | | | | | | | |
| Bromine test (lower layer) | | White turbidity | White turbidity | | | White turbidity | White turbidity | | White turbidity |
| Silver ammonium ni- trate (turbidity in 10 min.) | | None | None | Slight | Slight | Darkened aqueous layer | Blackened aqueous layer (much less for dis- tillate) | Turbid | Immediate turbidity |
| Chlorides (turbidity in 5 min.) | | None | None | Practically none | Practically none | Practically none | Practically none | None | None |
| Readily oxidizing sub- stances (chlorine, etc., blue color) | | None | None | None | None | None | None | None | None |
| Turbidity test (alcohol) | | Turbid | Turbid | | | None Turbid | None Turbid | None | None Turbid |
| ^a Davies, Rose & Co | ^b Schering Corp. | | | | | | | | |

Actions and Uses. The actions of trichloroethylene have not been investigated comprehensively, and it was introduced into therapeutics following some observations on man. Trichloroethylene appears to have a selective action on the sensory endings of the trigeminal nerve, whereby it affords relief in trigeminal neuralgia, but it is not clear that the action even of therapeutic doses is limited to these endings, and different individuals seem to show rather wide differences in susceptibility to this action; hence the dose necessary to afford relief varies correspondingly. Therapeutic doses sometimes cause transitory giddiness, with lassitude, distress, palpitation, and nausea. Large doses cause narcosis, and excessive doses cause death. There was no perceptible injury to the lungs, heart, or liver after narcosis repeated several times in the dog, but there was slight hyperemia of the gastric mucous membrane and marked reddening of the duodenum. The liquid is irritant; hence it should not be allowed to come in contact with the nose when the vapor is inhaled.

Dosage. Fifteen minims by inhalation, to be repeated after a few minutes if necessary; but it appears probable that not more than 60 minims should be inhaled within 24 hours when it is used for any considerable period of time.

Trichloroethylene occurs as a clear, colorless, mobile, and volatile liquid, possessing an odor similar to that of chloroform. It is miscible with ether and very soluble in alcohol; it is practically insoluble in water. The specific gravity is from 1.458 to 1.460 at 25° C. The refractive index is from 1.4770 to 1.4780 at 20° C.

Transfer 25 cc. of trichloroethylene to a distilling flask. Determine the distillation range according to Method I of U. S. Pharmacopeia X. Ninety-five per cent distills over at from 86° to 88° C. (corrected) at 760 mm. The refractive index of the distillate is the same as that of the material before distillation.

Transfer 5 cc. of trichloroethylene to a glass-stoppered cylinder, add 5 cc. of bromine water and shake the mixture vigorously at intervals of 15 minutes: at the end of an hour a white turbid solution forms in the lower layer. Agitate gently 5 cc. of trichloroethylene with 2 cc. of silver ammonium nitrate solution in a narrow glass-stoppered cylinder of from 10 to 15 cc. capacity: No turbidity or darkening is observed in either layer at the end of 10 minutes (acetylene, etc.).

Agitate 20 cc. of trichloroethylene with a 50-cc. portion of water and repeat, using a 25-cc. portion of water; transfer the combined aqueous layer to a flask and add to the aqueous solution 2 drops of methyl red indicator solution. If the color of the solution is yellow, not more than 0.1 cc. of 0.1 N hydrochloric acid is required to assume a pink color; if the color of the solu-

tion is pink, not more than 0.1 cc. of 0.1 N sodium hydroxide is required to assume a yellow color.

Agitate 10 cc. of trichloroethylene with 25 cc. of water and allow the liquid to separate completely. Separate 10-cc. portions of the aqueous layer are affected as follows: No turbidity is noted 5 minutes after the addition of 0.1 cc. of nitric acid and 0.1 cc. of silver nitrate solution (chlorides); no blue color is observed after the addition of 0.1 cc. of potassium iodide test solution and 0.1 cc. of starch test solution (readily oxidizing substances such as free chlorine).

Add 0.1 cc. of alcohol to 5 cc. of trichloroethylene: A turbid solution is formed (distinction from chloroform).

Evaporate 25 cc. of trichloroethylene in a platinum or porcelain dish on a steam bath and dry to constant weight at 100° C. No weighable residue is obtained.

SUMMARY

Comparative chemical examinations were made of several brands of medicinal trichloroethylene and of a specimen of a purified and of a technical grade. Two products were found to be markedly outside of the boiling point range and specific gravity range. The acidity of all samples but one examined was well within the range set. Four samples showed considerable turbidity in both layers when the silver ammonium nitrate test was applied. The presence of this turbidity gives rise to considerable doubt as to whether compounds such as acetylene are absent. All samples indicated a lack of chlorides and of readily oxidizing substances.

Standards for trichloroethylene for medicinal uses have been prepared, based upon the literature and upon the work herein reported.

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RECEIVED July 26, 1933.

CORRECTION. In the article on "Estimation of Total and Bound (D) Gossypol in Cottonseed Meal" by Smith and Halverson [*IND. ENG. CHEM., Anal. Ed.*, 5, 319 (1933)], 13th line from the bottom of the second column on the page, the sentence should read "Pipet (by suction) 4 cc. of aniline onto the meal."

Optical Density Color Measurement for Petroleum Oils

S. W. FERRIS AND J. M. McILVAIN, The Atlantic Refining Company, Philadelphia, Pa.

METHODS used in this country for assigning numerical color values to petroleum lubricating oils may be grouped as follows:

CLASS 1. A given thickness of oil is matched against one of a set of glass or liquid standards, primarily on the basis of hue. In this class fall the Lovibond (7) and the National Petroleum Association (1) scales.

CLASS 2. A variable thickness of oil is matched against a standard color disk, as in the method initially described by Delbridge (5) and later applied in the Tag-Robinson¹ colorimeter (13); or against a fixed depth of liquid standard, as in the methods of Rogers, Grimm, and Lemmon (10) and of Weir, Houghton, and Majewski (12). In at least one of these (12) the match is made on the basis of equality of brightness. A variant of methods of this class consists in matching a fixed thickness of the oil sample against a variable thickness of oil standard, as in the method of Parsons and Wilson (9). The color values derived from the

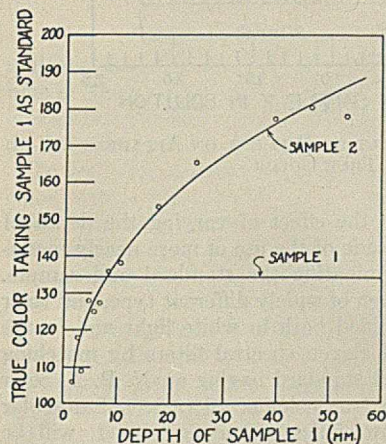


FIGURE 1. REVERSAL IN APPARENT TRUE COLOR WITH DIFFERENT DEPTHS OF OILS

methods of class 2, with the exception of the Tag-Robinson colorimeter, have been called "true colors."

CLASS 3. The fraction of light absorbed by a certain thickness of oil is determined photometrically. Examples of this class are the instrument proposed by Cox (3) which uses a sectored flicker disk, and that of Story and Kalichevsky (11) in which the distance between sample and illuminant is varied and the inverse-square law employed. Apparatus in which the relative transmission of unknown and standard oils are indicated by the response of photoelectric cells have been developed by several of the instrument companies. In all the methods cited except one (3) white light has been used as illuminant.

While several of these methods have been useful in the specification of color for sales work, from the viewpoint of the refiner each has more or less serious shortcomings. In order to serve him best, a color scale must meet six specifications:

1. Samples should be accorded values in agreement with ordinary visual inspection.

2. Values should be additive in the sense that the color C_m , of a mixture of two oils having colors C_a and C_b , will be given by the equation

$$C_m = \frac{C_a V_a + C_b V_b}{100} \quad (1)$$

where V_a and V_b are the respective percentages (by volume) of the oils whose colors are C_a and C_b .

3. Apparatus, standards, and color values should be reproducible in any laboratory.

4. Color values should be based on fundamental rather than arbitrary units.

5. The method should be usable in routine work.

6. Consistent color values should be obtainable on oils ranging from light finished products to the darkest tars and bottoms.

¹ The Saybolt chromometer for measuring the color of gaolines and naphthas falls in this class.

The methods of class 1 fail to meet specification 2. (For example, a mixture of equal parts of two finished oils from the same stock, which have respective N. P. A. colors of 4 and 8, may have an N. P. A. color of 6.5, whereas Equation 1 would require an N. P. A. color of 6 for the mixture. Story and Kalichevsky (11) show that the Lovibond scale leads to oil colors which are far from additive in the sense of Equation 1.) The methods of class 2 when restricted to matching a variable thickness of oil against a fixed thickness of one standard, as prescribed in the most recently published example (12) of the class, yield color values which satisfy specifications 1, 2, and 6, but do not meet specifications 3 and 4, and could be better with regard to specification 5. The methods of class 3 fail to meet either specification 1 (3) or specification 2 (11). (The method of Cox is open to objection because of his choice of blue light as illuminant, rather than because of his photometric arrangement.) When photocells are used with white light as illuminant it is well to remember that the response curve of the cell may vary markedly from that of the normal eye (the so-called visibility curve). O'Brien (8) has shown that filters can be devised for at least one type of photocell, such that the response curve of the combination is in satisfactory agreement with that of the eye.

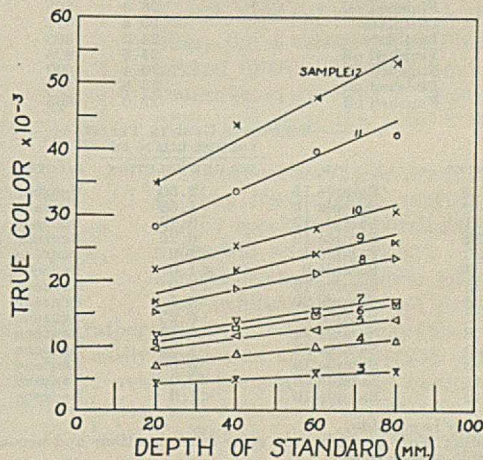


FIGURE 2. VARIATION OF APPARENT TRUE COLOR OF DARK OILS* MATCHED AGAINST VARIOUS DEPTHS OF STANDARD

* 0.1 to 2.0 per cent solution in ethylene dichloride.

This paper presents experimental data to show how a color scale for petroleum lubricating oils was developed, which meets all six of the above specifications. A complete description of the final method is also given, with examples of determinations on a large number of oils.

EXPERIMENTAL

One of the most serious objections to the true color method of determining oil colors is the change in apparent true color with the nature of the standard oil (10) or with the depth of standard against which the match is made. Figure 1 shows the results of an experiment in which two oils of nearly the same N. P. A. colors were compared in the Duboscq colorimeter, using white light. (These and subsequent

samples are described in Table I). Sample 1 is taken as standard and is therefore assigned the same true color at all depths. It is obvious that sample 2 will be assigned a true color less than, equal to, or greater than sample 1, if the depths matched are varied from lesser to greater. Furthermore these effects become greater when the difference of type between sample and standard increase. This is exemplified in Figure 2, which shows the results of matching ethylene dichloride solutions of various dark oils against a 2.5 + N. P. A. oil standard. Another difficulty with the true color method lies in the choice of a proper diluent for dark oils. Figure 3 illustrates the spread in true color values which may be introduced by the use of a poor solvent such as kerosene. It is evident that for this particular oil benzene is a superior diluent.

TABLE I. DESCRIPTION OF SAMPLES

| SAMPLE | TYPE | OILS USED IN TESTS | | |
|-----------------|---------------------------------|-----------------------|---------------|------|
| | | VISCOSITY | | |
| | | ° A. P. I. At 100° F. | S. U. SECONDS | |
| 1 | 7 N. P. A. oil standard | ... | ... | ... |
| 2 | 7.25 N. P. A. clayed distillate | ... | ... | ... |
| 3 ^a | Distillate | 20.4 | ... | 160 |
| 4 ^a | Crude residuum | 18.0 | ... | 270 |
| 5 ^a | Crude residuum | 17.1 | ... | 231 |
| 6 ^a | Crude residuum | 14.8 | ... | 401 |
| 7 ^a | Cracked tar | 10.8 | 196 | ... |
| 8 ^a | Crude residuum | 20.6 | ... | 310 |
| 9 ^a | Crude residuum | 17.2 | ... | 252 |
| 10 ^a | Crude residuum | 13.3 | ... | 2141 |
| 11 ^a | Crude residuum | 14.2 | ... | 632 |
| 12 ^a | Crude residuum | 22.8 | ... | 279 |
| 13 ^a | Finished oil | 21.5 | ... | 170 |
| 14 ^a | Finished oil | 21.5 | ... | 170 |
| 15 ^a | Finished oil | 19.4 | ... | 159 |
| 16 ^a | Distillate | 20.9 | ... | 123 |
| 17 ^a | Crude residuum | 8.2 | ... | 1816 |
| 18 | Finished oil | 26.0 | 145 | ... |
| 19 ^a | Finished oil | 22.0 | 505 | ... |
| 20 ^a | Finished oil | 25.0 | 294 | ... |
| 21 ^a | Finished oil | 24.6 | 278 | ... |
| 22 ^a | Finished oil | 28.4 | 503 | ... |
| 23 ^a | Distillate | 20.6 | 612 | ... |
| 24 | Distillate | 24.2 | 305 | ... |
| 25 | Finished oil | 24.6 | 906 | 79 |
| 26 | Finished oil | 20.4 | 590 | ... |
| 27 | Finished oil | 23.8 | 360 | ... |
| 28 | Finished oil | 22.0 | 505 | ... |

SOLUTIONS USED IN TESTS^b

| SAMPLE | OIL | VOLUME OIL X 100 | | DILUENT |
|--------|-----------|------------------|--|---------|
| | | VOLUME SOLUTION | | |
| 29 | Sample 15 | 2.50 | | Benzene |
| 30 | Sample 16 | 1.56 | | Benzene |
| 31 | Sample 17 | 0.10 | | Benzene |
| 32 | Sample 19 | 6.25 | | Benzene |
| 33 | Sample 4 | <1.0 | | Benzene |
| 34 | Sample 9 | <1.0 | | Benzene |
| 35 | Sample 10 | <1.0 | | Benzene |
| 36 | Sample 20 | 12.5 | | Benzene |
| 37 | Sample 21 | 6.25 | | Benzene |
| 38 | Sample 22 | 6.25 | | Benzene |
| 39 | Sample 23 | 3.33 | | Benzene |
| 40 | Sample 15 | 5.00 | | Benzene |
| 41 | Sample 26 | 50.0 | | Benzene |
| 42 | Sample 10 | <1.0 | | Benzene |

^a Used only in solution.

^b Excluding those made in true color determinations and accounted for in calculation of true color.

Effects such as these led to a preliminary comparison of several possible diluents—carbon tetrachloride, a narrow-boiling petroleum naphtha, kerosene, medicinal white oil, ethylene dichloride, and benzene. Of these the first three apparently gave incomplete solution, with considerable variation in true color at various dilutions. Medicinal white oil formed more satisfactory solutions but was too viscous for routine use. Ethylene dichloride and benzene were almost equally satisfactory and the latter was chosen for further tests. True color determinations (with fixed depth of standard, 12) were made on 31 samples each at several dilutions in benzene. Of the 155 determinations so made, 140 gave deviations of less than 5 per cent, 12 of from 5 to 10 per cent, and 3 of from 10 to 15 per cent, from exact proportionality between color and concentration. Figure 4 shows a few of the results. It was concluded that benzene is a highly satisfactory diluent for this purpose.

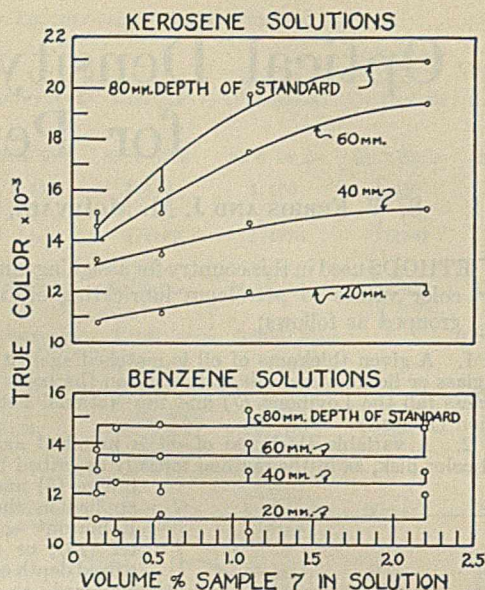


FIGURE 3. EFFECT OF DILUENT ON APPARENT TRUE COLOR

In order to eliminate the effect of varying the depth of standard, a study was made of the use of more nearly monochromatic light for illuminating the standard and sample. Three samples were chosen of widely different type, and their true colors were determined both in white light and in the light passed by each of eleven spectral filters by matching against 20 mm. of an oil standard having an N. P. A. color of 2.5+ and assigned a true color of 10 (12). (True color values referred to below, unless otherwise stated, will be understood to have been determined by this method. The necessity of defining so precisely the basis of the true color scale, on which these values are reported, emphasizes a major difficulty of the true color method in general—namely, that each investigator has been forced to choose an oil or glass, neither being reproducible, and assign thereto some arbitrary value of true color.) The results, plotted in Figure 5, showed that matching in green light (about 500 to 560 m μ) gave values similar to those obtained in white light. Red light

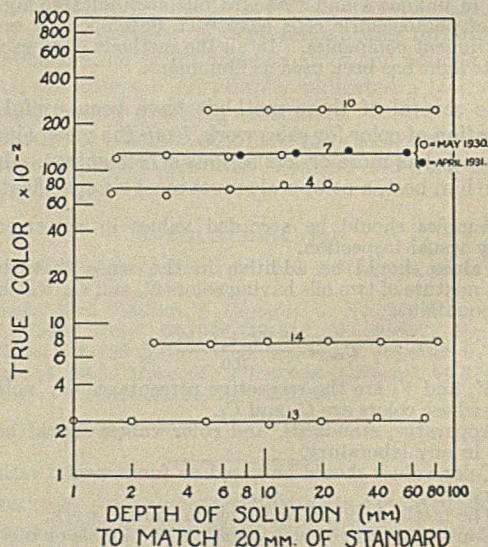


FIGURE 4. CONSTANCY OF TRUE COLOR OVER WIDE RANGE OF DILUTIONS

Benzene used as diluent.

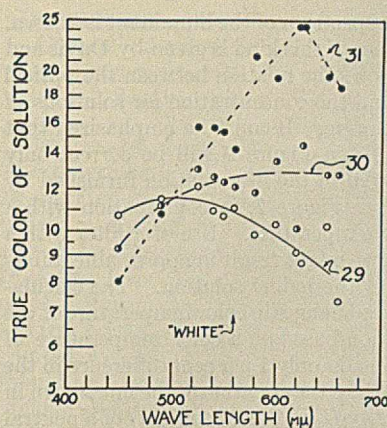


FIGURE 5. EFFECT OF COLOR OF ILLUMINANT ON APPARENT TRUE COLOR

indicate that the precision of reading is adequate in either blue or green (2 per cent or less average deviation), but decreases considerably in the red (as high as 12 per cent average deviation).

To verify the indication (Figure 5) that green light results in color values concordant with visual comparisons (white light), true color determinations were made on 15 samples in both white and green light. As a matter of interest determinations were also made in red and in blue light. The results, plotted in Figure 6, show a very satisfactory line-up between white and green light. Reversals of apparent color values appear in both the blue and the red (Table II).

Since in monochromatic light the only function of the standard is to absorb a fraction of the incident light, the oil standard was replaced by a neutral filter (gelatin-in-glass) which reduced the intensity to roughly the same extent as 20 mm. of the 2.5+ N. P. A. standard previously used. A cooperative test was then made in which each of two laboratories determined the colors of 79 samples. One laboratory used white light and 20 mm. of oil standard, the other green light and neutral filter standard. The results obtained by the two methods checked satisfactorily, with no trend toward a greater disagreement at either extreme of the color range covered (from 20 to 5100 true color). Since this range of colors required dilutions with benzene such that the resulting solutions contained from 10 to 0.05 per cent of oil, the agreement between the two laboratories also demonstrates that the dilution law holds as well in green light as in white light. Therefore no extensive program to prove this was considered necessary. However, for one case studied, the dilution law held satisfactorily, not only in green light, but also in red and blue. Thus the additivity relations between an oil with color and the proper colorless diluent, such as benzene, follow Equation 1 satisfactorily in green light and would probably do the same in any nearly monochromatic light.

In order to prove that Equation 1 is also satisfied by mixtures containing more than one oil, true colors were determined on four oils of widely different types, and on four two-component blends made from them. The calculated color of the blends agreed with that actually determined within 8 per cent, whether white light and oil standard, or green light and neutral filter standard, were used.

produced too great a spread in the color values, whereas the use of blue light resulted in actual reversals of color. Since each of the points on Figure 5 represents the mean of six readings, it is possible to compare the precision of reading in the several portions of the spectrum by calculating average per cent deviations for each set of six readings. The figures so obtained

TABLE II. REVERSALS OF APPARENT COLOR VALUES

| SAMPLE | TRUE COLOR | | | | N. P. A. COLOR |
|--------|-------------|-------------|-----------|------------|----------------|
| | White light | Green light | Red light | Blue light | |
| 27 | 65.4 | 65.5 | 12.2 | 254 | 5- |
| 25 | 49.9 | 52.2 | 17.6 | 180 | 4.75+ |
| 24 | 23.4 | 23.0 | 5.53 | 107 | 3.5+ |
| 26 | 22.9 | 24.2 | 5.85 | 90.3 | 3.75- |
| 40 | 22.5 | 23.7 | 3.33 | 130 | 3.5+ |
| 41 | 10.8 | 10.7 | 2.81 | 38.5 | 2.5+ |
| 18 | 10.1 | 9.32 | 2.04 | 47.2 | 2.5+ |
| 34 | 9.21 | 9.12 | 3.80 | 16.6 | 1.75 |
| 38 | 8.06 | 8.10 | ... | 38.4 | 2.25- |
| 33 | 7.63 | 7.15 | 2.51 | 14.5 | 1.5- |
| 37 | 7.60 | 7.40 | ... | 26.3 | 2.25- |
| 39 | 7.58 | 7.31 | 1.92 | 19.2 | 2- |
| 36 | 6.64 | 6.43 | ... | 30.6 | 2- |
| 35 | 5.76 | 5.16 | 1.85 | 9.75 | 1+ |
| 32 | 5.66 | 4.98 | ... | 17.7 | 1.75- |

The use of nearly monochromatic light effectively eliminates disturbing differences in color between sample and standard. This minimizes the influence of the personal factor of the observer, which is often troublesome in methods using white light, where the effect of both hue and brightness must be evaluated in deciding on a match. The beneficial effect on the precision of matching is illustrated by the following example: Determinations were made of the color of two samples by three observers using (A) white light and fixed depth of oil standard and (B) green light and fixed depth of oil standard. The average deviation from the mean for all observers on both samples was 2.5 per cent using method A and 1.0 per cent using method B.

Having shown that a satisfactory color method resulted when samples diluted with benzene were matched against a neutral filter standard in green light covering a narrow band of wave lengths, the next steps were to find a reproducible substitute for the green filter, and a means of calibrating the neutral filter in absolute units. The transmission curve of the green gelatin filter used up to this point is shown in Figure 7.²

It was considered that this curve would be duplicated with materials most readily specified and obtained and least dependent on the products of any one manufacturer, if a colored solution was used as filter. Preference was given to

inorganic salts, rather than organic dyes, since as a class the salts would be more easily duplicated and more stable with time. A survey of the available literature and an examination of some twenty solutions with a small direct-vision spectroscope resulted in the choice of a 30-mm. layer of a strong solution of

² The transmission curves given in Figure 7 were determined by Razek and Mulder, using the Razek-Mulder color analyzer.

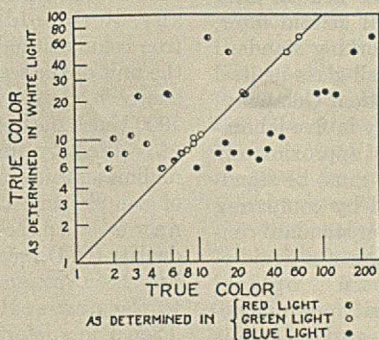


FIGURE 6. RELATION BETWEEN TRUE COLOR IN WHITE LIGHT AND IN RED, GREEN, OR BLUE LIGHT

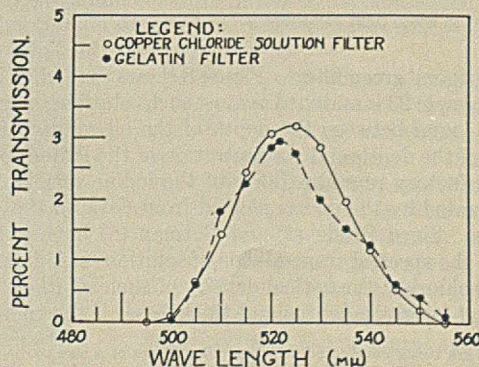


FIGURE 7. TRANSMISSION CURVES OF GREEN FILTERS

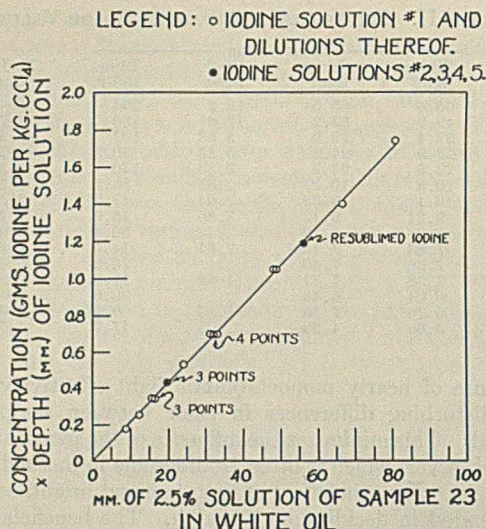


FIGURE 8. PROPORTIONALITY OF OIL COLOR AND IODINE COLOR IN GREEN LIGHT

cupric chloride in water. Figure 7 shows that the transmission curve of this solution in a clear glass cell is a close approximation to that of the gelatin-in-glass filter previously used.³

Having found a satisfactorily reproducible substitute for the green filter, the matter of calibrating the neutral filter standard was taken up. A Wratten neutral gelatin filter, cemented between glass flats, was used as working standard in the preliminary tests. For routine tests all-glass neutral filters (supplied by the Bausch & Lomb Optical Co.)⁴ have been substituted and used satisfactorily in five laboratories. These filters have an optical density of approximately 0.3, but for use in the proposed method they must be standardized more exactly. This is accomplished by comparing them, in the Dubosq colorimeter, with a master standard consisting of a liquid of known optical density per millimeter and which is known to change its optical density linearly with increasing depth. In the search for such a liquid, tests were made of some 28 solutions, with the result that dilute solutions of iodine in carbon tetrachloride were found to obey Beer's Law in the light passed

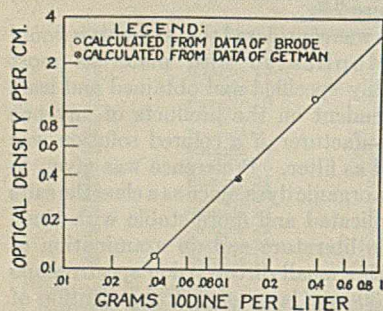


FIGURE 9. OPTICAL DENSITY OF SOLUTIONS OF IODINE IN CARBON TETRACHLORIDE

Used in green light colorimetry.

by the authors' green filter. Figure 8 shows that when a solution of sample 23 is matched against such solutions, a linear relation is found between the depth of the oil solution and the product of the depth and concentration of the iodine solution. The satisfactory reproducibility of the iodine solution is also demonstrated by the points plotted from data on the several solutions. Since Brode (2) and Getman (6) have published data on the spectral transmission of solutions of iodine in carbon tetrachloride, the optical density of such solutions can be calculated for given depths and thicknesses if the energy dis-

³ Tests are being conducted on glass color filters of a size to be conveniently slipped into the Dubosq eyepiece, but because of its reproducibility from specifications, the cupric chloride solution filter is considered as standard.

tribution throughout the spectrum of the illuminant is known. A discussion of calculations of this kind is given by Davis and Gibson (4). Figure 9 shows the relation between the optical density per centimeter and the concentration for solutions of iodine in carbon tetrachloride. It must be emphasized that the optical densities read from Figure 9 will be correct only when the solution is viewed in the illumination furnished by the green filter specified in Figure 7, in combination with a source of 1850° K. color temperature. Use of a filter with a different transmission curve might result in appreciable differences in optical density of the iodine solution. The calculations are not so sensitive to changes in color temperature of the source, since a recalculation based on a color temperature of 2600° K. for the source made only 1 per cent difference in the optical density figures. From the equation of the line shown in Figure 9, the optical density D (in the green light) of a neutral filter which is matched by X mm. of an iodine-in-carbon tetrachloride solution of concentration C mg. per liter is given by

$$D = 0.0003193 \times (\text{mg. iodine per liter}) \times (\text{depth in mm.}) \quad (2)$$

In order to express color values in more fundamental units and to differentiate between color determined by this method and by any of the older true color methods, the unit of the scale chosen as 1000 times the optical density per millimeter thickness of sample and the name optical density color has been assigned to the new scale.

Then if, in a determination, R mm. of a given oil sample match a neutral filter of optical density D , the optical density color of the oil is $1000 D/R$.

A comparison of several of the true color oil standards used in the method of Weir, Houghton, and Majewski (12) with a neutral filter calibrated for density has permitted the generalization that the following relation exists between true colors determined by their method and optical density colors

$$\text{Optical density color} = 1.57 \times \text{true color} \quad (3)$$

One of the disadvantages of the true color method using white light and oil standard was that it led to different color values if the depth of standard was changed. The method herein presented gives the same color values for any optical density of standard within the practicable working range. This is shown in Figure 10, where the optical density colors of one light and one dark oil remain constant regardless of the density of the neutral filter used in the determination. The points for the filter of lowest density are considered reasonable checks in view of the increased uncertainty in the determination of the density of this filter.

A detailed description of the method is given below. When it is followed exactly, the accuracy obtained is comparable to any photometric method, check determinations by several observers agreeing to within 2 per cent of the average. Under routine conditions, with identical samples distributed monthly by a control laboratory, four laboratories have consistently reported results within 5 per cent of the average.

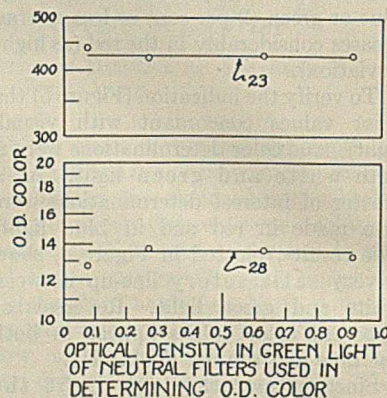


FIGURE 10. OPTICAL DENSITY COLORS DETERMINED IN GREEN LIGHT

Neutral filters of several densities.

DETERMINING ADDITIVE
COLORS ON OPTICAL
DENSITY COLOR
SCALE

SET-UP OF MACHINE.

The determinations should be carried out in a room which is completely dark except for the small light leakage from the instrument. Preferably, the entire room should be painted a dead black, and should be small enough to exclude other work or the presence of more than two men at a time. It is essential that the wall facing the operator, as he sits at the color machine, be non-reflecting. In locating and installing such a colorimeter room, proper ventilation should be provided and underground steam lines avoided as much as possible.

A table or stand for the instrument and stool for the operator are provided, of such relative heights that readings may be made without undue strain.

A Bausch & Lomb Duboscq colorimeter No. 2504, 100 mm., and Bausch & Lomb colorimeter lamp No. 2414 have been found satisfactory for this test. Purchasers of new instruments should specify that the Duboscq plungers be cemented in place with benzene-proof cement. The colorimeter with its removable shield is shown on the right of Figure 11.

For routine testing the oil to be examined is placed in a cup 25.4 mm. (1 inch) in diameter and 108 mm. (4.25 inches) deep, the bottom of which consists of a disk of optical glass sealed to the bottom of the tube with benzene-proof cement. When relatively few determinations are to be made, the cups furnished with the colorimeter suffice. Both types are shown in Figure 11 (left front).

A 60-watt, inside-frosted Mazda bulb is specified.

A distinctive feature of this procedure is that matches are made with use of green light, which is secured by placing between the light source and mirror of the colorimeter a glass cell containing a green solution. The solution in use at present is made by dissolving 326.0 grams of Baker's c. p. cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and 0.50 gram of Baker's c. p. mercuric chloride in 351.3 grams of distilled water and filtering once through Whatman No. 42 paper. The solution is contained in a glass cell such that the light passes through 30 mm. of solution. The cell specified for this purpose is a metal-glass-Bakelite cell using rubber gaskets instead of cement and made to order by the Arthur H. Thomas Company. (Duplicates may be ordered by referring to A. H. Thomas blueprint 587.) If this cell is used, the solution gradually darkens and should be replaced monthly. An alternative cell, which is more fragile but which does not darken the solution, is Arthur H.

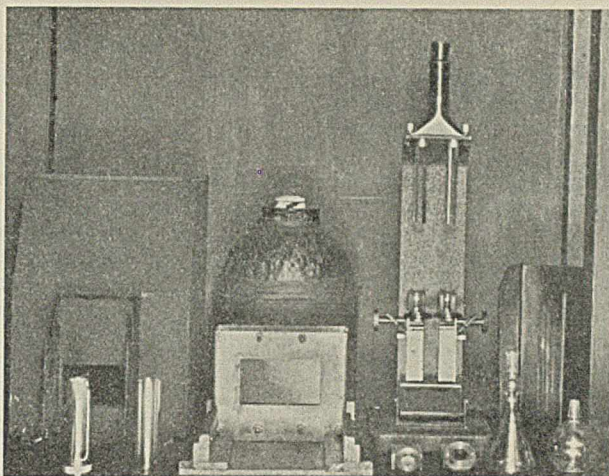


FIGURE 11. COLORIMETER AND AUXILIARY APPARATUS FOR DETERMINATION OF OPTICAL DENSITY COLORS

light screen is used, which also shields the eyes of the operator from stray light. Such a shield is shown in Figure 11 (left rear).

The working standard in this procedure is a 25.4-mm. (1-inch) square glass neutral filter. This is introduced into the system by replacing the left hand cup of the Duboscq by a specially made brass mounting which holds the neutral filter and a glass equivalent to the bottom of the removed cup.

Neutral filters are pieces of gray glass about $25.4 \times 25.4 \times 3.0$ mm. ($1 \times 1 \times 0.125$ inch), with an optical density of about 0.3. They are calibrated and issued by the control laboratory and periodic rechecks are made. Reasonable care must be exercised in handling these filters. They should be cleaned, if necessary, by wiping with soft lens paper. They must not be washed with solvents of any kind, nor scratched by rubbing with a gritty cloth.

In order to introduce the neutral filter and the special cup into the set-up, brass adapters are used. These are shown in Figure 11, propped up in front of the Duboscq colorimeter. Figure 12 shows the apparatus completely assembled.

PREPARATION OF SAMPLE. Oils which, in depths of from 8 to 90 mm., match the standard neutral filter need no further preparation.

Haze due to small quantities of suspended matter in the oil must be removed by filtering before taking the color. If this is not done the grayness imparted by the haze will be read as color and lead to erroneous conclusions for ordinary purposes. (This applies to haze produced by suspended salts, water, or small quantities of separated wax.)

Dark oils which flow readily are to be diluted with benzene of 30 Saybolt color in the ratio of one volume of oil to 10 volumes of solution. If this solution is still too dark to match the neutral filter at a depth greater than 8 mm., a second and if necessary further dilutions should be made, always in the 10 to 1 ratio. These dilutions are to be made in a special flask calibrated at two points so that the volumes indicated have a ratio of 9 to 10; and with volume between the two marks of 10.0 ± 0.05 ml. The flask is to be

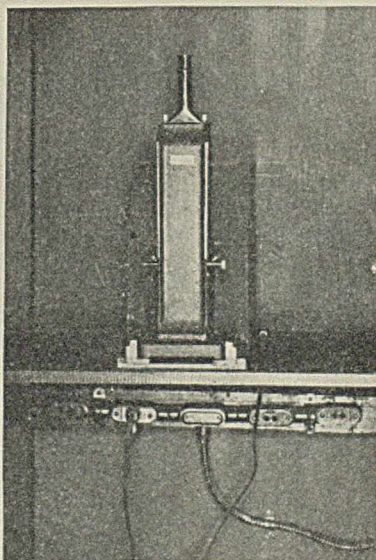


FIGURE 12. ASSEMBLED APPARATUS FOR DETERMINATION OF OPTICAL DENSITY COLORS

closed, while mixing, by a special bulb-type stopper with ground-glass joint, and not by cork or operator's thumb. The bulb-type stopper permits completion of mixing before transfer. Pyrex flasks of this type can be obtained from the Corning Glass Company. The flask and bulb-type stopper are shown in Figure 11 (right front).

The benzene used for the above dilutions should be steam-distilled and filtered through paper before use.

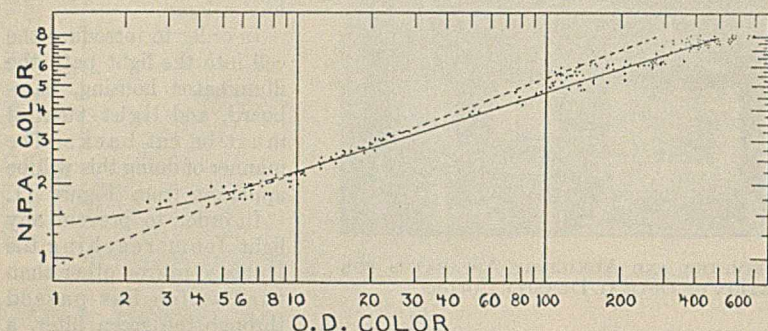


FIGURE 13. NATIONAL PETROLEUM ASSOCIATION AND OPTICAL DENSITY COLOR DATA FOR VARIOUS SAMPLES

Dark oils too viscous to flow readily and oils of high pour may be warmed sufficiently so that they will pour and then added to the benzene in the dilution flask, stopping a little short of the second mark. After the contents of the flask have cooled to room temperature the volume is adjusted to the mark by adding the necessary few drops of solute.

TAKING THE COLOR. The following parts are examined and cleaned if necessary: 2 plungers, cup on right side of machine, bottom glass and neutral filter on left, mirror (silvered side), large surfaces of green filtercell, bulb in illuminator, and inner reflecting surfaces of bulb housing, particularly the bottom. It will also be necessary occasionally to remove dust from the top section of the eyepiece which can be unscrewed for that purpose.

The clean cup is now placed on the right side of the instrument and the filter holder, without the filter but with the bottom glass, on the left. The light shield furnished with the machine is put in place, the light turned on, and the field observed. The eyepiece tube should be pushed in or out until the line of separation between the two sides of the field appears sharpest to the observer making the test. Both sides should appear equally bright. If they do not, then either the cleaning was inefficient or the optical system is out of balance. If the field appears equally bright on both sides, the cup on the right is racked up until the plunger touches its bottom. The scale on the right should now reach zero, and should be adjusted to do so if necessary. The neutral filter is placed in position in its holder, which is racked up until the plunger and neutral filter are nearly in contact.

The oil or solution to be tested is placed in the cup, which is then replaced on the right of the machine and racked up and down until the fields match in intensity. The eye should be held as nearly as possible on the axis of the eyepiece while matching, and the point of match should be approached from both sides by "bracketing." Six readings of the depth of match should be taken and averaged. However, on starting a series, it is well to discard the first few readings so as to give the eye time to adjust itself. If the average reading is below 8 mm., another set of readings should be taken on a more dilute sample. After each sample the cup and plunger should be washed with benzene and volatile naphtha. For this purpose a test tube which can be half-filled with solvent and then slipped up around the plunger eliminates the necessity of wiping the cup or plunger except occasionally.

CALCULATING THE COLOR. Color values on the optical density scale are calculated from

$$\text{Optical density color} = \frac{10^3 D \times 10^N}{R} \quad (4)$$

where D = optical density of neutral filter

$$= \frac{\log \text{incident light}}{\log \text{transmitted light}}$$

R = mm. depth of oil (or solution) to match neutral filter

N = number of dilutions (in 1 to 10 ratio)

These color values are named optical density colors (colors on the optical density scale) because they are calculated from the depth of oil (or solution) having an optical density equal to that of the neutral filter working standard. The neutral filters as purchased are not accurately calibrated and hence must not be used until a calibration has been supplied by the control laboratory. To illustrate the calculation in a few specific cases the following examples are given:

(1) **OIL NOT REQUIRING DILUTION.** Density neutral filter = 0.336 = D . Depth of undiluted oil to match = 12.0 mm. = R .

$$\text{Optical density color} = \frac{10^3 \times 0.336}{12.0} = 28.0$$

(2) **OIL REQUIRING DILUTION.** Same neutral filter, $D = 0.336$. Depth of solution at match = 27.0 mm. = R . Number of 1 to 10 dilutions = 2 = N .

$$\text{Optical density color} = \frac{10^3 \times 0.336 \times 10^2}{27.0} = 1244$$

Since the measurements are uncertain in the third figure, this result should be written 1240.

(3) **DILUTION FLASK NOT EXACTLY 1 TO 10 RATIO.** If the dilution flask used does not give exactly a 1 to 10 ratio the following formula is used:

$$\text{Optical density color} = \frac{10^3 D \times (\text{dilution factor})^N}{R} \quad (5)$$

For example: Density of neutral filter = 0.336.

$$\text{Dilution factor} = \frac{\text{volume of solution contained by flask}}{\text{volume of oil taken for dilution}} = 9.70$$

Number of dilutions = $N = 2$. Depth of final solution at match = 38.0 mm. = R .

$$\text{Optical density color} = \frac{10^3 \times 0.336 \times (9.70)^2}{38.0} = 832$$

RELATION OF O. D. COLOR TO N. P. A. COLOR

Figure 1 demonstrated that, comparing two oils in white light, various results may be obtained, depending upon the thickness of oil layer. Nor is this a phenomenon connected with a colorimeter of the Duboseq type. Samples 1 and 2 were placed in tubes of various diameters. In tubes of 2 to 5 mm. diameter, sample 2 was unquestionably lighter, although in 35-mm. tubes (4-oz. bottles) it was just as definitely darker than sample 1. N. P. A. color is, then, comparable to a white-light true color at a fixed depth (35 mm.), and since the optical density color eliminates this variation of color with depth, no strict correlation between N. P. A. and optical density color is possible.

That there is a rough correlation is demonstrated by Figure 13, which contains values for 190 diverse oils. The solid line between 2 and 8 N. P. A. was determined on another series of oils. Below 2 N. P. A. (broken line) the line seems to depart from linearity, which appears to be in agreement with (unpublished) color analyses of N. P. A. standards which reveal that below 2 N. P. A. the interrelationships between standards are of a different nature than those between the standards from 2 to 8 N. P. A.

The dotted line corresponds to that of Weir, Houghton,

and Majewski (12) for true color. It is not in good agreement with the data for the wide variety of oils included here, but there is evidence that it is valid for light distillates, finished by acid-treating alone, which was the type of oils considered by them.

ACKNOWLEDGMENT

Acknowledgment is due to H. M. Weir, who brought the advantages of the true color system to the authors' attention; to M. L. Wood for preliminary work on the problem and the suggestion of using monochromatic light; to W. F. Houghton, A. B. Guise, and S. S. Kurtz, Jr., for helpful discussion; to K. O. Brown and J. A. Kane who made many of the determinations during the development period; and to the many laboratory technicians who have assisted in making this method a success in routine work.

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Inverted Fractional-Distillation Analysis

Inversion Column

R. A. J. BOSSCHART, Laboratory of the N. V. De Bataafsche Petroleum Mij., Amsterdam, Holland

FOR the continuous splitting of a mixture of components—for instance, by distillation or extraction—when use is made of the difference in the coefficient of distribution of the components over two phases, three chief types are distinguishable. In the case of distillation these are (1) flash distillation, (2) rectifying dephlegmation, and (3) complete rectification.

In the first case the mixture is divided over two phases, which are then separated from each other. In the second case the mixture is introduced on one side of the column, while part of the product escaping on the other side is re-fed in another phase as reflux, which after being interchanged in the column flows away on the first side. In the third case the mixture to be split is introduced into the middle of the column. The column may here be looked upon as being constructed of two halves, each working according to the second type. It is of importance that the two phases in these two halves play an opposite part.

For the discontinuous separation, applied for analysis, three analogous cases are conceivable. The first is closely connected with analytical distillation, such as the A. S. T. M. distillation (D86-30); the second, with analytical rectification for distillation, as with the Podbielniak apparatus (1); the third case is also imaginable to a certain extent.

For the usual fractional-distillation analysis of the second type, the mixture to be separated is, as a rule, introduced as vapor at the bottom of the column, so that the lightest component is the first to be separated as the top product. It is, however, just as possible to introduce the mixture as liquid

A description is given of a rectifying apparatus for normal pressure, which allows analysis by distillation of mixtures of gases or liquids, commencing with the components with the highest boiling point.

The apparatus has a range of about +200° to -170° C.

The fractions can be collected in liquid or in gaseous condition, as desired.

The analysis can be terminated at any point, which shortens the duration of the analysis considerably in many cases, especially when determination of the fractions with the highest boiling points is of chief importance, which frequently happens in the petroleum industry.

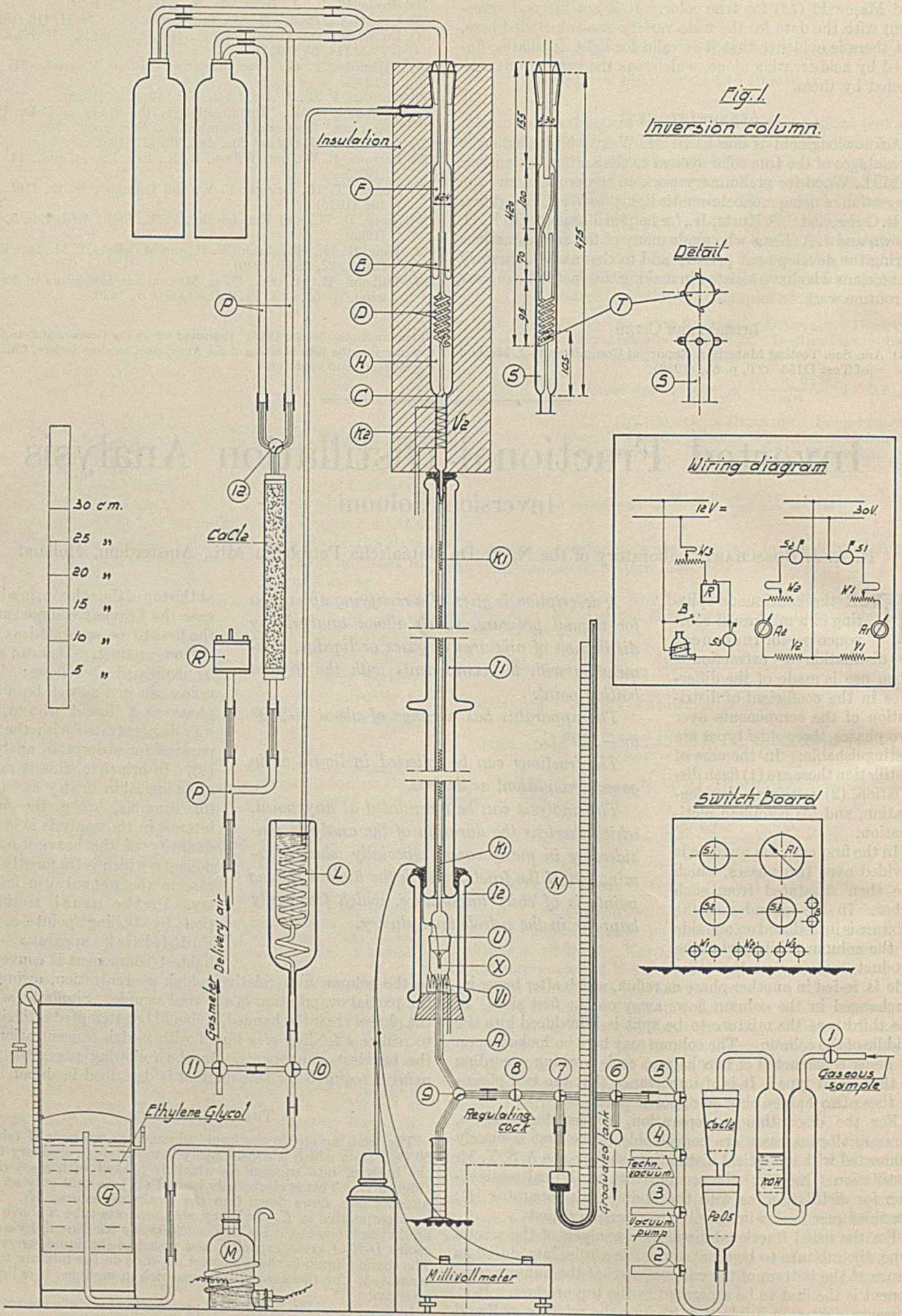
at the top of the column, in which case the heaviest component is the first to be separated as the bottom product. This can also be expressed as follows: The reflux can just as well be a gas phase as a liquid phase, as was demonstrated with the apparatus for absorption analysis (2). In principle, this is much more logical in many cases, as for example, when the main interest in the analysis is in the quantity of the heaviest components, which is frequently the case in the petroleum industry. In the usual rectification by boiling point—e. g., Podbielniak apparatus—the lightest component is conveyed

to the column in a relatively high concentration, owing to the partial evaporation of the trial sample. Similarly, when the phases are interchanged, it should be attempted artificially to realize a feeding of a liquid with a high concentration of the heaviest components. In the following pages the apparatus required for this method is described in detail.

THE TOP COOLING

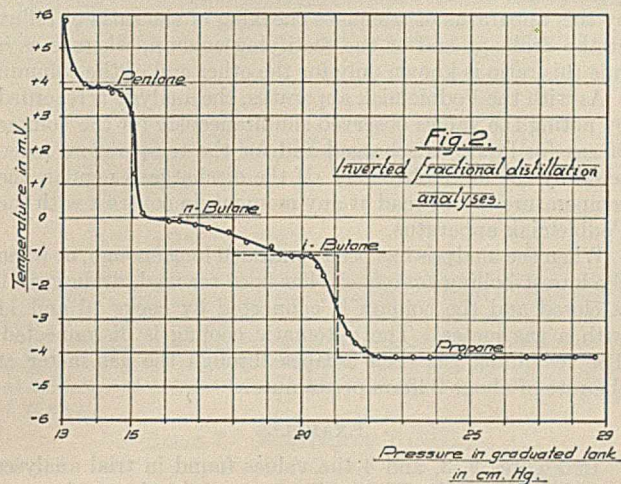
The trial sample, in the liquid phase, is in reservoir *H* (about 50 cc.), from which it continuously flows, through capillary *C* in the bottom, into column *K*₂ which is packed with glass rings (Figure 1). This is electrically heated (*V*₂), so that only an adjustable part flows down into the rectifying column *K*₁. The part evaporated in *K*₂ rises through a separate tube *S* above the liquid reservoir, but it is there continuously condensed, by a top cooler *D-E* of great capacity, and re-fed to the liquid reservoir. The cooling liquid in the top cooler depends on the mixture to be separated; for the analysis of gases rich in methane it is liquid nitrogen.

In order to maintain a normal pressure in the whole apparatus,



the space around the top cooler is connected with gas tank *G* (capacity about 2 liters), filled with a noncondensing gas (hydrogen) above ethylene glycol (low vapor pressure, slight solubility of hydrogen or hydrocarbons). This gas also surrounds the top cooler, in so far as it is not driven out by the condensing vapor. This makes it possible for the condensation level to rise or go down in connection with fluctuations in cooling, etc., constant pressure (2 cm. water of excess pressure) being guaranteed by the gas tank.

The condensation normally takes place at the cooling coil *D*, which is continuously filled with liquid nitrogen from the cooling vessel *F*. As soon as the stock in this vessel is exhausted, the condensation level rises to the test tubes *E*, which are now only just filled.



The accompanying expulsion of hydrogen to the gas meter is utilized in the contact manometer *M* to close an electric current. This closes in the relay *R* the outlet of the compressed air tube *P*. The current of compressed air, limited by capillaries, now presses the liquid nitrogen from one of the thermos flasks into the cooling vessel. Owing to this, the condensation level drops again and the expelled hydrogen reenters, passing through the Dewar tube *L*, in which, at -20°C . (ice and salt), the vapor of the ethylene glycol from the gas tank is sufficiently precipitated.

This automatic supply of nitrogen proved, in all the experiments, to insure a perfectly regular circulation of liquid and vapor above the rectifying column, entirely independent of the moistening of the column and the collection of the liquid regulated by the manipulator.

Some tentative experiments brought to light two difficulties in the required transmission of much heat: The rising vapor is easily cooled down so far that a stable, dense mist is formed; the mist drops may even pass the cooler. Also, too high a percentage of high-boiling constituents should be avoided, on account of the risk of freezing out at the cooler.

In the construction employed, these components are sufficiently removed from the vapor by a rectifying interchange in the top column *K*₂ and by dephlegmation on the wall of tube *S* in which the evaporated part rises. The vapor is then made to rotate strongly by the sprayer *T* near the cooling coil, by which the mist formed is effectively centrifugized. Moreover, the temperature on the wall of the (double-wound) cooling coil is adjusted to some extent, as the nitrogen vapor developing in it constantly prevents it from being entirely filled with the cooling agent. The difference in height between the two ends of the coil in the cooling vessel *F* acts like a gas-lift pump and causes the nitrogen to circulate through the coil.

RECTIFYING AND MEASURING APPARATUS

In order to render the results as comparable as possible, the rectifying column *K*₁ was chosen in

exactly the same shape as that used by Podbielniak in his apparatus (inside diameter 4 mm., length about 80 cm., wire coil packing); it is also surrounded by a silvered vacuum jacket *I*₁.

At the bottom the column ends in a wide ground joint *U*, the inside of which ends in a very thin-walled, narrow tube. In this are suspended the three thermoelements *X*. The liquid dropping down through it falls in drops onto the aperture of the discharge capillary *A*, which is heated by the heating device *V*₁. The vapor formed returns to the column through openings immediately above the thermoelements.

The circulation of air in the (unsilvered) vacuum jacket *I*₂ causes part of the dripping liquid to evaporate before it reaches the thermoelements, so that an excessive supply of heat to the capillary aperture can be avoided. This would easily give rise to errors in the reading of the temperature, owing to heat radiation to the thermoelements.

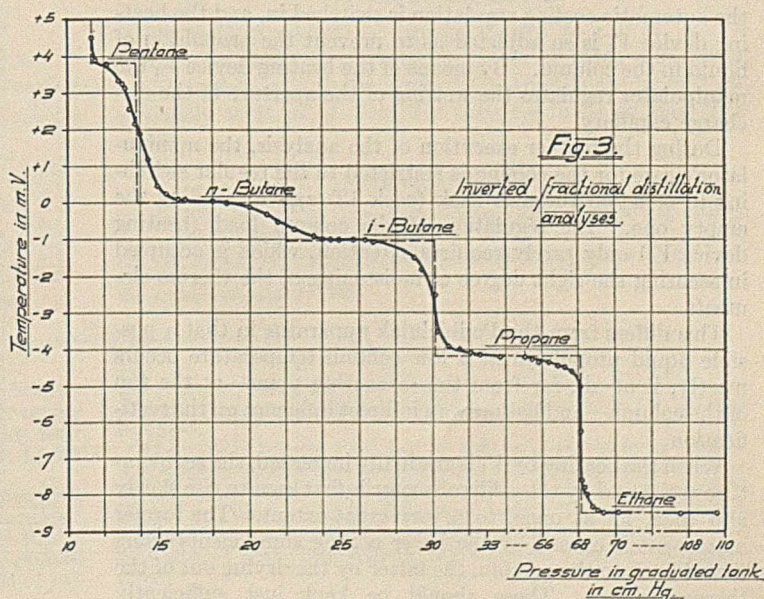
Through the very narrow discharge capillary *A* and the drain cock 9 the rectified product can be collected, as desired, as liquid in a graduated cylinder or as gas in the graduated tank *O*, the pressure in which is registered by the barometer *N*, which is closed on one side. (Tight shutting of cock 9, also after the liquid has passed, is insured by the use of gasoline-insoluble cock grease, such as "Resistol.")

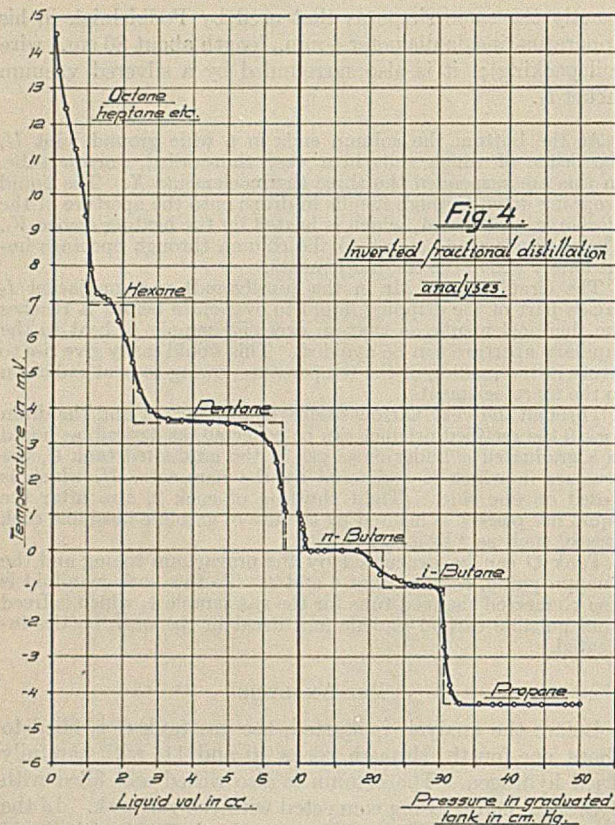
Tank *O* can be evacuated by the prevacuum tubing and the vacuum pump, connected at 4 and 3. To this cock manifold is also connected the feed tube for the gas sample *I*, which is freed from possible carbon dioxide and dried in the wash bottles indicated.

THE ANALYSIS

Before the analysis is started, the gas tank *G* is filled to about one-fourth, through cocks 10 and 11, with carefully dried hydrogen. The column is also rinsed and filled with hydrogen, before being connected with the gas tank. In the case of a light product, the top cooler is filled with liquid nitrogen, for which purpose the compressed air relay *R* is made to function by press button *B* (see wiring diagram). About 250 cc. of hydrogen then pass from the gas meter to the column.

A gaseous sample is introduced (after rinsing out the wash bottles and the cock manifold up to cock 5) through cocks 1 to 9, inclusive. About 100 cc. of hydrogen are driven out of the column by this. Immediately after this slight rise in the gas tank (during intense cooling), its reading should be noted. The feed of gaseous sample may now be increased to about 1.5 liters per minute. If the sample also contains hydrogen, oxygen, nitrogen, or the inert gases helium or argon, these will join the hydrogen present while the sample is introduced;





their volume is determined by reading the rise in the gas tank during the introduction. If this is more than 1 liter, a known volume can be quickly withdrawn from the gas tank through cocks 10 and 11. A concentration of oxygen of more than 10 per cent in the gas tank should be avoided because of condensation, which results in a strong development of mist and irregularity in the cooling.

If a liquid sample has to be introduced, some methane plus ethane (about 5 liters) should first be put in as conveyor gas for the top circulation to prevent freezing of the high-boiling components on the cooling coil. The liquid sample can subsequently be introduced under some excess pressure from the flask through the liquid draining capillary.

After introducing the trial sample, the drain cock is closed, the automatic cooling regulation is switched in, and the heating device V_2 is so adjusted as to prevent the propulsion of liquid in the column. By means of the heating device V_1 the manipulator regulates the wetting of the aperture of the discharge capillary.

During the further execution of the analysis, the manipulator's care for the cooling is restricted to the regular switching in of a full thermos flask (cock 12) and to refilling the empty one. The regulation of the column load (heating device V_2) only rarely requires attention, which is occupied in securing the right degree of moistening of the thermo-elements.

This differs from the Podbielniak apparatus in that a possible liquid propulsion at a low column temperature occurs mostly, if at all, far from the measuring point—at the top of the column—and has only an indirect influence on the rectification.

When the heating by V_1 is gradually increased, the temperature registered by the millivoltmeter is first seen to rise slowly and then, all at once, to a very great extent. The former movement is caused by the lower boiling components being forced back to the column, the latter by the drying out of the thermo-elements. These should be kept just sufficiently

moist, which requires less supply of heat in proportion as more rectificate is exhausted.

REFLUX RATIO. In the butane range (slight exchange of heat with the surroundings) the charge of the heating device V_1 was about 10 watts, equivalent to 2.4 gram calories per second (Figure 2). This means (molecular heat of evaporation of butane equals 5400 gram calories per gram molecule) a reflux of about 0.00044 gram molecules per second or about 10 cc. of gas per second.

The rate of flow to the graduated tank was about 0.28 cc. of gas per second. The ratio of reflux was therefore about 40.

Attention should here be drawn to the possibility afforded by this apparatus of adequate checking of the ratio of reflux at the drainage end of the rectifying column, whereas as a rule this ratio is known only for the other end of the column.

As with the Podbielniak apparatus, the analysis is recorded by noting the values observed simultaneously for the volume of gas (or liquid) discharged and for the temperature registered by the millivoltmeter. If the discharge is regular, the temperature can be read at any moment, in contrast with the Podbielniak apparatus.

When the analysis has been continued long enough, or when the lowest-boiling component has been reached, drain cock 9 is closed and the column is connected by cocks 10 and 11 with a gas meter. The automatic cooling is disconnected. The remaining gas then escapes through the gas meter at the rate of about 2 liters per minute.

EXAMPLES

In Figures 2, 3, and 4 the values found in trial analyses have been plotted. The millivoltage of the thermolements

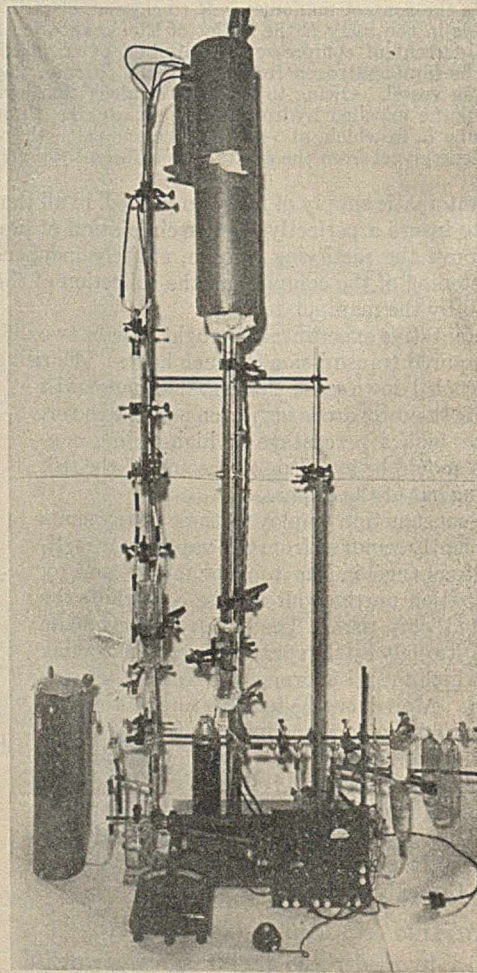


FIGURE 5. BOSSCHART INVERSION COLUMN

has in each case been taken as the ordinate (1 millivolt equals about 10° C.), the abscissa indicating the pressure in the graduated tank (or the volume of liquid drawn off).

Figure 2 represents a brief analysis of the top gas obtained in the industrial production of gasoline. The trial sample (about 15 liters) was introduced in about 20 minutes. The regulation of the heating took 15 minutes, the rectification itself 1 hour, hence the whole analysis took over 1.5 hours.

The product was measured exclusively in the gaseous condition.

RESULTS OF DETERMINATION. Rise in the gas tank during the introduction was 6.0 cm. Increase in pressure in the graduated tank while the separate components were rectified off (Figure 2) was:

| | MERCURY Cm. |
|------------------------------------|----------------|
| Initial reading of barometer | 13.0 |
| For pentanes and higher components | 2.0 |
| For normal butane | 3.0 |
| For isobutane | 3.1 |
| For propane | 7.6 |
| Final reading of barometer | 28.7 |

The quantity of gas (methane plus ethane plus propane) which subsequently passed through the gas meter (converted to dry gas at 20° C.) was 12.61 liters.

The measuring apparatus is so calibrated that 1 cm. rise in the gas tank gives an increase of 116 cc. of gas, and 1 cm. mercury rise of the pressure in the gas tank gives an increase of 71 c. of gas.

TABLE I. ANALYSIS OF TOP GAS

| COMPONENT | Gas Cc. | PER CENT BY VOLUME Bos- Podbielniak ap- paratus paratus | |
|--|------------|--|-----------------|
| | | Gas Cc. | paratus paratus |
| Pentanes and higher (2.0 × 71) | 142 | 1.0 | 1.1 |
| Normal butane | 213 | 1.5 | 3.2 |
| Isobutane | 220 | 1.5 | |
| Propane | >540 | >3.7 | 6.7 |
| Ethane plus methane | <12610 | <87.5 | 84.5 |
| Oxygen, hydrogen, nitrogen, etc. (6.0 × 116) | 696 | 4.8 | 4.5 |
| Total | 14421 | 100.0 | 100.0 |

Carbon dioxide, if present, should of course be determined chemically, like the composition of the noncondensable part.

Figure 3 shows a similar sample from the same plant, a trial sample about 45 liters. The analysis has been continued further. The duration was:

| | Min. |
|-----------------------------|---------|
| Introduction of sample | 40 |
| Establishing of equilibrium | 15 |
| Time of distillation | 3 hours |
| Total, about | 4 hours |

TABLE II. CONTINUED ANALYSIS OF SAME TOP GAS

| COMPONENT | INCREASE IN PRESSURE ^a | | PER CENT BY VOLUME |
|---|---|------------|--------------------------|
| | Cm. Hg | Gas Cc. | |
| Pentanes and higher | 2.4 | 171 | 0.4 |
| Normal butane | 8.2 | 582 | 1.3 |
| Isobutane | 8.1 | 575 | 1.3 |
| Propane | 38.1 | 2,710 | 6.1 |
| Ethane | >41.4 | >2,940 | >6.6 |
| Methane (gas meter reading, converted) | | <37,320 | <83.2 |
| Noncondensable (= 4.3 cm. rise in gas tank) | | 499 | 1.1 |
| Total trial sample (rounded off) | | 44,800 | 100.0 |

^a According to Figure 3.

Figure 4 represents the analysis of a gas which still contains gasoline. As the higher-boiling components have been collected and measured as liquids (left half of Figure 4), all the data have been converted to weight. The duration was:

| | Min. |
|---|-----------|
| Introduction of sample (about 20 grams) | 25 |
| Establishment of equilibrium | 20 |
| Rectification | 3.5 hours |
| Total, about | 4.5 hours |

TABLE III. ANALYSIS OF GAS CONTAINING GASOLINE

| COMPONENT | VOLUME OF LIQUID Cc. | SPECIFIC GRAVITY GAS Cc. | Grams | PER CENT WEIGHT |
|---|-------------------------------|-----------------------------------|--------|-----------------------|
| | | | | |
| DRAWN OFF AS LIQUID | | | | |
| Heptanes and higher | 1.0 | 0.70 | 0.70 | 3.5 |
| Hexanes | 1.3 | 0.66 | 0.86 | 4.3 |
| Pentanes (grad. cyl. 0° C.) | 4.2 | (0°) 0.65 | 2.74 | 13.9 |
| Normal butane (grad. cyl. 0° C.) | 0.1 | (0°) 0.60 | (0.06) | 2.20 |
| GAS | | | | |
| DRAWN OFF AS GAS | | | | |
| Normal butane | 12.1 | 800 | 2.67 | 7.8 |
| Isobutane | 8.8 | 583 | 2.67 | 1.55 |
| Propane | >19.5 | >1290 | 2.02 | >2.60 |
| Methane plus ethane (gas meter reading) | <8520 | abt. 1.0 | <8.52 | <43.2 |
| Noncondensable (rise of gas tank 4.1 cm.) | 444 | abt. 1.4 | 0.62 | 3.1 |
| Total weight of trial sample about | | | 19.80 | 100.0 |

^a Converted to 0° C.

CONCLUSION

The apparatus described makes it possible to rectify mixtures of gases or liquids at boiling points between +200° and -170° C.

Especially when chiefly the higher-boiling components have to be determined, or when the lowest-boiling component strongly preponderates in percentage, the analysis can be finished in a very short time.

Other advantages are simple regulation and sharp control of the exact moistening of the thermoelements, adequate control of the ratio of reflux, and reduction of the dead space. Between the place where the temperature is registered and that where the volume is determined the formation of liquid is greatly restricted.

Since all the systematic deviations must be about equal but opposite to those occurring with the Podbielniak apparatus, a careful comparison of the two methods on the same sample will afford a long-sought-for opportunity of surveying and eliminating these deviations.

ACKNOWLEDGMENT

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NEW NORWEGIAN PROCESS FOR MANUFACTURE OF SODIUM NITRATE. Details in connection with the new process for manufacturing sodium nitrate recently developed in Norway have just been given out, according to a report made public by the Commerce Department.

The process, which will be patented in all important countries, is based on the use of artificial zeolites. Seawater somewhat concentrated is pumped through a large container filled with a calcium base-exchange medium. When the reaction has occurred the sodium zeolite is treated with a concentrated solution of cal-

cium nitrate, resulting in the formation of sodium nitrate and a calcium zeolite. Seawater is again introduced and the process repeated.

The sodium nitrate produced by this process, the report states, is not much more expensive than the calcium nitrate now being produced, especially if it is considered that sodium nitrate can be packed and shipped in much cheaper sacks. The new product is stated to be practically the same as natural sodium nitrate and it is alleged that the synthetic can compete with the natural in price.

Qualitative Method for Selenium in Organic Compounds

M. J. HORN, Protein and Nutrition Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

WHEAT plants grown by the Bureau of Plant Industry at the Arlington Experiment Farm on normal soil to which had been added from 1 to 20 parts per million of selenium in the form of sodium selenate were believed to contain small quantities of selenium. Only a limited supply of these plants was available for analysis, and a quick method which would require only a gram or so of material was desired to test this material for selenium.

The method of Schmidt (3), used by Stover and Hopkins (4), seemed to be the quickest procedure available.

These workers digested powdered, dried leaves with 10 cc. of concentrated nitric acid until only 2 or 3 cc. remained. This operation with nitric acid was repeated. Then 5 cc. of sulfuric acid were added and the mixture was boiled, a few drops of nitric acid being added from time to time to hasten the oxidation. When a straw-colored solution was finally obtained, the boiling was continued until dense white fumes were evolved. The solution was cooled and brought up to definite volume and 0.01 gram of codeine was added. The presence of selenium was indicated by the formation of a green color, changing gradually to a blue-green and finally to a pure blue color.

The disadvantages of this method are (1) the possibility of losses of selenium on digestion with nitric acid, (2) the difficulty of removing all traces of the nitric acid, and (3) the time consumed in first digesting the material with nitric acid and then removing the nitric acid with sulfuric acid. It is necessary to remove all traces of nitric acid in the digest; otherwise a deep red color is obtained when codeine is added. It was desired, therefore, to eliminate the use of nitric acid if possible, and the Kjeldahl digestion method for nitrogen determination offered possibilities. Besides giving a smooth, quick method of oxidizing the organic material, digestion of the material with sulfuric acid and mercuric oxide offered advantages in the probable formation of a double salt of mercury with selenium, which lessens the possibility of a loss of selenium by volatilization, and in the change of the inorganic salts occurring in the plants to a state of oxidation that does not give a blue color with codeine.

Lyons and Shinn (1) showed that added salts, such as mercuric chloride and zinc chloride, appear to form a double salt with the selenium holding it in solution. Schmidt (3) showed that ferric iron in quantities of 1 drop of strong ferric chloride solution in 10 cc. of concentrated sulfuric acid will interfere with the test.

Weighed quantities (0.01 gram) of metallic selenium were digested for 1 hour with concentrated sulfuric acid and a little mercuric oxide, after the manner of Kjeldahl nitrogen digestions. The sulfuric acid digest was cooled and made up to 50 cc. with concentrated sulfuric acid. An aliquot of 5 cc. was taken and 4 drops of a 3 per cent aqueous solution of codeine sulfate were added. The color developed was compared in a Bock Benedict colorimeter against the color similarly developed in a standard solution containing 0.01 gram of metallic selenium dissolved at room temperature in 50 cc. of concentrated sulfuric acid. The standard solution was set in the comparator at 20 mm. The comparison of the color intensities showed that no loss of selenium had occurred during the digestion. Further comparisons made against the same standard with 5-cc. aliquots of the digest diluted 50 per cent and 100 per cent with concentrated sulfuric acid gave the same result.

Two grams of ferric sulfate were digested for 1 hour with 50 cc. of sulfuric acid and mercuric oxide in the manner described. A test of this digest with codeine sulfate gave no blue color, the solution remaining colorless to light yellow.

Solutions were made up with concentrated sulfuric acid containing 0.0005 to 1.0 gram per liter of selenium. These were digested with sulfuric acid and mercuric oxide, and a 5-cc. aliquot of each was tested in a test tube with 2 drops of 3 per cent codeine sulfate solution. All gave visible blue colors, the limit of detection by this method being less than 0.5 part per million.

Plants grown on soil to which selenium had been added and which were known to contain selenium and similar plants grown on normal soil were furnished by the Bureau of Plant Industry. In every test with these plants those known to contain selenium gave a blue color on addition of codeine sulfate solution, while the plants which contained no selenium remained colorless. Tests were then made on wheat straw, corn, wheat flour, wheat leaves and stalks, and soils, only 1 gram of the dried material being used. The test requires no more time than that required for a Kjeldahl digestion for nitrogen.

In order to ascertain just what salts might interfere with this test under the conditions of the experiment, Daniel Ready, of the Bureau of Chemistry and Soils, tested 17 inorganic elements: chromium, nickel, titanium, beryllium, molybdenum, thallium, tellurium, vanadium, boron, antimony, bismuth, arsenic, iodine, manganese, iron, silicon, and tungsten. Only vanadium interfered with the test, giving a dark greenish blue solution on addition of codeine sulfate. Arsenic on digestion with plants gave no color, but on digestion with soils it gave a blue color which rapidly disappeared, leaving the solution a light yellow. There is no evidence that vanadium salts are present in plant material, although they are present in some soils. Ready added 2 mg. of the salt of each element to 5 grams of the soil, and digested the mixture with 50 cc. of sulfuric acid.

This method can be made fairly accurate as a quantitative method if fresh solutions of definite quantities of selenium are made up in sulfuric acid and comparison is made with the unknowns. For quantities ranging from 1 to 5 parts per million it is quite accurate, but when larger quantities are present the color is not permanent. Also, on standing the codeine is gradually acted upon by the sulfuric acid, giving a brown color which interferes with the test. A digest on standing in the open air for several hours absorbs sufficient moisture to interfere with the test. It is of interest to note that the blue color developed by adding 2 drops of codeine sulfate solution in 5 cc. of concentrated sulfuric acid containing 10 parts per million of selenium will gradually disappear if water is added drop by drop. Digests which will not give a test with codeine sulfate, because of absorption of water on standing in the air, can be heated for 15 minutes to distill off the water. The digest will then give the test in the usual way. It is important, therefore, that the codeine be added to the cooled digest as soon after the digestion as possible.

EXPERIMENTAL

One gram of the dried sample is put in a Kjeldahl flask and 40 cc. of concentrated sulfuric acid are added, together with 0.2 gram of mercuric oxide. The mixture is then digested until colorless, and the digest is cooled and made up to definite volume, if desired, with concentrated sulfuric acid. To 5 cc. of the cooled digest in a test tube are added 2 drops of a 3 per cent aqueous solution of codeine sulfate, with cooling and shaking after each drop. If the digest contains selenium, a green color develops

and then rapidly changes to blue. When the method is applied to soils, the cooled digest should be centrifugalized, and the test made on the clear supernatant solution.

Table I shows the results of tests made on samples obtained from the Bureau of Plant Industry. The plus marks denote the relative intensities of color developed by the above test; the figures denote an approximate quantitative estimation made by comparison with fresh standards. All samples taken were 1 gram each in 50 cc. of sulfuric acid. Quantitative determinations made on some of these samples by other methods show the method to be fairly accurate.

TABLE I. TESTS ON WHEAT LEAVES AND STALKS CONTAINING VARIABLE AMOUNTS OF SELENIUM

| SAMPLE | QUALITATIVE ESTIMATION | APPROXIMATE QUANTITATIVE ESTIMATION |
|-------------------------------|------------------------|-------------------------------------|
| | | P. p. m. |
| 101 Wheat leaves | ++++ | 20 |
| 102 Wheat leaves | ++ | 10 |
| 103 Wheat leaves | + | 2 |
| 104 Wheat leaves | ++++ | 20 |
| 105 ^a Wheat leaves | 0 | 0 |
| 106 Wheat leaves | +++++ | 25 |
| 112 Stalks | +++++ | 25 |

^a Sample 105 was grown on soil containing no selenium, the others on soil containing different quantities of selenium.

Table II shows a comparison of substances containing selenium and the normal substance. (R) denotes samples containing selenium determined by Robinson's gravimetric method (2).

TABLE II. TESTS ON MATERIALS KNOWN TO CONTAIN SELENIUM AND OTHERS KNOWN TO CONTAIN NO SELENIUM

| | |
|--------------|----------|
| Straw (R) | Positive |
| Normal straw | Negative |
| Corn (R) | Positive |
| Normal corn | Negative |
| Wheat (R) | Positive |
| Normal wheat | Negative |
| Soil (R) | Positive |
| Normal soil | Negative |

A quick accurate method has been developed for the detection of selenium in organic compounds. The results on samples known to contain selenium and on those containing no selenium are described. Vanadium interferes with the test.

ACKNOWLEDGMENT

The author wishes to express his thanks to A. M. Hurd-Karrer for the numerous samples supplied in connection with this investigation.

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Platinized Silica Gel as a Catalyst in Gas Analysis

II. Oxidation of the Methane Hydrocarbons

KENNETH A. KOBE AND E. BRUCE BROOKBANK

Department of Chemical Engineering, University of Washington, Seattle, Wash.

IN A PREVIOUS paper (3) it has been shown that the copper oxide tube on the gas analysis apparatus may be replaced by a similar tube containing a commercial platinized silica gel which is an efficient catalyst for the oxidation of hydrogen and carbon monoxide. Hydrogen may be quantitatively oxidized at 100° C.; carbon monoxide acts as a catalyst poison at this temperature, making it necessary to raise the temperature to 300° C. to oxidize the carbon monoxide quantitatively. Although methane is not oxidized at 300° C., nothing is known of the oxidation of ethane and higher hydrocarbons under these conditions. It is common practice to determine hydrogen and carbon monoxide together by oxidation at 300° over copper oxide. In order to determine the possibility of oxidizing hydrogen and carbon monoxide together at 300° in the catalyst tube in the presence of hydrocarbons found in technical gases, the conditions under which methane, ethane, propane, and butane are catalytically oxidized over platinized silica gel were determined.

APPARATUS AND GASES

The apparatus was that used in the previous work (3). The catalyst is the commercial platinized silica gel containing 0.075 per cent of platinum produced by the Silica Gel Corporation for the oxidation of sulfur dioxide to trioxide. Methane was prepared by the action of an alcohol solution

of methyl iodide on a zinc-copper couple (7). Ethane was prepared by the hydrolysis of ethyl magnesium iodide. The propane was commercial Shellene obtained from the Shell Oil Company and was approximately 97 per cent propane. Butane was prepared by the hydrolysis of butyl magnesium bromide. The hydrocarbons after being prepared were analyzed for hydrocarbon content and then diluted with oxygen before use.

OXIDATION OF HYDROCARBONS

The hydrocarbon-oxygen mixture was passed through fuming sulfuric acid to remove any unsaturates, then over the catalyst at 100° C. to remove any hydrogen. The procedure in using the catalyst tube for hydrocarbon oxidation was exactly the same as that used in the determination of hydrogen. The gas mixture was passed at a rate of 30 to 50 cc. per minute through the catalyst tube heated to the desired temperature. Eight passes were made, as this is in excess of the number needed for the oxidation of hydrogen. The results are shown in Table I.

The results with methane show that it is possible to oxidize hydrogen and carbon monoxide in the catalyst tube at a temperature of 300° C. without oxidizing methane.

The oxidation products from methane and ethane were examined for unsaturated compounds, but none were found. Thus the high ratio of contraction to carbon dioxide is not

due to a dehydrogenation of the hydrocarbon. Adsorption may be one explanation for the larger contraction at the lower temperatures.

It was not found possible to oxidize propane or butane completely, even at a temperature of 400° C.

TABLE I. OXIDATION OF THE METHANE HYDROCARBONS

| METHANE | | | | | |
|--|-----|-----|-----|------|------|
| Analysis | 1 | 2 | 3 | 4 | 5 |
| Heater temp., ° C. | 300 | 325 | 350 | 375 | 400 |
| Contraction, cc. | 0.0 | 0.0 | 0.0 | 0.5 | 5.3 |
| Carbon dioxide, cc. | 0.0 | 0.0 | 0.0 | 0.3 | 4.9 |
| 9.3 per cent methane in the gas mixture | | | | | |
| ETHANE | | | | | |
| Analysis | 1 | 2 | 3 | 4 | |
| Heater temp., ° C. | 230 | 250 | 280 | 300 | |
| Contraction, cc. | 0.0 | 2.4 | 4.5 | 6.2 | |
| Carbon dioxide, cc. | 0.0 | 0.0 | 0.2 | 1.1 | |
| 3.4 per cent ethane in the gas mixture | | | | | |
| PROPANE | | | | | |
| Analysis | 1 | 2 | 3 | 4 | 5 |
| Heater temp., ° C. | 130 | 150 | 180 | 220 | 400 |
| Contraction, cc. | 0.0 | 1.2 | 2.1 | 2.7 | 11.3 |
| Carbon dioxide, cc. | 0.0 | 0.2 | 0.2 | 0.7 | 5.4 |
| 21.7 per cent propane in the gas mixture | | | | | |
| BUTANE | | | | | |
| Analysis | 1 | 2 | 3 | 4 | |
| Heater temp., ° C. | 120 | 140 | 160 | 400 | |
| Contraction, cc. | 0.0 | 1.5 | 2.8 | 12.9 | |
| Carbon dioxide, cc. | 0.0 | 0.9 | 1.1 | 7.1 | |
| 9.0 per cent butane in the gas mixture | | | | | |

OXIDATION OF CARBON MONOXIDE IN CITY GAS

Although ethane begins to oxidize at 250° C., the rate of oxidation of the small amount present in city gas might be so slow as not to affect the results when hydrogen and carbon monoxide are oxidized together over the catalyst. The residues from three samples of city gas, containing carbon monoxide, hydrogen, methane, ethane, and nitrogen, were used to determine this. One analysis was run in which the carbon monoxide was determined by absorption in acid cuprous chloride, and hydrogen by oxidation in the catalyst tube at 100°. Other analyses were run in which both carbon monoxide and hydrogen were oxidized in the catalyst tube at 250° and at 300° C. The results are shown in Table II.

TABLE II. OXIDATION OF CARBON MONOXIDE AND HYDROGEN IN THE CATALYST TUBE

| Analysis | CARBON MONOXIDE BY ABSORPTION | | CARBON MONOXIDE BY CATALYST TUBE | |
|---------------------------|-------------------------------|------|----------------------------------|--|
| | 1 | 2 | 3 | |
| Heater temp., ° C. | 100 | 250 | 300 | |
| Number of passes | 5 | 6 | 6 | |
| Hydrogen, per cent | 32.3 | 36.8 | 36.9 | |
| Carbon monoxide, per cent | 14.4 | 6.3 | 14.6 | |

These results show that the oxidation of the ethane present in city gas is sufficient to affect the results for hydrogen. The rate of oxidation of the carbon monoxide at 250° C. is so slow as to preclude using this or a lower temperature at which ethane is not oxidized.

OXIDATION OF HYDROCARBONS OVER COPPER OXIDE

The copper oxide method was extensively used with no knowledge of the oxidation of hydrocarbons other than methane, until the recent work of King and Edgcombe (2), who studied the oxidation of methane, ethane, propane, and butane over copper oxide. They found that ethane, propane, and butane were slowly oxidized at 280° C., the temperature used for the determination of hydrogen and carbon monoxide. When the hydrocarbon was circulated over the copper oxide at 280° C. for 10 minutes in the Bone and Wheeler gas analysis apparatus, the following amounts of oxidation were found to have taken place: methane, 0.0; ethane, 0.8; propane, 1.0; butane, 1.4 per cent by volume. Various gas mixtures were also oxidized over copper oxide to study the effect of the oxidation of hydrogen and carbon monoxide on the oxidation of the hydrocarbons. The results are shown in Table III.

TABLE III. OXIDATION OF PARAFFIN HYDROCARBONS (Oxidized over copper oxide at 280° C. in presence of hydrogen and/or carbon monoxide)

| COMPOSITION OF GAS MIXTURE | ANALYSIS BY COMBUSTION | | PARAFFIN HYDROCARBONS OXIDIZED | |
|--|------------------------|----------------|--------------------------------|----------------|
| | CO ₂ | H ₂ | Mixture % | Hydrocarbons % |
| CH ₄ C ₂ H ₆ C ₃ H ₈ CO H ₂ N ₂ | 17.3 | 51.1 | 0.25 | 0.8 |
| 16.8 51.6 0.6 | 0.7 | 69.2 | 0.23 | 0.8 |
| 29.7 69.8 0.5 | 14.5 | 59.3 | 0.17 | 0.7 |
| 25.8 14.0 59.8 0.4 | 1.0 | .. | 0.5 | 0.8 |
| 34.0 64.0 2.0 | .. | .. | .. | .. |

King and Edgcombe conclude that with city gas, which does not normally contain more than 5 per cent of ethane, the amount of oxidation of ethane and higher homologs does not cause an error greater than that of measurement. However, with gases containing higher hydrocarbons, such as the gases from the low-temperature carbonization or hydrogenation of coal, errors due to oxidation of hydrocarbons may appreciably affect the accuracy of the analysis. Although King and Edgcombe found no oxidation of methane at 280° C., Campbell and Gray (1) state that the temperature should not exceed 300°. This is in contrast to the catalyst tube method where no oxidation of hydrocarbon takes place under the conditions for oxidation of hydrogen.

In studying the oxidation of hydrogen and carbon monoxide, King and Edgcombe found that if the carbon monoxide/hydrogen ratio exceeded 0.22, carbon monoxide would remain after all the hydrogen had been oxidized. As no volume decrease occurs when carbon monoxide is oxidized by copper oxide, the analyst must use precautions to insure its complete oxidation. The catalytic oxidation of carbon monoxide gives a volume decrease, so that complete oxidation may easily be attained.

ADSORPTION OF GASES

The adsorption of carbon dioxide by copper oxide introduces an error into the method of oxidizing carbon monoxide over copper oxide. Scherb (6) states that this occurs at room temperature, decreases with rising temperature, and becomes negative through dissociation at a red heat. King and Edgcombe (1) found appreciable disappearance of carbon dioxide when carbon monoxide is oxidized at 280° C. In order to recover all carbon dioxide they found it necessary to evacuate the reaction tube.

The adsorption of carbon dioxide over clear and platinized silica gels was studied by Reyerson and Swearingen (5) for pressure of carbon dioxide of about 740 mm. At 138° no carbon dioxide remained on the platinized gel; 1.78 cc. per gram remained on the clear gel, but this volume became zero at 218°. The platinized gel used by these workers contained much more platinum than the commercial platinized gel, though the adsorptive capacity of the latter is considerably less than that of the clear gel. Thus hydrogen and carbon monoxide can be determined together at 300° C. with no adsorption of carbon dioxide. This was also shown by the experiments reported in the first paper of this series (3).

Nothing has been reported concerning the adsorption of hydrocarbons by copper oxide. The adsorption of methane on silica gel was investigated by Reyerson and Swearingen (5) who found 1.35 cc. per gram at 0° and 740 mm. The small amount adsorbed at this low temperature indicates that no adsorption would occur at 100°. The adsorption of butane was investigated by Patrick and Long (4). At 100° they found 1.87 cc. per gram at 145.4 mm., 3.44 cc. per gram at 294.7 mm., 6.16 cc. per gram at 566.9 mm., and 7.45 cc. per gram at 696.5 mm. No data are available concerning the adsorption of ethane and propane. From the small amounts (low partial pressures) of ethane and higher hydro-

carbons present in city gas it may be concluded that adsorption will not be enough to affect the results. With gases containing greater amounts of the higher hydrocarbons adsorption will remove an appreciable volume from the gas mixture. However, a similar decrease in volume is caused by solution in fresh liquid reagents the first time the gas is bubbled through. After the liquid has become saturated with the gases no further volume decrease is due to this cause. The same thing is true of adsorption of gases on the catalyst. Since this adsorption is nonspecific (dependent only on the partial pressure of the gas) the catalyst will adsorb and come into equilibrium with the hydrocarbon mixture, so that no adsorption will occur in the second sample. The catalyst tube may be considered as introducing no more error than the liquid reagents used.

CONCLUSIONS

1. The oxidation of methane, ethane, propane, and butane over a commercial platinized silica gel has been studied. No oxidation occurs with methane at 350°, ethane at 230°, propane at 130°, or butane at 120° C., but oxidation

does occur at temperatures 20° to 25° higher. Complete oxidation does not occur even at 400° C.

2. Hydrogen and carbon monoxide can be oxidized simultaneously at 300° C. in the presence of methane, but not when higher hydrocarbons are present, as in city gas.

3. A comparison of the copper oxide and catalyst tube methods has been made considering oxidation of higher hydrocarbons and adsorption of gases.

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Volume of Sugar-Beet Marc and Its Adsorptive Effect

S. J. OSBORN, Great Western Sugar Company, Denver, Colo.

THE volume allowance for marc in digestion methods for determining sugar in beets has recently received renewed attention on the part of a number of investigators. In a previous paper Osborn and Brown (3) described the centrifugation method for this purpose, which is free from many of the drawbacks of other methods, and reported some preliminary determinations made on three samples of cossettes, which indicated a value of 1.0 ml. for the volume of the marc and lead precipitate in the normal weight (26 grams) of cossettes under the conditions of the hot-water digestion method. As the literature has been extensively reviewed by other authors (3, 7, 8), mention will be made here only of a few recent references.

Saillard (5) determined the weight and specific gravity of the washed and dried marc from 3 samples of rasped beets, finding a value equivalent to 0.9 ml. of marc, inclusive of the lead precipitate, per 26 grams of beets. In a communication (6) to the International Commission for Uniform Methods of Sugar Analysis Saillard stated the value as 1.2 to 1.3 ml. for the French double normal weight (32.52 grams), which is equivalent to 1.0 ml. per 26 grams. In the same communication he referred to some work done at the Kief Institute, in which the marc volume was calculated from the comparative polarizations obtained by digestion and by aqueous extraction. The average volume, in this case also inclusive of the lead precipitate, was 0.70 ml. per 26 grams of beets.

This paper is a continuation of work to establish the volume allowance for marc in the determination of sugar in beets by hot-water digestion. Fifty-eight determinations on thirty samples of cossettes by the Brown centrifugation method gave an average value of 1.0 ml. per 26 grams of cossettes for the volume of the marc, inclusive of the lead precipitate. No difference was found in the marc volume with the use of 6, 7, or 8 ml. of lead subacetate per 26 grams of cossettes. Tests made to determine the adsorption of water by marc from sugar solutions indicated that this effect, if any, is small under the conditions of the hot-water digestion, but may be sufficient to justify a somewhat higher marc allowance, the absolute value of which it is difficult to determine with precision by polarimetric methods.

Spengler and Paar (7) have reported a number of tests in which the percentage of marc was calculated from the polarizations of sugar solutions made to volume with and without the presence of the normal amount of marc. In the presence of lead subacetate they found an average value of 0.83 ml. per 26 grams in the experiments made with pressed juice, and a little higher value with the use of pure sugar solutions. This value is not considered to include the lead precipitate, for which about 0.25 ml. should be added according to the author's data (2), and with this correction the volume would be 1.08 ml. Spengler and Paar also found marc volumes of about 1.5 to 2.5 ml. in the absence of lead subacetate, from

which they conclude that beet marc contains considerable colloid water which is largely eliminated by the effect of the lead reagent.

DETERMINATIONS BY CENTRIFUGATION METHOD

During the 1932-33 campaign 58 determinations were made on 30 samples of ground cossettes from northern Colorado beets by the Brown centrifugation method (3). The procedure was as follows:

A hot-water digestion was made in the usual manner, except that half proportions were employed on account of the necessity of using 100-ml. flasks in the centrifuge. The 0.5 N weight (13 grams) of ground cossettes was rinsed into a 100-ml. flask with 3 to 4 ml. of lead subacetate (55° Brix.) and water to make

a volume of about 75 ml. After thorough deaeration under vacuum to remove air, the contents were digested 30 minutes in a water bath at 80° C., the flask was then filled slightly above the mark with hot water, and the digestion was continued 10 minutes longer.

After cooling, making to volume at 20° C., and mixing, the flask was weighed and then centrifugalized. As much of the clear supernatant liquid as possible (usually about 70 ml.) was drawn off carefully by suction into a test tube serving as a receiver, care being taken to avoid the loss of particles of the pulp or precipitate. The specific gravity of the clear liquid was determined in a pycnometer. The weight of "pulp" remaining in the flask was determined, and the entire amount of pulp was then dried in the flask to determine its moisture content. In this operation the excess of water was first evaporated off on a water bath, and the flask was then heated at 80° C. at an absolute pressure of 175 mm. of mercury in a vacuum oven, about 18 hours being required to attain constant weight. During the drying a slow current of air was aspirated through a tube extending almost to the bottom of the flask, to facilitate the removal of vapor. From the weights and analytical data the volume of the marc and lead precipitate was then calculated as described in the previous paper (3).

An International Equipment Company Type C centrifuge was used with a carrier and trunnion cups suitable for two 100-ml. flasks. The radius measured to the middle of the globular part of the flask was about 6.25 inches. In tests 1 to 21 the centrifuge was operated at a speed of 1100 to 1200 revolutions per minute, in subsequent tests at 1800 revolutions. The latter speed was preferable and gave a good separation in 10 minutes. A speed of 2900 revolutions was also tried, but was abandoned because of the difficulty of finding flasks that would not collapse at this speed.

TABLE I. MARC VOLUME

(With use of 6 ml. of lead subacetate per 26 grams of cossettes)

| EXPT. | SUGAR % | MARC PER 26 GRAMS OF COSSETTES | | | Av. Ml. |
|-------|------------|--------------------------------|-----------|------------|------------|
| | | I Ml. | II Ml. | III Ml. | |
| 1 | 15.3 | 1.10 | .. | .. | 1.10 |
| 2 | 14.5 | 1.06 | .. | .. | 1.06 |
| 3 | 17.0 | 0.98 | 0.96 | .. | 0.97 |
| 4 | 16.3 | 0.84 | 1.06 | .. | 0.95 |
| 5 | 16.0 | 1.10 | .. | .. | 1.10 |
| 6 | 15.3 | 0.83 | 0.92 | .. | 0.88 |
| 7 | 16.0 | 0.85 | 0.91 | .. | 0.88 |
| 8 | 17.1 | 1.00 | 0.91 | .. | 0.96 |
| 9 | 17.6 | 1.05 | 1.06 | .. | 1.06 |
| 18 | 16.0 | 0.77 | 0.91 | .. | 0.84 |
| 20 | 14.8 | 0.87 | .. | .. | 0.87 |
| 21 | 16.9 | 0.99 | 1.00 | .. | 1.00 |
| 24 | 16.3 | 0.93 | .. | .. | 0.93 |
| 25 | 14.2 | 0.83 | 0.96 | 0.93 | 0.91 |
| 26 | 14.5 | 0.92 | 0.91 | .. | 0.92 |
| 31 | 16.3 | 0.98 | .. | .. | 0.98 |
| Av. | 15.9 | .. | .. | .. | 0.96 |

TABLE II. MARC VOLUME

(With use of 7 ml. of lead subacetate per 26 grams of cossettes)

| EXPT. | SUGAR % | MARC PER 26 GRAMS OF COSSETTES | | | Av. Ml. |
|-------|------------|--------------------------------|-----------|------------|------------|
| | | I Ml. | II Ml. | III Ml. | |
| 11 | 17.1 | 0.93 | 0.95 | 0.94 | 0.94 |
| 12 | 17.0 | 0.94 | 0.94 | 0.94 | 0.94 |
| 13 | 14.2 | 0.90 | 0.88 | 0.89 | 0.89 |
| 14 | 14.4 | 1.01 | 0.92 | 0.96 | 0.96 |
| 20 | 14.8 | 0.99 | .. | 0.99 | 0.99 |
| 28 | 16.0 | 0.93 | 0.94 | 0.94 | 0.94 |
| 29 | 16.1 | 1.06 | 1.10 | 1.08 | 1.08 |
| 30 | 15.4 | 1.03 | 0.97 | .. | 1.00 |
| 31 | 16.3 | 1.04 | .. | .. | 1.04 |
| Av. | 15.7 | .. | .. | .. | 0.98 |

The marc values found, which also include the lead precipitate, are given in detail in Tables I to IV. The agreement between duplicates was satisfactory with a very few exceptions, being less than 0.1 ml. in most cases. No determinable difference was found with lead addition varying from 6 to 8 ml. per normal weight of cossettes. The minimum amount was apparently sufficient for clarification and the use of a larger quantity did not increase the amount of lead precipitate. In Table IV, in which four different lead additions were used on the same cossette samples, no difference is definitely established within the range of experimental error.

The average of all determinations and of each series, ex-

pressed to the nearest single decimal place, gives a value of 1.0 ml. for the volume of marc and lead precipitate per 26 grams of beets. This agrees well with the author's former values (2, 3) and with the recent determinations by other methods of Saillard (5, 6), and of Spengler and Paar (7) when the latter are corrected to include the volume of the lead precipitate. The value of about 1.5 ml. of Stanek and Vondrak (9) is distinctly higher.

TABLE III. MARC VOLUME

(With use of 8 ml. of lead subacetate per 26 grams of cossettes)

| EXPT. | SUGAR % | MARC PER 26 GRAMS OF COSSETTES | | | Av. Ml. |
|-------|------------|--------------------------------|-----------|------------|------------|
| | | I Ml. | II Ml. | III Ml. | |
| 15 | 13.8 | 0.90 | 0.92 | 0.91 | 0.91 |
| 16 | 15.4 | 1.01 | 0.94 | 0.98 | 0.98 |
| 17 | 14.5 | 0.95 | 0.92 | 0.94 | 0.94 |
| 19 | 17.4 | 1.00 | 0.97 | 0.98 | 0.98 |
| 20 | 14.8 | 0.93 | .. | 0.93 | 0.93 |
| 22 | 16.7 | 0.92 | .. | 0.92 | 0.92 |
| 23 | 16.2 | 0.98 | 1.02 | 1.00 | 1.00 |
| 27 | 15.8 | 1.08 | 1.01 | 1.04 | 1.04 |
| 31 | 16.3 | 1.03 | .. | 1.03 | 1.03 |
| Av. | 15.7 | .. | .. | .. | 0.97 |

TABLE IV. MARC VOLUME

(With use of various amounts of lead subacetate)

| EXPT. | Lead subacetate, ml.: | MARC PER 26 GRAMS OF COSSETTES | | | |
|-------|-----------------------|--------------------------------|----------|----------|----------|
| | | 5 Ml. | 6 Ml. | 7 Ml. | 8 Ml. |
| 20 | | 0.78 | 0.87 | 0.99 | 0.93 |
| 31 | | 1.07 | 0.98 | 1.04 | 1.03 |

An effort to plot the marc values against percentage of sugar has indicated a tendency to slightly higher marc volume with increasing sugar percentage, but this is so slight that it cannot be regarded as definitely established by the tests here reported.

ADSORPTIVE EFFECT OF MARC

It was claimed by early investigators that beet marc selectively adsorbs water from a sugar solution, with consequent increase in volume. The water thus loosely held was variously designated as water of imbibition, water of hydration, and colloid water. A good review of this early work is given by Rümpler (4). Vondrak (10) objected to the centrifugation method of determining marc volume because it does not take account of possible sorption of water by the marc in contact with the sugar solution. Mintz, Kartashov, and Trofimovskii (1) claim that the marc and lead precipitate adsorb sugar, although this view does not seem to be held by others.

The question has been confused by the fact that the method of preparation of the marc used by different investigators has varied. Under the conditions of the hot-water digestion method, the marc is heated to 80° C. for 30 or 40 minutes in the presence of lead subacetate. The temperature is probably not of great influence on the character of the marc because the cold-water digestion method is a standard method for the determination of sugar in beets which, with properly rasped pulp, is recognized as giving accurate results. The work of Spengler and Paar (7) is illuminating, however, in showing that the presence of lead subacetate largely nullifies the water-adsorptive capacity of the marc.

In order to obtain some information on the adsorptive effect of beet marc applicable to the conditions of the hot-water digestion method, several hundred grams of the marc and lead precipitate from hot water digestions were prepared by filtering, washing free of sugar, and air-drying at about 45° C. For convenience this material will be hereafter referred to simply as "marc." The effect on the polarization of sugar solutions was then determined independently by two analysts. A summary of the results is given in Table V.

TABLE V. EFFECT OF MARC ON POLARIZATION OF SUGAR SOLUTIONS

| SERIES | DESCRIPTION OF MARC USED | TEMP. OF DIGESTION ^a ° C. | No. of tests | ANALYST A | | | No. of tests | ANALYST B | | |
|--------|--------------------------|---|--------------|--------------------|--------------------|------------|--------------|----------------|-------------|------------|
| | | | | Control series | Marc series | Difference | | Control series | Marc series | Difference |
| 1 | 1 gram, air-dried | Cold | 4 | 15.36 | 15.37 | 0.01 | 9 | 15.22 | 15.24 | 0.02 |
| 2 | 1 gram, dried at 80° | Cold | 10 | 15.38 | 15.39 | 0.01 | 9 | 15.23 | 15.23 | 0.00 |
| 3 | 1 gram, dried at 105° | Cold | 10 | 15.38 | 15.41 | 0.03 | 9 | 15.30 | 15.29 | -0.01 |
| 4 | 1 gram, dried at 80° | 80 | 10 | 15.38 | 15.39 | 0.01 | 6 | 15.29 | 15.28 | -0.01 |
| 5 | 1 gram, dried at 105° | 80 | 10 | 15.18 ^b | 15.18 ^b | 0.00 | 3 | 15.28 | 15.30 | 0.02 |
| 6 | 1 gram, air-dried | 80 | 6 | 13.04 ^b | 13.02 ^b | 0.02 | .. | .. | .. | .. |
| | | Av. | 50 | 14.80 | 14.81 | 0.01 | 36 | 15.26 | 15.26 | 0.00 |
| 7 | 5 grams, dried at 80° | Cold | .. | .. | .. | .. | 4 | 15.25 | 15.38 | 0.13 |
| 8 | 5 grams, air-dried | Cold | 10 | 15.35 | 15.47 | 0.12 | .. | .. | .. | .. |
| 9 | 5 grams, air-dried | 80 | 10 | 15.35 | 15.44 | 0.09 | .. | .. | .. | .. |

^a Period of 40 minutes in all cases.

^b Digestion juice used in these series, pure sugar solutions in all others.

Except in the two series in which digestion juice (filtrate from a hot-water digestion) was employed, the procedure was as follows:

Approximately 2 grams of high-grade sugar were weighed out, dissolved in water, and made up to 100 ml. in a volumetric flask. The marc was then added and after 40 minutes' standing in the cold, or after hot digestion, the solution was filtered and polarized. In the hot digestion tests the flask was weighed before and after digestion, and any water lost by evaporation was restored. In connection with every series an equal number of sugar solutions, to which no marc was added, was polarized to serve as controls.

As in all marc investigations by polarimetric methods, careful work and a large number of determinations are required to minimize accidental error. In order to eliminate personal bias in reading a number of solutions of approximately the same polarization, the weight of sugar taken was allowed to vary between 1.95 and 2.2 grams, and the readings were afterwards calculated to the equivalent polarization per 2 grams of sugar. Usually five determinations and the same number of controls were handled at one time, the work being repeated to form a series of 10 determinations. In each set of 5 polarizations the difference between the highest and lowest polarization was usually not essentially over 0.1° and was sometimes less. Careful temperature control was exercised in making to volume and in the polarizations, which were made in a 400-mm. tube.

TABLE VI. DETERMINATIONS OF MARC VOLUME BY ADDITION OF MARC TO SUGAR SOLUTIONS
(1 gram marc in 100 ml.)

| SERIES | NO. OF TESTS | POLARIZATION | | | CALCULATED VOLUME FOR 2 GRAMS OF MARC ML. |
|--------|--------------|----------------|-------------|------------|--|
| | | Control series | Marc series | Difference | |
| 1 | 5 | 15.31 | 15.40 | 0.09 | 1.2 |
| 2 | 5 | 15.37 | 15.48 | 0.11 | 1.4 |
| 3 | 5 | 15.34 | 15.46 | 0.12 | 1.6 |
| Av. | 15 | 15.342 | 15.448 | 0.106 | 1.37 |

The amount of sugar was chosen to give a polariscope reading about equal to that of a cossette polarization. In most of the work the marc was added in the same proportion to sugar in which it is present in a regular hot-water digestion of 0.5 *N* concentration. As the combined marc and lead precipitate have a specific gravity of about 2.0 (2), the calculated amount for 1.0 ml. of marc is accordingly 2 grams per 200 ml., or 1 gram per 100 ml. of solution, the amount used in these experiments. The average combined weight of the marc and lead precipitate from the digestion of 26 grams of cossettes was also found to be exactly 2 grams by direct weighing.

The air-dried marc showed about 2 per cent loss of moisture when heated at 80° and 3 per cent when heated at 105° C. The amount of moisture present in the marc dried at lower temperatures was therefore of negligible influence on the results. Several tests made by both analysts by extracting 1 and 5 grams of the marc with water and making up to 100 ml. showed zero polarization in all cases.

In the determinations of analyst A all solutions were made to volume and polarized at 20° C. The average polarizations of the control series in which sugar solutions were used are close to the theoretical value of 15.38 for pure sucrose. In the determinations of analyst B, various temperatures were employed to approximate the prevailing room temperature, but the same temperature was of course always employed for the parallel determinations and controls of each series.

The averages of all the tests and of each series made with 1 gram of marc show no determinable effect on the polarization. As the marc came from hot-water digestions, in which it had been heated at 80° C. for 40 minutes in the presence of lead subacetate, it was not expected that the variations in the temperature at which the prepared marc was dried, or the use of cold *vs.* hot digestion, would be of significance on the results, and this proved to be the case.

The three series made with the use of 5 grams of marc indicate consistently an adsorption of water equivalent to a polarization increase of the order of magnitude of about 0.1 sugar degree. This is equivalent to a polarization of 0.02° for each gram of marc, an amount which could hardly be definitely determined within the range of experimental error by polarizations made with the use of 1 gram of marc.

Some tests were also made in which the volume of the marc and lead precipitate was calculated from polarizations obtained in the following manner:

One gram of marc which had been dried at 105° C. and 1.95 to 2.2 grams of sugar were transferred to a 100-ml. flask, water was added, and the flask was evacuated to remove the air present in the marc, and then the regular hot-water digestion procedure was carried out, the solution finally being made up to 100 ml. at 20°. From the average polarization of a series of tests of this kind and of a control series composed of an equal number of determinations in which no marc was added, the equivalent marc volume was computed.

The averages of three series of this kind, which are given in Table VI, show consistently a higher value than that of 1.0 ml. obtained by the centrifugation method. Unfortunately the accuracy of polariscopic observation is not sufficient to establish the desired value with precision, as is illustrated by the fact that the difference of 0.4 ml. between the calculated volumes of the first and third series is due to a variation of only 0.03° in the polarization differences of the two series. It is therefore well not to attach too great importance to the absolute accuracy of these calculated marc volumes.

The difference between the use of a marc volume of 1.0 ml. or of 1.4 ml., the average of Table VI, would be equivalent to only 0.03° in the polarization of a beet containing 16 per cent sugar, so that within these limits the marc volume is established closely enough for practical purposes.

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Comparison of Extraction Formulas

CARROLL W. GRIFFIN, Vassar College, Poughkeepsie, N. Y.

THE process of extraction is frequently used for the removal of a desired compound from an impure solution of it. Thus the separation of an organic compound from an inorganic substance may usually be effected by extracting the aqueous solution with an organic solvent. A well-known general principle for the process is that, with a given quantity of extracting liquid, the use of many fractions of the liquid leads to a more nearly complete removal of the desired compound than does the use of the entire liquid in a single extraction. Formula 1 (1)

$$X_n = X_0 \left[\frac{KW}{KW + L} \right]^n \quad (1)$$

where W = cc. of solution
 X_0 = grams of substance dissolved therein
 L = cc. of extracting solvent used in each extraction
 K = distribution ratio of the substance for the two solvents
 X_n = grams of substance remaining unextracted after the n^{th} extraction

may be used to demonstrate the above principle and to compute the amount of substance which may be expected after a given number of operations.

As n is increased in the above formula X_n , the amount of substance remaining unextracted, will diminish and approach zero as a limit (X_0 , K , W , L , and n being positive). Sometimes numerical examples are used to demonstrate this, but that the conclusion is valid in general is obvious, for from Equation 1 we may say

$$\frac{X_n}{X_0} = \frac{1}{(1 + L/KW)^n}$$

and putting $L/KW = \alpha$ we know that for positive values of α $(1 + \alpha)^n = 1 + n\alpha + \dots$ positive terms

becomes infinite as $n \rightarrow +\infty$. Therefore $\frac{1}{(1 + \alpha)^n}$ and its equal $\frac{X_n}{X_0}$ must, as $n \rightarrow +\infty$, approach zero as a limit.

The above case should be clearly distinguished from that in which the quantity of extracting liquid is not unlimited, as is always true in practice. While in this case, too, subdivision of the available liquid into many portions is advantageous, the limit of the process is not zero. If, in such a case, we consider L cc. as the total volume of extracting liquid and that it is to be subdivided into n equal parts, and these successively used, the formula obviously should be written

$$X_n = X_0 \left[\frac{KW}{KW + L/n} \right]^n = f(n) \quad (2)$$

where, as before, X_0 , K , W , L , and n are positive. (In the

following differentiation, note that L is now a constant.) Proceeding on the basis that if the first derivative is negative the function is decreasing we seek to establish that

$$X_{n+1} < X_n \text{ or that } f'(n) < 0$$

$$f'(n) = X_0 \left[\frac{KW}{KW + L/n} \right]^n \left\{ \frac{L}{n(KW + L/n)} + \ln \left[\frac{KW}{KW + L/n} \right] \right\}$$

Since the first term in the above equation is positive it is sufficient to study the sign of the remainder of the expression, i. e., that in braces.

Let us make the change of variable

$$L/KWn = u \text{ so that } \lim_{n \rightarrow +\infty} u = 0$$

The first term (in braces) becomes $\frac{u}{1+u}$ and the second $-\ln(1+u)$, so that we study the sign of

$$\psi(u) = \frac{u}{1+u} - \ln(1+u) \text{ as } u \rightarrow 0 \text{ by positive values}$$

Now $\psi(0) = 0$

(In general it may not be a fact that when the derivative is negative the function is negative. Here, however, the function is zero for u zero, and since its derivative is negative for u positive, it follows that the function is negative for u positive.)

$$\psi'(u) = \frac{-u}{(1+u)^2}$$

Therefore $\psi(u) < 0$ for $u > 0$. Hence the function $\psi(u)$ has a graph below the axis of u for $u > 0$.

Thus also $f'(n) < 0$ and in particular

$$f(n+1) = X_{n+1} < f(n) = X_n$$

or

$$X_{n+1} < X_n$$

Whereas X_n in Equation 1 approaches zero as n increases towards plus infinity, such is not true of X_n of Equation 2. In the latter case X_n obviously cannot approach the limit zero since in this case the total quantity of liquid, L , is finite. We evaluate this limiting constant as follows:

Starting with Equation 2 we may write

$$\ln \frac{X_n}{X_0} = \frac{\ln \left[\frac{KW}{KW + L/n} \right]}{1/n}$$

which takes the form $0/0$ as $n \rightarrow +\infty$. Therefore, differentiating both numerator and denominator

$$\lim_{n \rightarrow +\infty} \ln \frac{X_n}{X_0} = \lim_{n \rightarrow +\infty} \left[\frac{-L}{KW + L/n} \right]$$

Thus $\lim_{n \rightarrow +\infty} \ln \frac{X_n}{X_0} = \frac{-L}{KW}$

and $\lim_{n \rightarrow +\infty} \frac{X_n}{X_0} = e^{-L/KW}$

The limiting value, $e^{-L/KW}$, may also be established thus:

$$\begin{aligned} \lim_{n \rightarrow +\infty} \left[\frac{KW}{KW + L/n} \right]^n &= \lim_{n \rightarrow +\infty} \left[1 + \frac{L}{KWn} \right]^{-n} \\ &= \lim_{n \rightarrow +\infty} \left[(1 + L/KWn)^{KWn/L} \right]^{-L/KW} = e^{-L/KW} \end{aligned}$$

However, the former method is necessary in order to show that $f(n)$ continuously—i. e., steadily or monotonically—decreases to its limiting value.

SUMMARY

Two formulas used in the process of extraction are compared as concerns variables involved, especially with reference to the limits of extraction with an infinite and with a finite quantity of extracting liquid. These limits have been evaluated.

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Determination of Small Quantities of Nitrobenzene in Oils

C. E. ANDING, JR., B. ZIEBER, AND W. M. MALISOFF, The Atlantic Refining Company, Philadelphia, Pa.

OCCASIONS arise in which it becomes necessary to determine small amounts of nitrobenzene in petroleum oils. An outstanding instance is the process (4) for the refining of lubricating oils by extraction with nitrobenzene, where both the refined oil and the extract must be freed from small amounts of residual nitrobenzene. A comparative study of various methods has been made, selecting as the most promising the reduction with standard solutions of titanous salts and back-titration with ferric alum.

It was felt that the known difficulties of nitrogen determinations by combustion in a furnace or by a Kjeldahl procedure would be accentuated in the case of heavy oils. Another major line of approach lay in the reduction of nitrobenzene to aniline. Two variants of this would be (a) reduction with an excess of reducing agent followed by the determination of the excess, or (b) reduction followed by the determination of aniline. Under procedure b one might consider diazotization, colorimetric methods, or bromometric methods. Actual tests, however, showed that side reactions take place with nitrous acid, bromine, or similar reagents on account

of the oil present, as was expected. The color of the oils precluded any hope of success by colorimetric methods. Variant a therefore was chosen. Under that head stannous chloride, titanous chloride, and titanous sulfate were chosen for consideration as reducing agents less likely to be affected by anything that may be present in the oils.

Titanous chloride was soon ruled out on account of the formation of chloramines (2). A comparison of the action of stannous chloride (5) and titanous sulfate with reflux (1) showed superiority of the latter. Using known solutions of pure nitrobenzene the authors have been able to obtain 98 per cent reduction with 20 per cent excess titanous solution, whereas even 150 per cent excess stannous chloride gives only 80 per cent reduction. The reduction with stannous chloride is much slower as well.

Figures 1, 2, and 3 represent the apparatus developed for this determination.

PROCEDURE

The procedure finally developed is as follows:

A sample of oil not exceeding 5 grams is weighed in the boiler, and 10 cc. of xylene, 25 cc. of methanol, and 25 cc. of 40 per cent sulfuric acid are

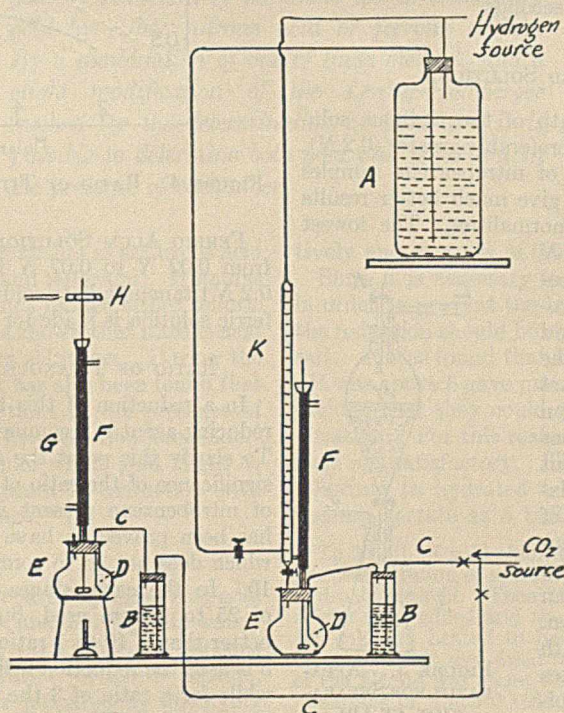


FIGURE 1. ASSEMBLED APPARATUS

- | | |
|--|-------------------------------|
| A. Titanous sulfate storage | F. Condenser |
| B. Carbon dioxide wash tower with spiral | G. Set-up in boiling position |
| C. Carbon dioxide lines | H. Turbine |
| D. Carbon dioxide inlet | K. Titanous sulfate buret |
| E. Boiling flask | |

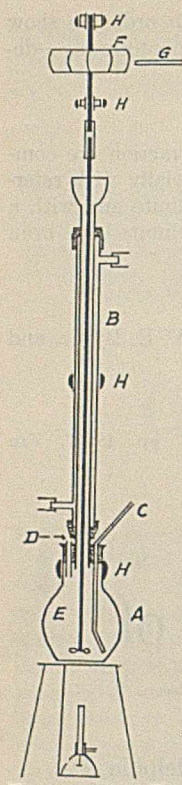


FIGURE 2. DIAGRAM OF APPARATUS

- A. Boiling flask
 B. Condenser
 C. Carbon dioxide inlet
 D. Hole for buret
 E. Propeller
 F. Turbine
 G. Air jet
 H. Clamps

added. The stopper containing the condenser, stirring rod, etc., is placed in the flask and carbon dioxide is bubbled through for 5 minutes. The flask is attached to the buret containing the reducing solution. The titanous sulfate is added in such a quantity that there will be a large excess present after the reduction. The flask is removed from the buret, the hole is plugged with the glass rod, and the stirrer is connected to the motor and the water circuit to the condenser. The mixture is gently boiled for 10 to 20 minutes with constant agitation. After heating it is cooled with cracked ice (to save time) and when cool is titrated with the ferric alum solution. When the blue of the titanous sulfate is almost completely removed, 10 cc. of 10 per cent ammonium thiocyanate are added through the top of the condenser as the indicator, and the titration is continued to the appearance of a pink end point lasting at least one minute. Carbon dioxide is bubbled through the apparatus during the entire procedure.

In most cases the separation of the oil was found not to be necessary. In the authors' experience, however, black tar-like samples were encountered which did not give consistent results with some observers unless the oil was separated after the reduction. This was referred to as the interference of the color with that of the end point. For such observers the end point is easier to define when the oil is separated. The apparatus in Figure 3 is used, and the separation is made when the end point color persists for only 15 or 20 seconds.

STRENGTH OF STANDARD SOLUTIONS

TITANOUS SULFATE. The strength of the titanous solution should be at least 0.08 *N* and preferably greater (0.2 *N*). As indicated in Table I, analyses of nitrobenzene samples and of oil containing nitrobenzene give much better results with the solutions of the higher normalities. The lowest results are obtained with a 0.05 *N* solution. The effect is more noticeable as the concentration of nitrobenzene increases. This decreased amount of reduction still held for the 0.05 *N* solution in spite of the fact that the amount of titanous solution was considerably increased, as well as the time of contact. It is apparent that the increased dilution of the mixture with water, due to the use of larger volumes of dilute titanous solution to obtain approximately the same amount of salt for contact, had an inhibitory effect on the reaction. This confirms Sampey's (5) work with stannous chloride wherein he states that the presence of water is inhibitory. With regard to the strength of titanous chloride solutions used in reductions, English (3) states that even for more accurate results a 0.25 *N* solution may be used

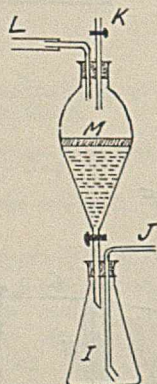


FIGURE 3. APPARATUS FOR SEPARATION OF OIL

- I. Final titration flask
 J. Carbon dioxide inlet
 K. Outlet for carbon dioxide
 L. Connection to C
 M. Separatory funnel

without increasing the time of analysis. The author's experience has confirmed this and for the best results over a wide range of nitrobenzene concentrations they found a 0.2 *N* solution to be effective.

TABLE I. NITROBENZENE IN OIL

| NITROBENZENE (Approx.) % | TITANOUS SULFATE <i>N</i> | NITROBENZENE | | DEVIATION ^a |
|--------------------------|---------------------------|--------------|------------|------------------------|
| | | Present Gram | Found Gram | |
| 0.01 | 0.20 | 0.0005 | 0.007 | ±0.0005 |
| 0.025 | 0.08 | 0.0013 | 0.0013 | ±0.0001 |
| 0.05 | 0.05 | 0.0021 | 0.0022 | ±0.0001 |
| 0.05 | 0.08 | 0.0020 | 0.0021 | ±0.0001 |
| 0.05 | 0.20 | 0.0023 | 0.0025 | ±0.0004 |
| 0.100 | 0.05 | 0.0036 | 0.0035 | ±0.0006 |
| 0.100 | 0.08 | 0.0049 | 0.0050 | ±0.0004 |
| 0.100 | 0.20 | 0.0057 | 0.0061 | ±0.0005 |
| 0.30 | 0.05 | 0.0137 | 0.0132 | -0.0005 |
| 0.30 | 0.08 | 0.0127 | 0.0125 | -0.0014 |
| 0.60 | 0.05 | 0.0240 | 0.0228 | -0.0012 |
| 0.60 | 0.08 | 0.0198 | 0.0193 | -0.0014 |
| 0.60 | 0.20 | 0.0245 | 0.0246 | ±0.0008 |
| 1.06 | 0.20 | 0.0191 | 0.0189 | ±0.0004 |
| 5.00 | 0.20 | 0.0300 | 0.0300 | ±0.0004 |
| 25.00 | 0.20 | 0.0300 | 0.0302 | ±0.0004 |
| 95.00 | 0.20 | 0.0285 | 0.0285 | ±0.0005 |

^a Av. of 3 or more analyses.

Redistilled and recrystallized nitrobenzene is recommended for standardization. Ferric alum solutions of known strength have likewise been used.

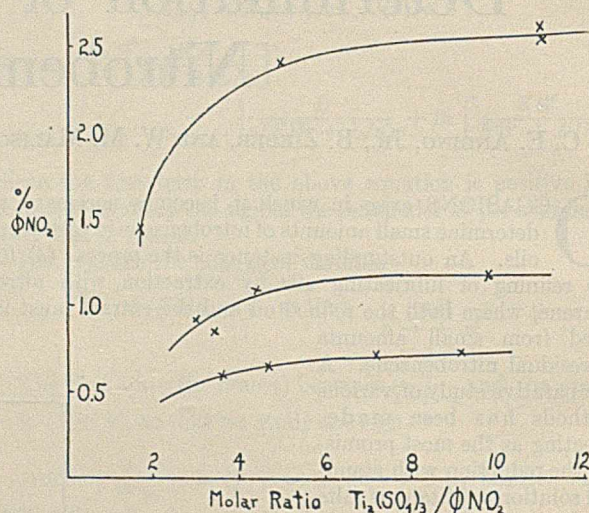


FIGURE 4. RATIO OF TITANOUS SULFATE TO NITROBENZENE

FERRIC ALUM SOLUTION. Ferric alum solutions varying from 0.02 *N* to 0.07 *N* have been used. For use with a 0.2 *N* titanous sulfate solution, the choice of a 0.05 *N* or 0.07 *N* ferric solution is made for obvious reasons.

RATIO OF TITANOUS SULFATE TO NITROBENZENE

In a reduction of this type wherein a large excess of the reducing agent is recommended, the question of limits arises. To clarify this point the authors have made a study of the significance of the ratio of moles of titanous sulfate to moles of nitrobenzene present in an analysis. This molar ratio has been proved to have a direct bearing on the reaction, which does not go to completion when the ratio is less than 10. In the early stages of the investigation molar ratios of 25 to 1 were used, but the results are not appreciably better than a 10 to 1 ratio. On the other hand, if a ratio of 5 is used the reduction will be less than 95 per cent complete, while for a ratio of 3 the reduction will be less than 80 per cent complete (Figure 4).

SIZE OF SAMPLE

For the sake of convenience and accuracy the size of the sample of oil is limited to not more than 5 grams. Table II

is presented as a guide, tabulating the convenient sized sample, with the volume of titanous sulfate solution required to give a molar ratio of at least 10 to 1.

TABLE II. CHOICE OF SAMPLE SIZE

| NITROBENZENE PRESENT % | SAMPLE USED Grams | 0.2 N $Ti_2(SO_4)_3$ Cc. |
|---------------------------|----------------------|-----------------------------|
| 0.1 | 4 | 8 |
| 1 | 1.8 | 15 |
| 5 | 0.6 | 24 |
| 25 | 0.12 | 25 |
| 100 | 0.03 | 25 |

If the odor of nitrobenzene is pronounced, the sample will contain as a minimum approximately 0.1 per cent of nitrobenzene.

DISCUSSION

The oil has no appreciable effect on the titanous sulfate. A number of samples of oil were selected as typical of those actually encountered in practice. The average variation was equivalent to 0.005 per cent (0.0002 gram from 5-gram sample) of nitrobenzene = 0.005 per cent, the variation tending largely in the negative direction. An average accuracy of 98 ± 10 per cent may be expected for concentrations of nitrobenzene from 0.025 to 0.65 per cent, when an 0.08 N solution is used and for higher concentrations of

nitrobenzene greater accuracy is attained with a 0.2 N solution. The variations may seem large when considered from the standpoint of the per cent accuracy. On the other hand, if one considers the actual weights of nitrobenzene present and found as indicated in Table I, the values are indeed small. In the light of the authors' experience there is no doubt that a much higher degree of accuracy could be obtained by using a larger sample and a much stronger titanous solution, but the procedure would be entirely precluded from use as a control method, because of the expense of the titanous sulfate.

For further details on technic one is referred to English's work (3). Other provisions made involved the treating of the rubber stoppers with boiling sodium hydroxide and dilute sulfuric acid and the use of a sodium carbonate solution containing pyrogallic acid for scrubbing the carbon dioxide.

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RECEIVED September 25, 1933.

Separation of Gold from Tellurium

VICTOR LENHER, G. B. L. SMITH, AND D. C. KNOWLES, JR.

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

THE common gravimetric methods used for the determination of gold and tellurium consist of reducing the gold or tellurium ion to the elementary state and weighing as the element. The separation of gold from tellurium may be accomplished if we have a system of sufficiently low potential to reduce gold but high enough not to reduce tellurium. Such reducing agents as sulfurous acid and hydrazine will reduce both gold and tellurium. Hutchins (2) found that nitrous acid would not reduce either telluric or tellurous acids, but Fisher (1) has shown that nitrous acid quantitatively reduces gold from its solutions. During the course of the present investigation it has also been found that gold may be reduced from its solutions in the presence of tellurium by ferrous sulfate. This investigation was undertaken to establish the conditions under which gold might be separated quantitatively from tellurium by reduction with nitrous acid and with ferrous sulfate.

MATERIALS

Solutions of gold chloride were prepared by dissolving gold in aqua regia, evaporating to dryness, and diluting with water. These solutions were standardized, taking aliquot portions and reducing with an aqueous solution of sulfur dioxide. Solutions of tellurium chloride were prepared by dissolving pure tellurium dioxide in concentrated hydrochloric acid and diluting with water. The hydrogen chloride content of the solutions of tellurium was adjusted to approximately 12 per cent (3.3 M). The tellurium solutions were analyzed according to the method of Lenher and Homberger (3).

Tellurium can be separated satisfactorily from gold by reduction of the auric ion to elementary gold by either nitrous acid or ferrous sulfate. By a combination of one of these methods and a slight modification of the Lenher-Homberger method for the determination of tellurium it is possible to determine both gold and tellurium in the presence of each other.

PRECIPITATION OF GOLD WITH NITROUS ACID

When a solution of auric chloride is reduced with sodium nitrite the quantity of gold precipitated is a function of the hydrochloric acid content of the solution and probably more specifically of the pH of the solution. If the pH is less than 1 the gold is not precipitated quantitatively and at a pH of 0.67 the error is about 3 per cent.

Since it is necessary to have hydrochloric acid in solution in order to prevent the hydrolysis of tellurium tetrachloride, the reduction should be carried out in the presence of a buffer salt. It was found that buffers which gave a solution whose pH was above 5 gave precipitates of gold which were so finely divided that they could not be quantitatively separated by filtration. For this reason borax and sodium acid phthalate were not satisfactory. There also is danger of hydrolysis of tellurium to hydrated tellurium dioxide at the higher pH. Sodium acetate as a buffer gave fairly satisfactory results.

To 20 ml. of gold chloride solution were added 50 ml. of a 10 per cent solution of sodium acetate and 5 ml. of constant-boiling hydrochloric acid. Then 25 ml. of a 4 per cent solution of sodium nitrite were added and the total volume was brought to about 150 ml. and heated to boiling. The gold was filtered onto a Gooch crucible and dried to constant weight at 110°. The pH of the filtrate was about 1.6. The error in a series of six determinations, in which 0.1568 gram of gold was taken varied from one to three parts per thousand low, probably because of the loss of a small amount of precipitated metal through the asbestos mat of the Gooch.

Better results were obtained by using Rochelle salts, sodium potassium tartrate, as a buffer.

To 100 ml. of a solution of gold chloride were added 100 ml. of a 20 per cent solution of Rochelle salts, and 25 ml. of a 4 per cent solution of sodium nitrite, and the volume was adjusted to 250 to 275 ml. The solution was allowed to stand until the gold had settled and was then brought to boiling and the gold was filtered onto a tared Gooch crucible, washed, dried at 110°, and weighed. The filtrate from such a precipitation had the following pH when the respective amount of constant-boiling hydrochloric acid had been added: 1 ml., 2.4; 5 ml., 1.8; 10 ml., 1.5; 25 ml. 0.65. When the pH is less than 1 the gold is not quantitatively precipitated, but at a pH of 1 to 3 the error is from one to two parts per thousand low.

These results clearly indicate that Rochelle salts are a satisfactory buffer for use in the precipitation of gold with nitrous acid in the presence of a limited amount of hydrochloric acid.

PRECIPITATION OF GOLD WITH FERROUS SULFATE

Although the precipitation of gold with ferrous sulfate is frequently referred to, textbooks and the literature do not give details which are essential for the success of an analysis by this method. The following procedure was found to give satisfactory results:

A solution of gold chloride containing a known amount of gold was taken and to this were added 10 to 12 ml. of concentrated hydrochloric acid and sufficient distilled water to bring the total volume to about 175 ml. The solution was heated to boiling and 1.5 grams of ferrous sulfate were added. The solution was now boiled for 10 to 15 minutes or allowed to stand on the sand bath at 80° C. for 24 hours and the precipitated gold was filtered onto a tared Gooch crucible, washed, dried at 110°, and weighed.

In a series of six experiments, taking 0.0948 gram of gold in each, the error in gold found varied from -0.0002 to +0.0003 gram.

SEPARATION OF GOLD FROM TELLURIUM WITH NITROUS ACID

An attempt was made to precipitate gold in the presence of tellurium, using sodium acetate as a buffer.

To 20 ml. of a solution of gold chloride and 10 ml. of tellurium tetrachloride were added 50 ml. of a 10 per cent solution of sodium acetate. This caused a hydrolysis of tellurium which resulted in the precipitation of hydrated tellurium dioxide, and it was necessary to add 2 to 3 ml. of concentrated hydrochloric acid in order to dissolve the tellurium. The solution was heated almost to boiling, and 25 ml. of a 4 per cent solution of sodium nitrite were added. The precipitated gold was filtered on a tared Gooch crucible, washed, dried at 110°, and weighed.

The pH of the filtrate from these precipitations was usually somewhat less than 1, and it was necessary to have a sufficient excess of hydrochloric acid to give this pH and thus prevent the hydrolysis of tellurium tetrachloride. The method is not applicable to the separation of gold from tellurium, since the errors were of the order of three to five parts per thousand low in a series of five determinations.

TABLE I. SEPARATION OF GOLD FROM TELLURIUM BY PRECIPITATION WITH NITROUS ACID IN THE PRESENCE OF ROCHELLE SALTS AS BUFFER

| GOLD TAKEN Gram | TELLURIUM TAKEN Gram | GOLD FOUND Gram | ERROR Gram |
|--------------------|-------------------------|--------------------|---------------|
| 0.1450 | 0.1283 | 0.1449 | -0.0001 |
| 0.1450 | 0.1283 | 0.1451 | +0.0001 |
| 0.1450 | 0.1283 | 0.1449 | -0.0001 |
| 0.1941 | 0.5000 | 0.1940 | -0.0001 |
| 0.1941 | 1.0000 | 0.1937 | -0.0004 |
| 0.1941 | 1.0000 | 0.1941 | 0.0000 |

The use of Rochelle salts as a buffer proved more satisfactory, however. The method developed is as follows:

One hundred milliliters of a 20 per cent solution of Rochelle salts are added to the solution containing gold and tellurium, and then followed by 25 ml. of a solution of sodium nitrite.

The volume of the solution should not exceed 275 to 300 ml. and the hydrochloric acid content must be below 1 to 1.5 per cent. After the gold has separated, the solution is brought to boiling and the gold is filtered and weighed. The results of a typical series of determinations are given in Table I.

SEPARATION OF GOLD FROM TELLURIUM WITH FERROUS SULFATE

The following procedure was developed for the separation of gold from tellurium with ferrous sulfate:

To a solution containing gold and tellurium, sufficient hydrochloric acid was added to bring its concentration to 1.5 to 2 per cent hydrogen chloride. The total volume of the solution was adjusted to about 175 ml., heated to boiling, 1 to 1.5 grams of ferrous sulfate were added, and the solution was boiled for 10 to 15 minutes. The gold was filtered onto tared Gooch crucibles, dried and weighed or filtered onto filter paper, ignited, and weighed. The results are tabulated in Table II.

TABLE II. SEPARATION OF GOLD FROM TELLURIUM BY PRECIPITATION WITH FERROUS SULFATE

| GOLD TAKEN Gram | TELLURIUM TAKEN Gram | GOLD FOUND Gram | ERROR Gram |
|--------------------|-------------------------|--------------------|---------------|
| 0.1084 | 0.1281 | 0.1083 | -0.0001 |
| 0.1084 | 0.1281 | 0.1082 | -0.0002 |
| 0.1084 | 0.1281 | 0.1084 | 0.0000 |
| 0.1084 | 0.1140 | 0.1082 | -0.0002 |
| 0.1496 | 0.1140 | 0.1495 | -0.0001 |
| 0.1496 | 0.1140 | 0.1497 | +0.0001 |

DETERMINATION OF GOLD AND TELLURIUM IN PRESENCE OF EACH OTHER

The simultaneous precipitation of gold and tellurium may be effected by following the method of Lenher and Homberger (3) with the modification of using double the volumes of reducing agents suggested by them.

Twenty millimeters of a solution containing gold and tellurium were taken and the concentration of hydrochloric acid was adjusted to 12 per cent (3.3 M). The solution was heated to boiling, and double the volumes of reagents (solutions of 15 per cent hydrazine hydrochloride and saturated solution of sulfur dioxide) were added as called for by Lenher and Homberger (3). The gold and tellurium were filtered, dried, and weighed. The precipitate was dissolved in aqua regia and evaporated several times with hydrochloric acid; the gold was separated as described above, using Rochelle salts and nitrous acid, and the weight of tellurium was obtained by difference. The results are tabulated in Table III.

TABLE III. DETERMINATION OF GOLD AND TELLURIUM

| GOLD TAKEN Gram | TELLURIUM TAKEN Gram | GOLD AND TELLURIUM FOUND Gram | | ERROR Gram | TELLURIUM FOUND Gram | ERROR Gram |
|--------------------|-------------------------|----------------------------------|--------|---------------|-------------------------|---------------|
| 0.0760 | 0.0593 | 0.1351 | 0.0759 | -0.0001 | 0.0592 | -0.0001 |
| 0.0760 | 0.0593 | 0.1352 | 0.0758 | -0.0002 | 0.0594 | +0.0001 |
| 0.0760 | 0.0593 | 0.1351 | 0.0759 | -0.0001 | 0.0592 | -0.0001 |
| 0.0760 | 0.0593 | 0.1351 | 0.0759 | -0.0001 | 0.0592 | -0.0001 |
| 0.0760 | 0.0593 | 0.1352 | 0.0761 | +0.0001 | 0.0591 | -0.0002 |
| 0.0760 | 0.0593 | 0.1352 | 0.0760 | 0.0000 | 0.0592 | -0.0001 |

SUMMARY

Gold may be precipitated quantitatively in the presence of limited amounts of hydrochloric acid (about 1.5 per cent of hydrogen chloride, 0.45 M) with nitrous acid, using sodium potassium tartrate (Rochelle salts) as a buffer. The pH of the solution should be greater than 1, but in the higher pH region gold is precipitated in such a finely divided form that it cannot be filtered.

Gold may be precipitated quantitatively in the presence of hydrogen chloride (1 to 2 per cent) with ferrous sulfate.

Gold may be separated from tellurium by reduction with nitrous acid in a solution buffered with Rochelle salts and having a hydrogen chloride content of 1.5 per cent or less (0.45 M), or by reduction with ferrous sulfate in a solution having a hydrogen chloride content of 1 to 2 per cent (0.3 to 0.6 M).

Gold and tellurium may be determined in the presence of each other by first precipitating the gold and tellurium together and then separating the gold by reduction with nitrous acid.

ACKNOWLEDGMENT

The subject for this investigation was suggested in 1917 by the late Victor Lenher. The experimental work was started in Professor Lenher's laboratory at the University of Wisconsin in 1917, was continued with Professor Lenher's permission by D. C. Knowles in 1926-27, and part of this paper is based upon the thesis presented by Mr. Knowles in partial fulfillment of requirements for the degree of Bachelor

of Science at the Polytechnic Institute of Brooklyn, in June, 1927. The authors are pleased to acknowledge their indebtedness to Douglas Fronmuller, who has made several series of determinations. Publication in the present form is with the permission of Samuel Lenher.

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RECEIVED April 7, 1933. Contribution from the Laboratory of Inorganic Chemistry of the University of Wisconsin and Contribution 20 from the Department of Chemistry of the Polytechnic Institute of Brooklyn.

Determination of Borate Ion in Ores of Borax

H. L. PAYNE, 552 Figueroa St., Los Angeles, Calif.

IN 1932, Scott (3) published the results of research on the determination of boric acid in the ores and mill products so abundantly produced from the mines in Kern County, Calif., which at the present time are the only source of borax ore in the United States. He concluded with a formal method based upon the results of these researches. The death of Doctor Scott prevented further research along the original lines, but as one of the participants in these investigations, the present author has continued the work and now offers a completed analytical method differing from Scott's directions in some essential particulars.

In general it is the method originally proposed by Thomson in 1893 and presented in revised form in 1908 by Wherry (5). In so far as it relates to titrating boric acid it has been officially accepted by the Association of Official Agricultural Chemists and by the American Ceramic Society, and for routine work has been approved by Hillebrand and Lundell, of the U. S. Bureau of Standards. With more or less incomplete detail it has been copied by standard books on chemical analysis, and is merely elaborated here. It is offered as a procedure applicable to all borate ores, to partially refined products, and to completely crystallized borax. By a more drastic decomposition treatment it may be applied to the analysis of the borosilicate minerals and glasses (4).

Borate minerals—borate ores and mill products—need not be ground finer than 30 mesh. Finer grinding of many of the calcined products results in a loss of values by dusting. All milled material is hygroscopic, cannot be dried to any permanently constant weight, and samples should be kept in tightly stoppered containers. Close checks by different laboratories are practically impossible.

The method is based upon the precipitation of the bases of the iron-alumina group from an acid borate solution and titration of the liberated boric acid with sodium hydroxide. Wherry (5) used calcium carbonate in neutral or alkaline solution as the precipitant, reprecipitating two or three times and washing carefully. Sullivan and Taylor (4) did the same, but separation under these alkaline conditions was never quite satisfactory and Wherry says that the method is not to be recommended. Wherry also tried an acid separation but did not follow it up. Scott's researches included acid precipitation using phenolphthalein indicator as control, demonstrating in this way that no aluminate passed into the filtrate to interfere with the boric titration, but he did not include this plan in his final method. The author follows Scott's sodium hydroxide-acid separation but with a modified procedure which involves only one precipitation and avoids all error by occlusion.

PROCEDURE

To 2.5 grams of the suitably prepared sample in a 100-ml. tall plain covered beaker add 5 or 10 ml. of water to wet the mineral and then 10 ml., pipet measure, of 6 N hydrochloric acid (1 to 1). Digest for at least 30 minutes on top of the water bath, with occasional agitation but without removing the cover. All borate ores are thus readily decomposed without loss of boron or the use of an excessive amount of acid (2). Remove from the bath, wash down the cover and beaker with plenty of cold water, and filter into a 250-ml. graduated flask, washing the insoluble matter with hot water only. (Ignite and weigh the insoluble mineral matter if that item is desired.) It may be tested qualitatively for boron; but the author has never found any, and such insoluble borate would not be considered available boric acid.

To the filtrate, which will amount to about 200 ml., add carefully, preferably from a buret, a strong sodium hydroxide solution until the liquid is nearly neutralized, using methyl red as indicator. This condition is necessary for the removal of carbon dioxide by boiling. A precipitate of iron and aluminum hydroxides will appear just before neutrality is reached and if the liquid is still acid to methyl red a proper condition obtains for the removal of carbonate by boiling. Adapt an air-condenser tube to the flask, such as the inner tube of a 24-inch (60-cm.) Liebig condenser, and heat to gentle boiling for at least 15 minutes, allowing the steam to rise not higher than half way up the condenser. All carbon dioxide will be removed without loss of boron and the iron-alumina hydroxide precipitate will occlude no boric acid. Under these conditions methyl red in the presence of free boric acid shows an acid reaction at pH of 6, and both iron and aluminum hydroxides are precipitated. Borates do not form until a pH of about 11; hence the precipitates carry no boron.

Remove the flask from the heat, wash down the condenser with cold water, and cool the flask as rapidly as possible without undue exposure to the air. As soon as cool, add at once sufficient calcium hydroxide solution to fill the flask to the mark. This will make the solution alkaline without introducing any soluble carbonate and any residual iron or alumina will precipitate. Mix thoroughly and filter on a dry paper and into a dry beaker. Do not wash, but as quickly as possible pipet off two aliquots for the final titration.

TITRATION

Titrations should be conducted as quickly as possible after the aliquots are taken, using a standard hydroxide practically

free from carbonate. To each aliquot in a flask add methyl red and a drop of hydrochloric acid just sufficient to turn it red. Then from the titration buret add hydroxide until the methyl red just turns a full lemon-yellow. Do not stop at the so-called neutral tint. The solution will then be alkaline to hydrochloric acid, at a pH of about 10, and will be practically neutral to phenolphthalein and boric acid at about the same pH. The differences are well within the color indicator errors of titration. (Allen and Zies (1) working on borosilicate glass found a difference of 0.3 mg. B_2O_3 between the end point with *p*-nitrophenol and the beginning with phenolphthalein. The author has not been able to confirm this error using methyl red, although theoretically some alkali should be consumed.)

To this neutralized solution add an excess of mannite and titrate to a permanent red with phenolphthalein, a color which is not bleached by further addition of mannite. If sufficient mannite is added at the beginning, the solution will be nearly colorless until the final red. In absence of excess mannite a pink color will maintain during much of

the titration and a true end point will be reached only when a single drop of the alkali gives a red that does not fade. Using 0.2 *N* alkali, titrations will habitually check to 0.1 cc. equivalent to 0.7 mg. of B_2O_3 or less than 0.1 per cent on 1 gram titrated.

Check analyses in this laboratory recently ran as follows: 38.80, 33.07, 29.67, 29.55, 44.61, 44.10, 41.01, 42.19, 42.07, 38.81, 33.22, 29.77, 29.62, 44.69, 44.25, 41.15, 42.19, 42.14, routine work. Two drops of 0.2 *N* alkali will always indicate an end point and the quantitative reaction between sodium hydroxide and boric acid in the presence of a polyhydric alcohol has never been brought into dispute.

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Determination of Iron

Adaptation of the Mercaptoacetic Acid Colorimetric Method to Milk and Blood

GLADYS LEAVELL AND N. R. ELLIS

Nutrition Laboratory, Animal Husbandry Division, Bureau of Animal Industry,
U. S. Department of Agriculture, Washington, D. C.

THE mercaptoacetic acid colorimetric method of Lyons (9) for the determination of small quantities of iron offers advantages over the thiocyanate colorimetric method of Elvehjem (3) as adapted from Kennedy (6), in that smaller samples may be used, thus making wet-ashing practicable and avoiding the losses and contaminations encountered in the dry-ashing procedure, and in that the color produced is more stable.

The authors' experiments confirmed observations of Andreasch (1), Ginsburg and Bondzynski (4), and Claesson (2) on the formation of an intensely blue or purple compound by the reaction of mercaptoacetic acid (thioglycolic acid) with ferric chloride in ammoniacal solution, the tendency of the color to fade, and the ready restoration of the color when the solution is shaken with air.

Preliminary experiments with a standard iron solution (0.005 mg. of iron per cc.) showed that for quantities of iron between 0.0025 and 0.025 mg., the colored solutions could be conveniently compared in tubes of uniform diameter, such as Nessler tubes, and that it was not necessary to dilute to volume, as the addition of distilled water to the solutions in the tubes caused no noticeable change in color intensities of the columns when observed through their entire depths. For quantities of iron from 0.015 to 0.1 mg., dilution to volume and the use of the colorimeter are recommended. Larger quantities of iron necessitate dilution and the production of color in convenient aliquots.

Comparison of color-development by the use of 2 drops of undiluted mercaptoacetic acid, 1 cc. of a 1 to 15 aqueous solution of the acid, 1 cc. of a 1 to 15 alcoholic solution, and 1 cc. of a 1 to 15 aqueous solution rendered alkaline with ammonium hydroxide (the reagent described in the next section) favored the last as it combines the advantages of nearly

eliminating the unpleasant odor of the mercaptoacetic acid with good control of the amount of reagent added.

Experiments on wet-ashing of milk with sulfuric acid, sulfuric and nitric acids (8, 10), and sulfuric and perchloric acids (5, 7) were performed. The ashing with sulfuric acid alone was too slow, and with nitric acid resulted in muddiness and other irregularities in the colors developed, whereas the colors with perchloric acid were like those developed when standard iron solutions were used.

METHOD

REAGENTS. Iron-free concentrated sulfuric acid, 60 per cent perchloric acid, concentrated ammonium hydroxide, standard iron solutions, and the mercaptoacetic acid reagent are necessary.

The standard iron solutions are prepared by dissolving 1 gram of pure iron wire in dilute sulfuric acid and oxidizing with concentrated nitric acid. The oxides of nitrogen and excess nitric acid are expelled by boiling. The solution is diluted to 1 liter, with further dilution as needed. In all dilutions it is advisable to add extra sulfuric acid to prevent hydrolysis of the dissolved iron salts to insoluble basic compounds.

The mercaptoacetic acid reagent is prepared by the addition of 4 cc. of mercaptoacetic acid to a solution of 8 cc. of concentrated ammonium hydroxide in 50 cc. of water.

DETERMINATION OF IRON IN MILK. Samples¹ of 5 cc. of milk (or 0.5 gram dried milk) are digested with 3 cc. of con-

¹ With samples of this size, there was rarely any turbidity from precipitation of alkaline earth phosphates in the final ammoniacal solution. Filtration of occasional turbid samples through small iron-free filter paper gave clear solutions with colors matching those of the duplicates which were not turbid. Filtration of very turbid solutions from larger samples gave entirely satisfactory results.

concentrated sulfuric acid and 2 cc. of perchloric acid in micro-Kjeldahl flasks on an electric heater until colorless and the excess of perchloric acid has been driven off. The perchloric acid is added in 0.5-cc. portions, one after the sulfuric acid, the second to the cooled flask after the charring is quite decided, and the remaining portions if, and as, needed. The digestion requires from 30 minutes to 2 hours. When the digestion is complete, the contents of the flask are transferred to a 150-cc. beaker, the flask is rinsed two or three times with small volumes of distilled water, the liquid cooled, and the acidity adjusted by the addition of concentrated ammonium hydroxide from a dropping bottle until just alkaline to litmus (a very small piece of litmus paper may be kept in the solution), then made just acid with concentrated sulfuric acid and an excess of from 5 to 10 drops of acid added. One cubic centimeter of the mercaptoacetic acid reagent is added and the solution made strongly alkaline by the addition of 1 to 2 cc. of concentrated ammonium hydroxide. The colored solution thus formed is compared with a series of standards in narrow tubes (12 × 20 mm.); therefore the volume should be kept below 20 cc. If the volume is too large for these tubes, other tubes of uniform diameter and appropriate capacity, such as Nessler tubes, may be used.

TABLE I. RESULTS OF IRON DETERMINATIONS BY MERCAPTOACETIC ACID METHOD

| SAMPLE | VOLUME | IRON ADDED | | IRON ^a |
|---------------------------------|-------------------|------------|----------------------|-------------------|
| | | IRON ADDED | IRON FOUND | |
| | Cc. | Mg. | Mg. | Mg./100 cc. |
| Goat's milk A | 5 | ... | 0.0035, 0.0035 | 0.07 |
| Goat's milk A | 5 | 0.005 | 0.008+ | 0.06+ |
| Goat's milk B | 5 | ... | 0.004-, 0.004- | 0.08- |
| Goat's milk B | 5 | 0.003 | 0.0065+ | 0.07+ |
| Goat's milk C | 5 | ... | 0.003, 0.0035 | 0.065 |
| Goat's milk C | 5 | 0.003 | 0.006 | 0.06 |
| Goat's milk D | 5 | ... | 0.0035, 0.003, 0.003 | 0.0063 |
| Jersey cow's milk | 5 | ... | 0.0035, 0.004 | 0.075 |
| Jersey cow's milk | 5 | 0.003 | 0.0065 | 0.07 |
| Milk from local market | 5 | ... | 0.0035 | 0.06 |
| | | | 0.003, 0.003- | |
| Dried milk | Gram | ... | 0.0058 | 1.03 |
| Dried milk | 0.563 | ... | 0.0058 | 1.10 |
| Dried milk | 0.507 | ... | 0.0058 | 0.995 |
| Dried milk | 0.584 | ... | 0.0059 | 1.02 |
| Dried milk | 0.577 | ... | 0.0059 | 1.02 |
| Hog's blood ^b | Cc. | ... | 0.0100, 0.0104 | 51.0 |
| Hog's blood ^b | 0.02 ^c | ... | 0.0050, 0.0053 | 52.3 |
| Hog's blood ^b | 0.01 ^c | ... | 0.0053, 0.0052 | ... |
| | | | 0.0054, 0.0052 | ... |
| | | | 0.0052 | ... |
| Hog's blood ^b | 0.02 ^d | ... | 0.0100, 0.0103 | ... |
| | | | 0.0104, 0.0104 | 52.8 |
| Guinea pig's blood ^b | 0.2 ^e | ... | 0.080, 0.086, 0.080 | 41.0 |
| Guinea pig's blood ^b | 0.1 ^f | ... | 0.045, 0.045, 0.045 | 45.0 |
| Guinea pig's blood ^b | 0.1 ^f | 0.02 | 0.06, 0.063 | 41.5 |

^a The added iron was subtracted before the calculation of mg. per 100 and the results are for 100 cc. excepting in the case of dried milk where they are for 100 grams.

^b See also section "Comparison with Other Methods."

^c Measured with blood pipet.

^d 2 cc. of 1 to 100 dilution.

^e 2 cc. of 1 to 10 dilution.

^f 1 cc. of 1 to 10 dilution.

The standards for color comparison are prepared by the substitution of 1 to 5 cc. of appropriate standard iron solutions for the sample to be analyzed. The entire procedure in the preparation of the colored standards must be identical with that for the sample.

The standards occasionally fade within an hour; however, the color is satisfactorily restored if the solution is then shaken with air. Standards are often satisfactorily revived even after they have been allowed to stand for 24 hours or more. It is, however, advisable to replace some of the members of the series of standards every day to verify the values of the older solutions.

Table I gives results obtained by the application of this procedure to goat's milk, cow's milk, and milk powder.

DETERMINATION OF IRON IN BLOOD. Samples of 0.01 or 0.02 cc. of blood are taken with the blood pipet, transferred with dilution to the micro-Kjeldahl flasks, and digested with 1 cc. each of concentrated sulfuric and perchloric acids. The remainder of the procedure is the same as described above.

Table I includes data for determinations on hog's blood by this procedure, and by using 1- and 2-cc. portions of a 1 to 100 dilution, and also data from some earlier experiments with guinea pig's blood in which amounts equivalent to 0.1 and 0.2 cc. were taken from a 1 to 10 dilution. In the latter case, the final volume of the colored solutions was 25 cc. and the colors were compared in the colorimeter.

COMPARISON WITH OTHER METHODS. Kennedy's thiocyanate method applied to the sample of guinea pig's blood, ranging from 0.1 to 0.4 cc., with and without added iron, gave results which when calculated for 1-cc. samples are 0.42, 0.39, 0.40, 0.395, 0.435, and 0.414 mg., respectively. The average is 0.412 mg., compared with an average of 0.423 mg. for nine determinations by the mercaptoacetic acid method, which are given in the table.

Hog's blood was used for a macrodetermination of iron by the digestion of 25-cc. samples with 60 cc. of concentrated sulfuric acid, dilution, reduction of the ferric iron to ferrous by pure zinc, and titration with standard permanganate solution. The iron found was 13.375 and 13.350 mg., respectively. Calculated for 100-cc. samples, the average is 53.75 mg., compared with 52.0 mg. for the mercaptoacetic acid method (Table I).

OTHER APPLICATIONS. This method was applied to eggs and to feces. Because of the larger quantities of iron the procedure for milk was modified as follows: two-gram samples were used, the product of digestion was diluted to 50 cc., and 10-cc. aliquots were used for color development without the adjustment of the acidity prior to the addition of the mercaptoacetic acid reagent. Either tubes or the colorimeter may be used.

SUMMARY

The mercaptoacetic acid method for the determination of small amounts of iron has been adapted to the analysis of milk and blood.

Wet-ashing with sulfuric acid and perchloric acid has been found satisfactory and avoids the contaminations and losses encountered in the dry-ashing procedures.

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JAPAN TO MANUFACTURE SILICON CARBIDE. Large-scale production of silicon carbide is proposed by Japanese interests, according to the Department of Commerce. Last year Japan's imports of "mineral substance for grinding or polishing" amounted to 3120 metric tons, valued at 939,000 yen, of which the United States supplied approximately 50 per cent. Annual consumption of silicon carbide in Japan is approximately 1000 metric tons. Two Japanese companies have started production on a commercial basis, and it is expected that their combined output will materially reduce imports of artificial abrasives.

Direct Determination of Chromium and of Vanadium in Steel

o-Phenanthroline Ferrous Complex as Indicator

HOBART H. WILLARD AND PHILENA YOUNG

Department of Chemistry, University of Michigan, Ann Arbor, Mich.

THE most exact methods at the present time for chromium involve the direct titration of the chromic acid, obtained from a persulfate or similar oxidation, with standard ferrous sulfate. The end point may be determined either potentiometrically or with an oxidation-reduction indicator. If vanadium is present in the steel, as is very often the case, vanadic acid is formed in the oxidation process, and this substance is titrated along with the chromic acid. It is necessary, then, to determine vanadium before the percentage of chromium can be estimated.

The desirability of the direct determination of chromium and of vanadium in steels has led to the suggestion of a number of methods, among which the following may be mentioned:

1. The excess of ferrous sulfate, remaining after the reduction of the chromic and vanadic acids, and the vanadyl salt may be titrated with standard permanganate (5). The accurate determination of this end point is difficult, especially if there is a large quantity of chromic salt in the solution, and a blank correction of rather indefinite value must always be applied. This titration has been made potentiometrically (6), but such a method cannot be recommended because of the very unsatisfactory character of the end point. If excess of ferrous sulfate is next added to reduce the slight excess of permanganate and the vanadic acid, and the excess removed by ammonium persulfate (1), a back-titration of the vanadyl salt with standard permanganate affords a method of obtaining vanadium on the same sample. The same difficulty with the end point, however, is encountered in this titration also.

2. Chromic acid may be titrated in the presence of vanadic acid with standard arsenite solution, the end point being determined potentiometrically (13). A very small amount of manganese must be present as catalyst, but the larger amounts usually present in steels lead to low results for chromium. All but a trace of manganese must be removed, therefore, before the titration, and it is desirable to remove most of the iron. After the chromium has been determined, the vanadic acid may be titrated potentiometrically in the same solution. Such a method for these elements is, obviously, not rapid.

3. After chromic and vanadic acids have been reduced with excess ferrous sulfate, the latter may be titrated potentiometrically at room temperature with standard ceric sulfate. The temperature of the solution is then raised to 70° to 75° C. and the vanadyl ion titrated potentiometrically with the same oxidizing agent (11).

4. Chromic acid may be reduced selectively in the presence of vanadic acid by a measured excess of standard arsenite (2).

*After oxidizing chromium and vanadium in a steel by the perchloric acid method and adding a measured excess of ferrous sulfate to reduce the chromic and vanadic acids, the excess may be titrated at room temperature with standard permanganate, using *o*-phenanthroline ferrous complex as an oxidation-reduction indicator. The reaction between permanganate and vanadyl ions in this solution of high acidity is sufficiently slow so that an excellent end point is obtained. If the hydrogen-ion concentration of this solution is reduced and the temperature raised somewhat, the vanadyl ion may then be titrated with standard permanganate because the indicator has such a high oxidation potential that it is not affected by the vanadic acid formed in this reaction. This gives a rapid indicator method of determining both chromium and vanadium in a single sample.*

The same double titration may be used after oxidation of the chromium and vanadium in a steel by the permanganate-azide or persulfate-hydrochloric acid method. Neither of these methods is as rapid as the perchloric acid method.

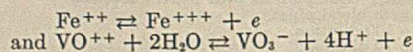
The excess of arsenite as well as any trace of vanadium which may have been reduced is titrated with standard permanganate, and a direct determination of chromium thereby obtained. The end point which is determined visually is described as satisfactory; a blank correction is required. A drop of arsenite is then added to the solution to reduce the slight excess of permanganate and the vanadic acid is titrated with standard ferrous sulfate, using diphenylbenzidine as an oxidation-reduction indicator. The results listed by the authors for chromium and vanadium in standard steels indicate that this method for chromium is fairly accurate.

5. Lang and Kurtz (4) have described a number of procedures for chromium and vanadium. Their results on steels, however, are not compared with those obtained by standard methods.

It is evident that direct indicator methods for chromium and for vanadium which are rapid and exact are needed, and the object of the present investigation has been to develop such methods.

THEORETICAL CONSIDERATIONS

From the reactions:



one would conclude that the oxidation potential of the ferric-ferrous system should not be appreciably influenced by a change in hydrogen-ion concentration of the solution, whereas that of the vanadate-vanadyl system should be considerably altered under similar conditions. Figure 1 illustrates this point for the latter system.

With an indicator of such high oxidation potential that it is not oxidized by vanadic acid, it should be possible in a mixture of ferrous, vanadyl, and chromic salts to obtain under proper experimental conditions two end points when titrating with a strong oxidizing agent. If the titration is commenced at room temperature in a solution of high hydrogen-ion concentration, the reaction between ferrous ion and the oxidizing agent should be rapid, while that between vanadyl ion and the oxidizing agent should be sufficiently slow, due to the lower reducing power of the vanadyl ion in such a solution, so that a good end point could be obtained when all ferrous ion is oxidized. This has been shown to be true when ceric sulfate is the oxidizing agent used in a solution 5 *M* in sulfuric

acid (7). In the following pages it will be shown that when permanganate is used, the same effect is obtained in a solution only 1 *M* in sulfuric acid. As the velocity of the reaction between vanadyl and permanganate ions is largely a function of the hydrogen-ion concentration of the solution and of its temperature, it should be possible, after reducing the acidity and raising the temperature of the solution, to titrate the vanadyl ion with permanganate, the indicator already present serving for this second end point.

o-Phenanthroline ferrous complex, an indicator of unusually high oxidation potential which has recently been described (8), appears to meet the necessary requirements, as it is not oxidized by vanadic acid in a moderately acid solution and is sufficiently stable for use at a temperature as high as 50° C. The indicator is red in color in reduced form and a very pale blue in oxidized form.

The experimental work which follows substantiates these theoretical considerations and shows their applicability to direct indicator methods for both chromium and vanadium in steel.

EXPERIMENTAL METHODS FOR STEELS WITHOUT TUNGSTEN

REAGENTS AND SOLUTIONS. The 0.05 *N* potassium permanganate was standardized by potentiometric titration against sodium oxalate from the U. S. Bureau of Standards.

The ferrous sulfate solution, prepared either from ferrous sulfate or from ferrous ammonium sulfate, contained 20 cc. of sulfuric acid (specific gravity, 1.5) per liter and was standardized each day against the 0.05 *N* potassium permanganate. If the perchloric acid method for chromium is used, the standardization of the ferrous sulfate should be carried out in a dilute perchloric acid solution with *o*-phenanthroline ferrous complex as indicator; with the permanganate-azide or persulfate method for chromium, the same titration should be made in a dilute sulfuric acid medium. A ferrous sulfate solution standardized by the former method was found to be 0.09949 *N*, and by the latter method 0.09919 *N*. This discrepancy, which is probably due to the fact that the indicator dissolves only slowly in the perchloric acid solution, is insignificant except with small samples of steels of high chromium content, and in any event disappears if the proper acid medium is used in standardizing the ferrous sulfate.

Since, in the reaction between *o*-phenanthroline and ferrous ion, three molecules of the former combine with one of the latter, a 0.025 *M* solution of the indicator may be prepared by dissolving the correct amount of *o*-phenanthroline (C₁₂H₈N₂·H₂O) in a 0.025 *M* aqueous solution of ferrous sulfate. Ordinarily two drops of this 0.025 *M* indicator solution are sufficient to afford a very sharp color change in steel analyses.

PERCHLORIC ACID METHOD. This method for chromium in steels without tungsten has been developed by Willard and Gibson (9). Their procedure, using perchloric acid both as solvent and oxidizing agent, was followed. After the oxidation was complete, the solution was cooled quickly,¹ diluted somewhat, boiled to remove chlorine, and then diluted further and cooled in running water. Experiments showed that after a measured excess of ferrous sulfate had been added to reduce the chromic and vanadic acids, the ferrous sulfate alone could be titrated at room temperature with standard permanganate, with *o*-phenanthroline ferrous complex as indicator, and a rapid and very sharp end point obtained, because at this acidity and temperature the reaction between vanadyl and permanganate ions is quite slow. If the hydrogen-ion concentration of the solution is then reduced by adding sodium acetate, and the temperature raised to 50° C., the red color of the reduced indicator returns and the vanadyl ion is easily titrated with further permanganate solution. A temperature of 50° C. seemed most satisfactory, for at higher temperatures too much of the indicator was destroyed, while at much lower temperatures the reaction was not sufficiently rapid. The end point in this second titration was

¹ G. F. Smith in a private communication to the authors has pointed out the desirability of cooling the solution quickly to prevent any reduction of chromium, which may be caused by the per-acid properties of the perchloric acid in a hot, concentrated solution.

considered as reached when the solution was a clear bluish green in color and when there was no return of any pink color after an interval of a minute. From the total volume of permanganate solution used, the percentage of chromium may be calculated directly, and from the difference between the first and second volumes of the permanganate, the percentage of vanadium may be determined. Obviously this procedure, which affords a determination of both chromium and vanadium in one sample, is very rapid—not more than a half-hour is required to weigh and prepare samples for the final

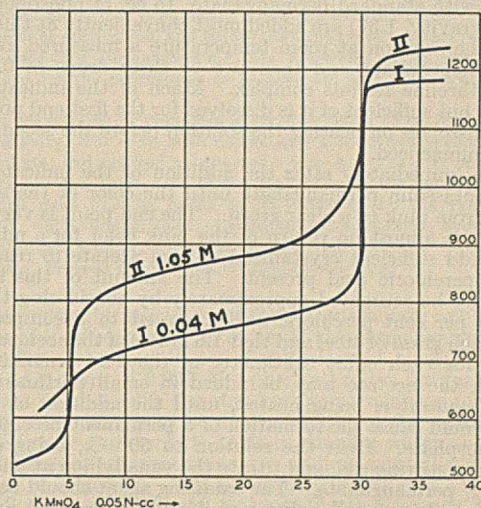


FIGURE 1. TITRATION OF MIXTURE OF FERROUS SULFATE AND VANADYL SULFATE WITH POTASSIUM PERMANGANATE

Solution I, 0.04 *M* in sulfuric acid; solution II, 1.05 *M* in sulfuric acid; temperature, 25° C.

titration. This method has the further advantage of giving an excellent end point at room temperature in the first step in the titration, while with the permanganate-azide or persulfate method either considerable acid must be added or the solution cooled to 5° to 6° C. before the titration of the excess ferrous sulfate. If the amount of vanadium is so small that large samples must be taken, the color of the chromic salt will be so intense as to render the end point indistinct. Results obtained on a number of steels by the perchloric acid method are given in Table I.

TABLE I. DIRECT DETERMINATION OF CHROMIUM AND OF VANADIUM IN STEELS WITHOUT TUNGSTEN. PERCHLORIC ACID METHOD

| STEEL | | SAMPLES | | | |
|-----------------------|-----|---------|-------|-------|-------|
| | | I | II | III | IV |
| | | % | % | % | % |
| B. S. 30 (c) | {Cr | 0.973 | 0.971 | 0.972 | 0.973 |
| (0.977% Cr; 0.235% V) | {V | 0.234 | 0.239 | 0.237 | 0.237 |
| B. S. 30 (a) | {Cr | 1.022 | 1.024 | 1.024 | 1.025 |
| (1.02% Cr; 0.20% V) | {V | 0.208 | 0.201 | 0.201 | 0.203 |
| Cr-V Steel* | {Cr | 0.917 | 0.925 | 0.919 | 0.920 |
| (0.918% Cr; 0.134% V) | {V | 0.140 | 0.142 | 0.142 | 0.137 |
| B. S. 72 | Cr† | 0.917 | 0.918 | 0.918 | 0.916 |
| (0.911% Cr; 0.012% V) | | | | | |
| B. S. 73 | Cr | 13.89 | 13.85 | 13.84 | 13.94 |
| (13.93% Cr; 0.034% V) | | | | | |

* Chromium plus vanadium determined after persulfate oxidation by titration with ferrous sulfate, using diphenylbenzidine as indicator (10). Vanadium determined by permanganate-azide method (12).

† The vanadium is equivalent to 0.004 per cent of chromium and this value should be subtracted from each of those listed to obtain the correct percentage of chromium.

Two-gram samples of the first four and 0.25-gram samples of the last steel were used. The titration was made only to the first end point in analyzing the last two steels.

RECOMMENDED PROCEDURE, PERCHLORIC ACID METHOD. Weigh a sample of suitable size, varying from 2 grams with low chromium to 0.25 gram with stainless steels, into a 500-cc. lipped beaker of tall form or into a 500-cc. Soxhlet flask. If the latter is used, the watch glass should be placed on very thin glass hooks

or on a bent platinum wire about 1 mm. in diameter to prevent the formation of a liquid seal when the contents of the flask are heated. Add 20 to 25 cc. of 70 per cent perchloric acid (depending on the size of the sample) and heat very slowly to prevent the reaction from becoming violent. After the steel has dissolved (usually only 3 to 5 minutes will be required) boil the solution for 15 to 20 minutes. The longer period is better for high-chromium steels. Cool the flask and contents a moment in the air and then in a stream of running water. Add 25 cc. of water, rinse off the watch cover into the beaker, and boil the solution for 3 minutes to remove all chlorine. Dilute the liquid to 250 to 300 cc. and cool in running water. If the steel contains more than a trace of vanadium so that two end points are to be determined in the titration with standard permanganate, 15 cc. of phosphoric acid (specific gravity, 1.37) are added most conveniently at this point. Add to the solution at room temperature a measured excess of 0.1 *N* ferrous sulfate, and then two or three drops of 0.025 *M* *o*-phenanthroline ferrous complex. Much of the indicator precipitates, but sufficient of it is dissolved for the first end point and all of it dissolves on heating the solution before the second titration is commenced.

Titrate immediately after the addition of the indicator with 0.05 *N* potassium permanganate until the color of the solution changes from pink to a clear green. The end point is very sharp and there is almost no return of the pink color for a minute or more. Add sufficient crystallized sodium acetate to react with the free perchloric acid present. The amount of this salt required may be estimated approximately by considering that 5.4 cc. of 70 per cent perchloric acid are used to decompose and oxidize each gram of steel and that 1.6 grams of the acetate will be required for each cubic centimeter of the acid remaining. If preferred, the acetate may be added in small portions to the solution while it is being heated, until the addition of further acetate would cause the formation of a permanent precipitate of ferric phosphate. Heat the solution to 50° C., using a thermometer as stirring rod, and titrate the vanadyl ion at once with the 0.05 *N* permanganate. The oxidizing agent should be added slowly, as only a small volume of it will be required and also because the reaction between vanadyl and permanganate ions is not instantaneous. The color change at the end point is the same as in the first titration and the end point is considered as reached when there is no return of a pale pink shade during an interval of a minute. It is sometimes advisable to add a drop more of indicator before titrating the vanadium.

To determine the normality of the ferrous sulfate solution, add sufficient of it to require 35 to 50 cc. of the permanganate to 250 cc. of water containing 10 to 15 cc. of 70 per cent perchloric acid. Add 2 drops of 0.025 *M* *o*-phenanthroline ferrous complex and titrate at once with the standard permanganate solution.

PERMANGANATE-AZIDE AND PERSULFATE METHODS. In a previous paper (12) the authors have pointed to the possibility of using sodium azide to destroy all permanganate and thus of avoiding a filtration in the permanganate method (6) for chromium plus vanadium in steels without tungsten. Since the procedure for the permanganate method in this modified form is shorter than that for the persulfate method, it seemed important to ascertain the conditions under which the former might be used for the direct determination of chromium or of both chromium and vanadium on the same sample.

Samples of steel were dissolved in a mixture of sulfuric and phosphoric acids, and the ferrous salts and carbonaceous matter oxidized in the usual way with nitric acid. After dilution, the vanadyl and chromic salts were oxidized in hot solution with potassium permanganate, and the excess of the latter removed by careful addition of sodium azide to the boiling hot solution. All hydrazoic acid was removed by boiling, and the solution was then cooled in running water. A measured excess of ferrous sulfate was added at room temperature and an attempt was made to titrate the ferrous and vanadyl salts with a standard permanganate solution, using *o*-phenanthroline ferrous complex as indicator. After the ferrous sulfate was oxidized, the reaction, as was to be expected, became very slow. If the hydrogen-ion concentration of the solution was then reduced by the addition of sodium acetate and the temperature raised to 50° C., the vanadyl ion was easily titrated and a satisfactory end point obtained. The hydrogen-ion concentration of the solution

may be reduced, if preferred, before any ferrous sulfate is added. The results for chromium on a number of steels which were analyzed in this way are recorded in the first column of Table II.

Since the oxidation by persulfate in the presence of silver ion is a standard procedure for chromium, analyses were made using this method. After the excess of persulfate had been removed by boiling, 1 to 3 hydrochloric acid was added to destroy the permanganate formed during the oxidation process, and the solution was then boiled to remove all chlorine. From this point the procedure was the same as that just given for the permanganate-azide method. Results are shown in the second column of Table II.

Experiments in which sodium azide was substituted for the hydrochloric acid after a persulfate oxidation (12) always led to high results for chromium. In such a procedure the silver ion is not precipitated, and may possibly cause interference later either by acting catalytically or as an oxidizing agent in the solution of low acidity. A study of the action of silver ion in synthetic mixtures similar to steels did not confirm either of these suppositions and the cause for high results here is still unexplained.

TABLE II. DIRECT DETERMINATION OF CHROMIUM IN STEELS WITHOUT TUNGSTEN. PERMANGANATE-AZIDE AND PERSULFATE-HYDROCHLORIC ACID METHODS

| STEEL | METHOD FOR CHROMIUM | | | | | | |
|---|-------------------------------------|----------------------------|--|--|--|--|--|
| | KMnO ₄ -NaN ₃ | | | (NH ₄) ₂ S ₂ O ₈ -HCl | | | |
| B. S. 30 (c) (0.977% Cr; 0.235% V) | 0.970, 0.992, 0.980, 0.966 | 0.996, 0.981, 0.985, 0.981 | | | | | |
| B. S. 30 (a) (1.02% Cr; 0.20% V) | 1.04, 1.02, 1.02, 1.02 | 1.03, 1.05, 1.03, 1.03 | | | | | |
| B. S. 72 (0.911% Cr; 0.012% V) | 0.908, 0.915, 0.912, 0.905 | 0.916, 0.920, 0.921, 0.931 | | | | | |
| B. S. 73 (13.93% Cr; 0.034% V) | 13.95, 13.94, 13.93, 13.89 | 13.71, 13.79, 13.84, 13.87 | | | | | |
| B. S. 101 (17.54% Cr; 0.044% V; 8.44% Ni) | 17.56, 17.60, 17.54, 17.51 | 17.42, 17.66, 17.58, 17.52 | | | | | |
| B. S. 64 (67.9% Cr; 0.11% V) | 67.83, 67.83 | | | | | | |

* After the steel had dissolved, vanadium equivalent to 2.5 per cent was added and the usual permanganate-azide procedure followed.

Two-gram samples of the first three steels, 0.25-gram samples of the fourth and fifth, and an aliquot portion of a 0.5-gram sample of the last were used.

Because of the low percentage of vanadium in Nos. 72, 73, 101, and 64 (as compared with the chromium content), it is unnecessary to reduce the hydrogen-ion concentration of the solution or to raise the temperature before the end point is reached. In fact, the ferrous sulfate must be titrated at room temperature and the volume of permanganate for this titration may be considered the final volume.

TABLE III. EFFECT OF VARYING ACIDITY ON DETERMINATION OF CHROMIUM

| Sp. Gr. | H ₂ SO ₄ Sp. Gr. | Fe | V | NaAc-3H ₂ O Gram | FeSO ₄ 0.05 N | KMnO ₄ 0.05 N | CHROMIUM PRESENT Gram | CHROMIUM FOUND Gram |
|---------|--|------|-------|-----------------------------|--------------------------|--------------------------|-----------------------|---------------------|
| | | | | | | | | |
| 6 | 0 | 0 | 0 | 0 | 20 | 15.54 | 0.02252 | 0.02244 |
| 6 | 0 | 0 | 0 | 15 | 20 | 15.82 | 0.02252 | 0.02221 |
| 6 | 10 | 0 | 0 | 0 | 50 | 16.09 | 0.07505 | 0.70507 |
| 6 | 10 | 0 | 0 | 15 | 50 | 16.36 | 0.07505 | 0.07482 |
| 6 | 10 | 1 | 0 | 0 | 20 | 15.56 | 0.02252 | 0.02242 |
| 6 | 10 | 1 | 0 | 15 | 20 | 15.87 | 0.02252 | 0.02215 |
| 6 | 10 | 1 | 0.005 | 15 | 20 | 15.84 | 0.02252 | 0.02218 |
| 6 | 10 | 0.25 | 0.005 | 15 | 20 | 15.82 | 0.02252 | 0.02221 |

In the analysis of steel 64, results which were 0.4 to 0.5 per cent low were invariably obtained if the excess of ferrous sulfate was titrated in a solution of low acidity. This error, which corresponds to 0.2 mg. of chromium for the size of sample used, would therefore be negligible for low-chromium steels.

To investigate this error a standard dichromate solution was treated with sulfuric acid, and in some cases with sodium acetate, phosphoric acid, ferric alum, chromic sulfate, and

vanadyl sulfate solutions before a measured excess of ferrous sulfate was added. The volume of the solution in every case after the addition of the ferrous sulfate was 300 cc. Two drops of 0.025 *M* *o*-phenanthroline ferrous complex were added and the titration with permanganate was carried out, the solution being heated to 50° C. after the ferrous sulfate had been oxidized if there was any vanadium present. The results of a number of experiments are given in Table III.

These experiments indicate that the error caused by titrating the ferrous and vanadyl salts with permanganate in a solution of low acidity is an absolute error and so small as to be negligible except in cases such as B. S. steel 64, where the chromium content is very high.

Only the permanganate-azide method was used in investigating the possibility of determining both chromium and vanadium on the same sample of steel, as this method is more rapid than the persulfate method. Steel samples were prepared as just described and the final solution containing chromic and vanadic acids was cooled in running water. If a measured excess of ferrous sulfate was added to such a solution, followed by two drops of the indicator, and the ferrous sulfate alone was titrated with permanganate, it was impossible to obtain an end point because the hydrogen-ion concentration of the solution was not high enough to make the rate of oxidation of the vanadyl ion by the oxidized indicator sufficiently low. Numerous experiments, however, indicated that a sharp end point could be obtained in the titration of the ferrous sulfate in either of two ways: by cooling the solution so that its temperature at the end of the titration was not above 6° to 8° C., or by titrating at room temperature after the addition of considerable sulfuric acid. The first method is preferable, as the hydrogen-ion concentration of the solution must in any case be reduced before the titration of the vanadyl salt. The necessary concentration of acid for a titration at room temperature is indicated in the procedure given later. In the analyses listed in Table IV, the temperature of the solution at the first end point was 6° to 8° C. The hydrogen-ion concentration was then reduced by adding sodium acetate and the temperature of the solution raised to 50° C. before the titration of the vanadyl salt was made.

TABLE IV. DIRECT DETERMINATION OF CHROMIUM AND OF VANADIUM IN STEELS WITHOUT TUNGSTEN. PERMANGANATE-AZIDE METHOD

| STEEL | | SAMPLES | | | |
|---------------------------------------|----|---------|-------|-------|-------|
| | | I | II | III | IV |
| B. S. 30 (c) (0.977% Cr; 0.235% V) | Cr | 0.972 | 0.977 | 0.977 | 0.973 |
| | V | 0.232 | 0.226 | 0.230 | 0.236 |
| B. S. 30 (a) (1.02% Cr; 0.20% V) | Cr | 1.019 | 1.028 | 1.030 | 1.015 |
| | V | 0.203 | 0.206 | 0.194 | 0.206 |

RECOMMENDED PROCEDURE, PERMANGANATE-AZIDE METHOD. Place a 2-gram sample in a 600-cc. beaker, add 15 cc. of water and 15 cc. of phosphoric acid (specific gravity, 1.37), and run in a measured volume of sulfuric acid (specific gravity, 1.83) from a buret. Allow 1.5 cc. of the latter for each gram of steel and 3 cc. excess. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 cc. of water and heat until the salts have dissolved. Add nitric acid (specific gravity, 1.42) in small portions to the hot liquid until the violent oxidation of ferrous sulfate is over (2 to 3 cc. of acid are sufficient). Avoid any appreciable excess. Boil the solution to destroy oxides of nitrogen and dilute to 300 cc. A few small pieces of broken porcelain in the solution will prevent bumping later. Heat to boiling, add a 2 per cent permanganate solution until a deep purple color remains, and boil the solution for 2 minutes. Add 0.1 *M* sodium azide (do this in a hood) to the boiling hot solution until a few drops excess are present. It is very important that the solution be boiling hot during the addition of the azide, especially if manganese dioxide is present. The azide will destroy the permanganate color first. Then add further azide, drop by drop, while stirring constantly until the solution clears. Boil for 5 minutes to remove all hydrazoic acid and cool the solution in running water. From this point either of two

procedures may be used if both chromium and vanadium are to be determined on the same sample:

A. After adding 10 cc. of sulfuric acid (specific gravity, 1.5), cool the solution in ice to 5° C. or lower. Add a measured excess of 0.1 *N* ferrous sulfate and two drops of 0.025 *M* *o*-phenanthroline ferrous complex. Titrate the ferrous sulfate at once with 0.05 *N* permanganate solution. The change in color from pink to a clear green at the end point is very sharp. In a short time, however, the pink shade begins to return. To reduce the hydrogen-ion concentration of the solution, add slowly while stirring 10 cc. of concentrated ammonium hydroxide and then crystallized sodium acetate until more would cause a permanent precipitate of ferric phosphate. Twenty grams will be found the correct amount if the quantity of sulfuric acid specified above has been used. Heat the solution to 50° C., using a thermometer as stirring rod, and titrate the vanadyl salt at this temperature with the standard permanganate. (See procedure under the perchloric acid method for the precautions to be observed and the character of the end point.)

B. To the solution at room temperature to which 35 cc. of sulfuric acid (specific gravity, 1.5) have been added, add a measured excess of 0.1 *N* ferrous sulfate, and proceed as directed under A. The first end point is sharp here but less permanent as the pink color of the indicator appears again much more quickly, owing to its reduction by the vanadyl salt. Add slowly, while stirring, 25 cc. of concentrated ammonium hydroxide and then crystallized sodium acetate as in A. Approximately 30 grams will be required. Proceed from this point as directed under A.

To determine the normality of the ferrous sulfate solution, add sufficient of it to require 35 to 50 cc. of the permanganate to 250 cc. of water containing 10 cc. of sulfuric acid (specific gravity, 1.5). Add 2 drops of 0.025 *M* *o*-phenanthroline ferrous complex and titrate at once with the standard permanganate solution.

If only chromium is to be determined, cool the solution containing chromic and vanadic acids in running water and reduce the hydrogen-ion concentration by adding crystallized sodium acetate as in A above. Add a measured excess of 0.1 *N* ferrous sulfate, 2 drops of 0.025 *M* *o*-phenanthroline ferrous complex, and titrate at room temperature with 0.05 *N* permanganate. If it is impossible to obtain an accurate end point, the presence of vanadium is indicated. In such a case heat the solution, after the ferrous iron has been titrated, to 50° C. and complete the titration as directed in A. If a sharp and permanent end point is obtained at room temperature, heat the solution as usual to 50° C. to determine whether there is any return of the pink color. If there is, complete the titration of the vanadyl salt at 50° C. with the permanganate. If no pink color appears in the solution on heating, the end point obtained at room temperature is considered the final end point. In such a case, the acidity of duplicate samples of the same steel should not be decreased before the titration with the standard permanganate.

APPLICATION OF METHODS TO STEELS CONTAINING TUNGSTEN

Attempts to develop an indicator method for the direct determination of chromium and of vanadium in chrome-vanadium-tungsten steels were not successful. If the tungsten was kept in solution as a complex fluoride and the persulfate-hydrochloric acid method was used to obtain chromic and vanadic acids (12), it was found that, after the addition of a measured excess of ferrous sulfate, the determination of the excess of this reducing agent by titration with standard permanganate was not satisfactory, as the color change at the end point was not sharp. Quantitative results can be obtained in this titration if the solution is cooled to 5° to 8° C., or if the acidity is high, but the direct titration of the chromic and vanadic acids in such a solution with standard ferrous sulfate, using oxidized diphenylamine sulfonic acid as indicator, is much to be preferred, as in this case a very sharp end point is obtained. As was to be expected, it was impossible in continuing the titration with permanganate to obtain an end point in the titration of the vanadyl salt, because of the formation of a complex manganic fluoride.

When phosphoric acid was used instead of hydrofluoric acid to keep the tungsten in solution, a dark brown color developed upon the addition of excess ferrous sulfate. This color, which was caused possibly by a complex phospho-vanado-tungstic acid, disappeared only slowly when permanganate was added to the solution. An end point when

all ferrous and vanadyl ions were oxidized could not be detected.

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Iodine Value of Rubber and Gutta-Percha Hydrocarbons

As Determined by Iodine Chloride

A. R. KEMP AND G. S. MUELLER, Bell Telephone Laboratories, 463 West St., New York, N. Y.

HALOGEN absorption methods employing solutions of bromine, iodine bromide, or iodine chloride are widely used for determining the unsaturation of organic compounds. In the use of these methods the choice of halogen reagent, the amount employed, and the time and temperature for the reaction are all important factors which must be given careful consideration in order that the best results may be obtained. Certain structural differences in unsaturated organic compounds may have a decided influence on the reactivity of these substances toward halogens. For example, the presence of negative groups on one or both of the unsaturated carbon atoms protects against halogen addition; thus maleic or fumaric acids do not add iodine chloride (7). Styrene adds iodine chloride quantitatively, but in the case of cinnamic acid only a slight reaction takes place (4). No addition of iodine chloride occurs with dichloroethylene and very little with vinyl bromide (3). The authors have found that polyvinyl chloride (Du-Prene) adds iodine chloride to only 30 per cent of theory. A triple-bonded compound, such as diphenylacetylene (4), shows only partial addition of iodine chloride, as would be expected from the negative effect of the first additive halogen. The unsaturated terpenes vary widely in their reactivity with halogens, extensive substitution occurring along with addition (5), particularly in the case of pinene. Aside from these complications, however, numerous investigators have shown that one or more of the halogens add quantitatively to a wide range of unsaturated hydrocarbons, acids, glycerides, alcohols, esters, etc. Of the many methods proposed the well-known Wijs procedure involving the use of 0.2 *N* iodine chloride in

The reactivity of various halogens towards rubber and gutta-percha hydrocarbons has been studied quantitatively. The behavior of both hydrocarbons toward halogens is very similar. The order of reactivity of the halogens is chlorine, bromine, iodine chloride, iodine bromide, and iodine. The results show that gutta-percha possesses a greater initial reactivity towards iodine than does rubber.

Data and detailed procedure are presented which offer further refinements to the iodine chloride method for the determination of the unsaturation of rubber and gutta-percha hydrocarbons.

Methods for the preparation of pure rubber and gutta-percha hydrocarbons are included and the corresponding iodine values found by the use of modified iodine chloride procedure are shown to be in close agreement with the theoretical.

It is recommended, in the case of gutta-percha hydrocarbon, that a greater excess of iodine chloride be used and that the reaction be carried on at room temperature for a longer period of time than that required for rubber.

glacial acetic acid has been widely used and accepted.

In a previous investigation (5), various halogen absorption methods for determining the unsaturation of rubber and gutta-percha were studied and it was found that the Wijs reagent (iodine chloride in glacial acetic acid) was the most satisfactory for this purpose. It was shown that under suitable conditions iodine chloride adds quantitatively to the double bonds in rubber hydrocarbon in close agreement with theory—i. e., one molecule of iodine chloride adds to each C_2H_3 grouping. This is equivalent to a theoretical iodine value of 372.8 and values found by the iodine chloride method for pure rubber hydrocarbon agree to within less than 0.5 per cent of this figure.

The method previously described (5) involves swelling 0.10-gram samples of rubber, etc., in 75 cc. of carbon bisulfide, adding 25 cc. of 0.2 *N* iodine chloride in glacial acetic acid, allowing the solution to stand 2 hours at 0° C., and titrating the excess iodine chloride with 0.1 *N* sodium thiosulfate immediately after addition of potassium iodide solution, using starch as the indicator. Excellent results were also obtained by allowing the reaction to proceed at room temperature for one hour, although substitution occurred slowly at this temperature. Since conducting the reaction under ice-cooling is a troublesome feature, one of the purposes of the present investigation was to determine the best conditions for operating at room temperature without sacrifice in the accuracy of the method. Another related objective was to determine if any differences exist between rubber and gutta-percha hydrocarbons with respect to their reactivity towards iodine chloride and other halogens. This phase of the study is of

particular interest with respect to the chemistry of these complicated hydrocarbons.

Since its publication, the original method (5) has been employed by numerous investigators to determine the purity as well as to follow the changes in unsaturation of rubber and gutta-percha when these substances were subjected to various treatments. Staudinger and Bondy (12) have followed the reduction in iodine value and thereby the cyclization of rubber and gutta-percha when subjected to elevated temperatures in various solvents. Fisher and McCollm (1) treated rubber with sulfuric and sulfonic acids and determined the reduction in unsaturation using the iodine chloride method. The effect of high tension alternating currents in producing cyclization has been correspondingly studied by Fromandi (2). Kemp, Bishop, and Lasselle (6) similarly followed the change in unsaturation resulting from oxidation of rubber and gutta-percha hydrocarbons.

MATERIALS

The rubber hydrocarbon employed for this work was prepared by repeatedly extracting 10 grams of pale crepe at room temperature with 100 cc. of a mixture of three parts acetone and one part c. p. petroleum ether (boiling point, 35° to 52° C.) in order to insure thorough removal of the resin. The acetone was removed by washing quickly with petroleum ether and the rubber was then covered with 1000 cc. of the same solvent. As a precaution against oxidation, an atmosphere of carbon dioxide was maintained over the surface of the solution. After 10 days' storage at room temperature in a dark cabinet the petroleum ether solution of rubber was decanted from the gel and about 90 per cent of the solvent distilled off. The remainder of the solvent was removed with a stream of carbon dioxide at room temperature and finally by heating in a vacuum (0.1 mm. residual pressure) at 50° C. until a constant weight was attained. The product was colorless, crystal clear, tough, and elastic. Analyses indicated the absence of ash and nitrogen.

TABLE I. REACTIVITY OF VARIOUS HALOGENS WITH RUBBER AND GUTTA-PERCHA HYDROCARBONS^a

| HYDROCARBON | HALOGEN USED | REACTION PERIOD Hrs. | REACTION | IODINE VALUE | UNSATURATION % |
|-----------------------------|-----------------|-------------------------|---------------------|--------------|-------------------|
| | | | TEMPERATURE ° C. | | |
| Rubber | Cl ₂ | 3 | 0 | 570 | 153 |
| Rubber | Br ₂ | 0.5 | 0 | 399 | 104 |
| Rubber | Br ₂ | 3 | 0 | 421 | 113 |
| Rubber | I ₂ | 3 | 0 | 1.3 | 0.35 |
| Rubber | ICl | 2 | 0 | 371.0 | 99.5 |
| Gutta (Pahang) ^b | ICl | 2 | 0 | 366.4 | 98.3 |
| Rubber | IBr | 0.5 | 0 | 286 | 76.7 |
| Rubber | IBr | 16 | 0 | 326 | 87.4 |
| Gutta (Pahang) | IBr | 0.5 | 0 | 292 | 78.3 |
| Gutta (Pahang) | IBr | 16 | 0 | 324 | 86.9 |
| Gutta (Balata) | IBr | 0.5 | 0 | 292 | 78.3 |
| Gutta (Balata) | IBr | 16 | 0 | 324 | 86.9 |
| Gutta (Balata) | IBr | 3 | 25 | 316 | 84.7 |
| Rubber | I ₂ | 0.16 | 25 | 1.08 | 0.29 |
| Rubber | I ₂ | 1 | 25 | 4.55 | 1.22 |
| Rubber | I ₂ | 3.125 | 25 | 9.20 | 2.47 |
| Rubber | I ₂ | 7 | 25 | 15.6 | 4.18 |
| Rubber | I ₂ | 18 | 25 | 23.7 | 6.36 |
| Rubber | I ₂ | 40 | 25 | 27.9 | 7.47 |
| Gutta (Balata) | I ₂ | 1 | 25 | 6.74 | 1.81 |
| Gutta (Balata) | I ₂ | 3.25 | 25 | 14.8 | 3.97 |
| Gutta (Balata) | I ₂ | 7.1 | 25 | 17.6 | 4.71 |
| Gutta (Balata) | I ₂ | 18 | 25 | 23.2 | 6.22 |
| Gutta (Balata) | I ₂ | 40 | 25 | 26.8 | 7.18 |

^a A 0.10-gram sample of hydrocarbon was dissolved in 75 cc. of c. p. carbon disulfide, and 25 cc. of the 0.2 N halogen in glacial acetic acid were added. At the end of the reaction period, after the addition of 15 per cent aqueous KI, the excess halogen was titrated with 0.1 N Na₂S₂O₄, using starch as the indicator. The flasks were kept in the dark during the reaction period.

^b See Kemp, Bishop, and Lasselle (6) for method of preparation. Carbon (found) 87.82 per cent; (theory) 88.15 per cent. Hydrogen (found) 11.73 per cent; (theory) 11.85 per cent.

Balata hydrocarbon was prepared separately from samples of both the "red" and "white" latices representing two common varieties of the *Mimusops Balata* which were obtained by Weise and Company of Rotterdam. In each case the balata was coagulated by adding an excess of 50 per cent

alcohol to the latex. The coagulum was washed in hot 50 per cent alcohol, then in hot water, and finally was dried in vacuum over calcium chloride. The resin was removed by repeated extraction with petroleum ether (boiling point, 35° to 52° C.) and the gutta was then dissolved in carbon disulfide, carbon dioxide being used to replace the air over the

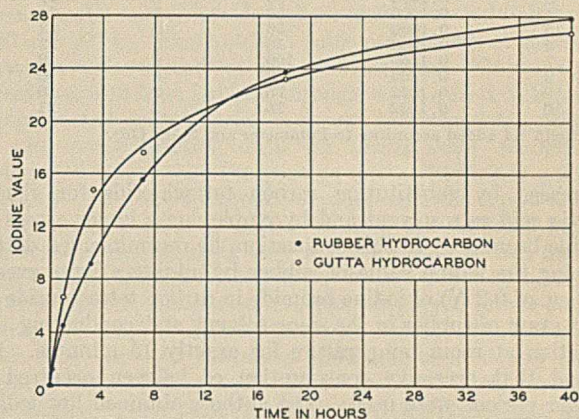


FIGURE 1. RATE OF REACTION OF IODINE WITH RUBBER AND GUTTA-PERCHA HYDROCARBONS

solution. After about 1 week the insoluble matter had completely settled, leaving a water-white clear solution of gutta which was decanted. The gutta was then precipitated with absolute alcohol. The alcohol was removed from the gutta by washing with petroleum ether and the absorbed petroleum ether evaporated in a stream of carbon dioxide. The hydrocarbon was finally heated to constant weight in a high vacuum at 60° C. In this connection it was observed that the last traces of solvent were more difficult to remove from the gutta than from the rubber hydrocarbon. The resulting product was milky white at room temperature and softened at 61° C., finally becoming colorless and crystal clear at 70° C. The product was free from ash and nitrogen.

REACTIVITY OF HALOGENS WITH RUBBER AND GUTTA-PERCHA HYDROCARBONS

Although some data were presented in the earlier publication (5) to illustrate the relative reactivity of various halogen solutions toward rubber, the data shown in Table I are more complete and include experiments with gutta-percha hydrocarbon. This information is of particular interest because of the relationship shown between rubber and gutta-percha hydrocarbons in their reactivity towards iodine chloride, iodine bromide, and iodine.

The most significant difference between these hydrocarbons in respect to their reactivity with halogens is the more rapid initial reaction of gutta with iodine as shown by the results in Table I which are plotted on Figure 1. Further evidence on this point has been obtained in connection with the separate refluxing of 10 grams of crepe rubber and gutta in 100 cc. of tetrachloroethane for 10 hours in an atmosphere of carbon dioxide. The gutta was found to undergo extensive cyclization as shown by a reduction in iodine value to 247, while rubber remained practically unchanged with an iodine value of 344. Staudinger and Bondy's (12) results also indicate that gutta-percha has a greater tendency to cyclize than does rubber.

The results in Table I also clearly show the superiority of iodine chloride as compared with other halogens for use in determining the unsaturation of rubber and gutta-percha hydrocarbons.

Gorgas (3) found that the activity of iodine bromide was

TABLE II. IODINE VALUE OF RUBBER HYDROCARBON

(Using 0.2 N iodine chloride in carbon tetrachloride followed by McIlhiney (8) procedure)

| NUMBER | WEIGHT OF SAMPLE Gram | RUBBER SOLVENT USED CHCl ₃ Cc. | REACTION PERIOD Hrs. | REACTION TEMPERATURE ° C. | EXCESS OF 0.2 N ICl ₂ IN CCl ₄ USED % | TOTAL IODINE VALUE | ADDITIVE IODINE VALUE | SUBSTITUTIVE IODINE VALUE | TOTAL |
|----------------|--------------------------|---|-------------------------|------------------------------|--|--------------------|-----------------------|---------------------------|-------------------|
| | | | | | | | | | UNSATURATION % |
| 1 | 0.1432 | 75 | 6 | 0 | 17 | 369.6 | 359.6 | 9.9 | 99.1 |
| 2 | 0.1419 | 75 | 6 | 25 | 17 | 371.1 | 347.2 | 23.9 | 99.5 |
| 3 ^a | 0.1000 | 50 | 6 | 22 | 22 | 369.1 | 326.8 | 42.3 | 99.0 |
| 4 ^a | 0.1000 | 50 | 6 | 22 | 22 | 371.6 | 323.6 | 48.0 | 99.6 |
| 5 | 0.1000 | 50 | 6 | 22 | 22 | 373.0 | 310.7 | 62.7 | 100.1 |
| 6 | 0.1000 | 50 | 6 | 22 | 22 | 374.5 | 317.9 | 56.7 | 100.4 |
| 7 | 0.1355 | 100 | 6 | 0 | 24 | 372.0 | 350.0 | 22.2 | 99.7 |
| 8 | 0.1356 | 100 | 6 | 0 | 24 | 370.6 | 348.4 | 22.2 | 99.4 |
| 9 | 0.1052 | 75 | 2 | 0 | 60 | 381.5 | 342.7 | 38.7 | 102.3 |
| 10 | 0.1032 | 75 | 2 | 21 | 62 | 391.4 | 348.9 | 42.4 | 104.9 |

^a Solid KI added according to Pummerer and Stärk (10).

increased by substituting carbon tetrachloride for glacial acetic acid as a solvent and by employing a larger excess of iodine bromide. In this connection, he recommended determining the iodine value of rubber by adding a large excess (50 cc. of 0.2 N) of iodine bromide in carbon tetrachloride to 0.15 gram of rubber in the same solvent and conducting the reaction at room temperature for exactly 15 minutes. He found that excessive consumption of halogen occurred if longer periods were used. The authors obtained low iodine values (316) for rubber when employing the Gorgas procedure; but by using 0.1 gram of rubber, 50 cc. of 0.2 N iodine bromide, in carbon tetrachloride, and 30 minutes at room temperature were able to obtain more consistent results. It was found, however, that under these conditions the results were variable and could not be relied upon where a high degree of accuracy was necessary.

USE OF IODINE CHLORIDE IN CARBON TETRACHLORIDE

Pummerer and Mann (10) determined the unsaturation of sol and gel rubber by adding iodine chloride in carbon tetrachloride to a chloroform dispersion of the rubber and allowing the solution to stand at room temperature for various intervals of time. These authors state, but do not show, that it is immaterial whether the various kinds of rubber are

bon disulfide in that cooling is unnecessary, but no results were given to support this contention. Later, Pummerer and Stärk (11) found that more consistent results could be obtained by limiting the excess of iodine chloride to 10 to 20 per cent and the reaction period to 6 hours at room temperature. Increased substitution was found to occur when more than the 20 per cent excess of iodine chloride was used. Their results were in good agreement with theory. However, when corrected for halogen acid present at the end of the reaction, as a gage of the extent of substitution, the values were in some cases as much as 6 per cent below the theoretical. Halogen acid was estimated by direct titration with sodium hydroxide following the titration with sodium thiosulfate.

The authors have carried out a series of experiments similar to those of Pummerer and Stärk (11) except that the liberated halogen acid was determined by the well-known McIlhiney (8) procedure involving the addition of potassium iodate solution immediately after the first titration with 0.1 N sodium thiosulfate. The iodine liberated by the halogen acid was then titrated with the sodium thiosulfate. Pure sol rubber hydrocarbon prepared by diffusion into petroleum ether from acetone extracted crepe was employed for these determinations. This preparation was transparent, colorless, and free from ash. The results given in Table II are in good agreement with those of Pummerer and Stärk, except that larger quantities of halogen acid were liberated. The close agreement of the total iodine values with theory is an indication that the halogen acid is formed largely as a result of hydrolysis of the rubber iodochloride addition product and not from substitution. Ingle (4) has noted that certain iodochlorides can be readily hydrolyzed. In the presence of too great an excess of iodine chloride, substitution apparently does occur at both 0° and 25° C. and is manifested by total iodine values which are higher than the theoretical.

When compared with the modified Wijs procedure as previously described (5), the method of Pummerer and Stärk appears to have certain disadvantages. For example, 6 hours are required as compared with 1 or 2 for the Wijs solution. The end points are not sharp and the variations in results therefore somewhat greater. Close attention must be paid to the amount of excess iodine chloride used, whereas with iodine chloride in glacial acetic acid variations of 70 to 200 per cent give practically the same results and the time of reaction is not so critical. In glacial acetic acid the solution of iodine chloride is more stable and permits of easier manipulation with less danger of loss of halogen due to volatilization than when carbon tetrachloride is used as the solvent. Hydrolysis of the iodochloride is undoubtedly a disturbing factor in the Pummerer procedure, but the use of a glacial acetic acid solution of iodine chloride in conjunction with carbon disulfide as the rubber solvent seems to exert a powerful repressing influence on side reactions such as substitution and hydrolysis.

The use of the McIlhiney or Pummerer procedure is of

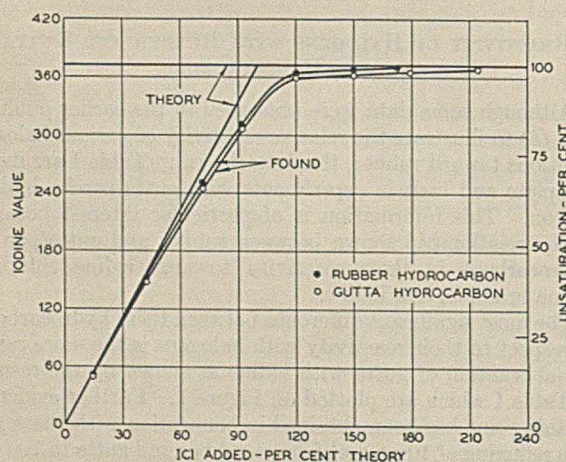


FIGURE 2. EFFECT OF AMOUNT OF ADDED IODINE CHLORIDE ON IODINE VALUE OF RUBBER AND GUTTA-PERCHA HYDROCARBONS

tested in the chloroform solution at 0° C. or at room temperature, whether they are left to stand for 6 or 96 hours, and whether 0.7 per cent or 0.2 per cent solution of rubber is treated. Although results on tests run at 0° were not published, their data showed that considerable substitution occurred at room temperature, gel rubber, for example, showing an unsaturation value 10 per cent in excess of the theoretical. It was stated that chloroform has the advantage over car-

advantage in case one wishes to determine the extent of substitution and hydrolysis by estimating the halogen acid split off during the reaction. This advantage was pointed out in the earlier publication by Kemp (5), particularly with respect to the study of the reaction of various terpenes with halogens.

EFFECT OF TIME AND TEMPERATURE

It was previously shown (5) in the case of pure rubber hydrocarbon at 0° C. that reaction periods ranging from 1 to 20 hours had no effect on the resulting iodine values and that these latter were equivalent to 99.7 per cent of the theoretical. The iodine value found for 15-minute periods at room temperature was the same as the 20-hour period at 0°, but after 20 hours at room temperature the iodine value rose to 102.3 per cent of theory. Since no similar data were obtained for gutta hydrocarbon at that time, it was decided to investigate the effect of time and temperature on the iodine value of gutta-percha. Further study was also made on the accuracy of results obtained with rubber for the shorter periods at room temperature since this procedure has manipulative advantages over the one previously recommended in which 2 hours at 0° C. was employed. These results are shown in Table III.

TABLE III. EFFECT OF TIME AND TEMPERATURE ON IODINE VALUE OF RUBBER AND GUTTA HYDROCARBON^a

| HYDROCARBON | WEIGHT OF SAMPLE Gram | REACTION PERIOD | | REACTION TEMPERATURE ° C. | IODINE VALUE | UNSATURATION % |
|----------------|--------------------------|-----------------|------|------------------------------|--------------|-------------------|
| | | Hrs. | ° C. | | | |
| Rubber | 0.0798 | 1 | 25 | 372.1 | 99.81 | |
| | 0.0798 | 1 | 25 | 371.8 | 99.70 | |
| | 0.0798 | 1 | 25 | 371.7 | 99.68 | |
| Rubber (4) | 0.1033 | 1 | 0 | 371.7 | 99.68 | |
| Rubber (4) | 0.1024 | 1 | 0 | 371.2 | 99.57 | |
| Balata (red) | 0.0999 | 1.25 | 25 | 366.1 | 98.20 | |
| Balata (white) | 0.1012 | 1.25 | 25 | 365.8 | 98.12 | |
| Balata (red) | 0.0502 | 1.33 | 25 | 368.2 | 98.76 | |
| Balata (white) | 0.0507 | 1.33 | 25 | 369.1 | 99.01 | |
| Balata (red) | 0.0503 | 2.33 | 25 | 370.0 | 99.24 | |
| Balata (white) | 0.0510 | 2.2 | 25 | 372.0 | 99.79 | |
| Balata (red) | 0.0857 | 2 | 0 | 364.2 | 97.69 | |
| Balata (red) | 0.0855 | 2 | 0 | 363.2 | 97.42 | |
| Balata (red) | 0.1011 | 2 | 0 | 362.3 | 97.18 | |
| Balata (red) | 0.0998 | 2 | 0 | 362.2 | 97.16 | |

^a Hydrocarbon dissolved in 75 cc. of CS₂ and 25 cc. of 0.2 N iodine chloride in glacial acetic acid added.

In determining the iodine value of balata hydrocarbon by the modified Wijs method at 0° C. it was noted that upon cooling, after the addition of the iodine chloride, a finely divided precipitate separated out. This precipitation does not take place with rubber. If room temperature is employed when determining the unsaturation of gutta-percha, precipitation is avoided. As can be seen from the results in Table III, gutta-percha appears to require a greater excess of Wijs reagent and a longer period of time for the completion of the reaction than does rubber. The use of a 0.05-gram sample and 25 cc. of Wijs solution for a 2-hour period at room temperature appears to be suitable for determining the iodine value of gutta-percha hydrocarbon. These results indicate that gutta-percha hydrocarbon does not absorb iodine chloride as rapidly as rubber hydrocarbon during the latter stages of the reaction.

In order to determine the relative rates of reaction of rubber and gutta-percha hydrocarbon with iodine chloride, 0.5000-gram samples of each were dissolved in 500 cc. of carbon disulfide in a volumetric flask, 50-cc. portions were pipetted into iodination flasks, and varying quantities of 0.2 N Wijs solution were added from a buret. The flasks were allowed to stand 10 minutes in the dark at 25° C. and the unreacted iodine chloride was determined by titration with 0.1 N sodium thiosulfate after the addition of aqueous potassium iodide and starch solution. These results are given in Figure 2 and show that the gutta-percha requires a greater excess of iodine

chloride for the completion of the reaction than the rubber hydrocarbon.

RECOMMENDED PROCEDURES

PREPARATION OF 0.2 N WIJS SOLUTION. Thirteen grams of pure iodine in powdered form are dissolved in a liter of glacial acetic acid (Merck's highest purity) heated to between 80° and 90° C. One hundred cubic centimeters of this solution are removed and set aside for use later. Chlorine gas, which has first been bubbled through water and then through concentrated sulfuric acid, is passed into the main portion of the iodine solution until the brown color changes to orange, at which time the passage of the chlorine is quickly stopped. The 100-cc. portion of iodine solution is now added to the main portion of iodine solution until a faint brown color remains, indicating only a slight excess of free iodine. The solution is then heated at 80° to 90° C. for 20 minutes, allowed to cool, and placed in a glass-stoppered brown bottle. Great care must be exercised to avoid contact of this solution with moisture. All containers should be scrupulously clean and dry before being used. When prepared in this manner, the solution is very stable and will keep several months without change.

PREPARATION OF 0.1 N SODIUM THIOSULFATE SOLUTION. Twenty-five grams of pure Na₂S₂O₃·10H₂O are dissolved in a liter of boiled distilled water and kept in a ground-glass stoppered bottle. It is standardized against pure potassium biniodate, iodine, or potassium dichromate in the usual manner as described in textbooks on analytical procedure (9). The present authors prefer the use of pure iodine for this standardization.

PROCEDURE FOR DETERMINATION OF IODINE VALUE OF RUBBER, GUTTA-PERCHA, ETC. In determining the iodine value or hydrocarbon content of crude rubber, balata, gutta-percha, or latex these substances must first be freed from moisture and resins. Tenth-gram samples (0.05 gram in case of gutta-percha) are placed in 500-cc. flared lipped ground-glass stoppered iodination flasks and covered with 75 cc. of carbon disulfide (Merck's highest purity). After standing overnight, 25 cc. of the 0.2 N Wijs solution are added from a pipet, while the flask is shaken so as to impart a rotating motion to the carbon disulfide solution during this operation. The solution should be clear and free from precipitate after addition of the iodine chloride. The stoppers are wetted with a drop of 15 per cent potassium iodide solution and the flask is placed in a dark place and allowed to stand for 1 hour (2 hours in the case of guttas). Twenty-five cubic centimeters of 15 per cent freshly prepared potassium iodide solution and 50 cc. of recently boiled and cooled distilled water are then added and the liberated iodine is titrated immediately with 0.1 N sodium thiosulfate. Toward the end of the titration 5 cc. of a freshly prepared 1 per cent solution of soluble starch are added as an indicator. The solution is rapidly rotated during titration and as the end point is approached, the color changes are from blue to brown to yellow. From this point on, the titration must proceed with caution. The solution should be shaken after the addition of every half drop and when the end point is reached the canary yellow color of the contents of the flask will fade out to a milky whiteness. A blank is run simultaneously with the sample. The difference in cubic centimeters of 0.1 N thiosulfate between the blank and sample titration is used to calculate the iodine value and per cent unsaturation in the following manner:

$$\text{Iodine value} = \frac{\text{cc. } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3 \times 1.2692}{\text{wt. of sample in grams}}$$

$$\text{Unsaturation (per cent)} = \frac{\text{iodine value found}}{3.728}$$

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Testing Reclaimed Rubber

HENRY F. PALMER, The Xylos Rubber Company, Akron, Ohio

A description and interpretation of physical tests on raw reclaimed rubber are presented. A discussion of the merits of tests on reclaim-sulfur cured compounds versus tests of typical compounds containing the reclaims shows that the former are of little value, except in the case of specific gravity.

A testing procedure is recommended for the consumer of reclaimed rubber, which stresses processing and physical tests on cured compounds from a factory test run (preceded by laboratory tests only if they can be interpreted accurately), using a specific and suitable recipe.

A CONSIDERATION of the testing of raw material such as reclaimed rubber should include both the manufacturer's tests for control purposes and tests applied by the consumer to insure himself against variations in raw material purchases. These tests may be identical in many cases, but the consumer may also run actual processing tests in his product and factory.

All the larger rubber companies and most smaller ones with a technical staff run tests on incoming raw materials. The problem here is to determine the minimum number of tests involving the minimum of time and labor which will assure the consumer that his raw material is uniform and comparable to previous shipments. It is decidedly unfortunate and costly for both producer and consumer if the consumer's specification tests on many rubber compounding ingredients are incorrectly chosen, carelessly performed, and too critically interpreted. These faults may be found singly or together, and the technologist responsible for the condition may not be receptive to the introduction of new ideas. Any of the above conditions necessarily means unwarranted rejections, inconvenience, and expense.

The object of this paper is to evaluate both manufacturer's and consumer's tests applied to reclaimed rubber, and to suggest a simple, rational, and practical procedure for testing this compounding ingredient.

A résumé of the chemical and physical tests applied to reclaimed rubber is as follows:

I. CHEMICAL TESTS

A. Raw or uncured reclaim

1. Acetone extract
2. Chloroform extract
3. Alcoholic potash extract
4. Total and free sulfur
5. Carbon black
6. Cellulose
7. Alkalinity or acidity
8. Moisture
9. Ash
10. Ash analysis
11. Special tests—e. g., manganese, lead

II. PHYSICAL TESTS

A. Raw or uncured reclaim

1. Manual or visual
2. Smoothness
3. Milling
4. Tubing

5. Plasticity and recovery
6. Load capacity
7. Color

B. Reclaim cured with sulfur

1. Specific gravity
2. Tensile, elongation, and stress
3. Permanent set
4. Resistance to tear
5. Rate of cure

C. Reclaim in special test formulas

1. Any usual cured rubber tests
2. Any of the tests listed under II-A on the uncured compound

Generally speaking, chemical tests are run for the purpose of ascertaining the constituents of the reclaim for efficient compounding. These analyses in detail are supplied by the manufacturer as representative of his product. Occasionally purchasing specifications will limit some chemical constituents, such as manganese content or alkalinity. Inasmuch as most analytical procedures are or can be based on fundamental chemical methods, the figures are reproducible from one laboratory to another. While chemical tests and laboratory procedures are important, they are not, with few exceptions, usually a serious or much disputed factor in control testing as compared to physical tests. The results of chemical analysis are generally accepted as an innate characteristic of the reclaim, and are so used by compounders.

Physical tests must be classified according to the state of the reclaim when tested.

RAW OR UNCURED RECLAIM

The processing of reclaimed rubber depends upon its condition in the raw state. Therefore, any tests which will indicate its processing qualities are of great value.

A manual and visual test of reclaim should be the first and is the simplest test to which it may be subjected after manufacture or upon purchase. This is primarily a manufacturer's preliminary control method, but is, of course, applicable to qualitative differentiation of various types of reclaim. Depending upon the expertness of the inspector, this test reveals qualitatively the softness, nerve, color, odor, and smoothness of the product. In a given production run, an experienced inspector can very accurately eliminate material which is irregular and not comparable to a control. This test is most valuable as an index of smoothness.

The smoothness of a reclaim is easily noted by visual examination of slabs finished from refiners in thin sheets. However, for reclaims finished from slabbing mills in thicker sheets (0.010 to 0.025 inch, 0.25 to 0.62 mm.) some other test is necessary. Mixing the reclaim in equal quantity with clean smoked sheets offers the simplest method. When a sheet of this mixture is stretched thin with the fingers, the presence of any lumps will be revealed. Further, if a piece of the mixture about 2 cm. thick is cut while hot, the lumps will be pushed out in subsequent contraction upon cooling and will be visible on the outer surface. Another method is to mix 50 parts of reclaim with about 10 parts of mineral rubber and 40 parts of whiting, after which it is tubed. Any unrefined lumps will show upon the tubed surface.

The test of most value would be one for judging the processing qualities, and for this purpose, milling tests offer a great deal of information in a short time. Any laboratory can set up a procedure (4) suitable to its equipment for running this test, using a uniform volume of sample, roll setting, roll speed, number of cuts, and temperature. A general recommendation of a sheet 10 mm. (0.25 inch) in thickness, low bank, low speed, and cool rolls is made. Naturally a control should always be run. The number of minutes required to reach a definite degree of smoothness and to adhere to the back roll of the mill allows a numerical record. The former indicates inertness or speed of break-down preparatory to pigment incorporation and the latter indicates the degree of tackiness. This test can be of immense value in gaging nerve or inertness, and degree of tackiness.

Reclaim suitable for tubing work may be evaluated by extrusion through a 3.2-mm. (0.125-inch) die. Visual examination of the surface waviness indicates the comparative inertness. This test on a reclaim of high nerve such as first-grade alkali whole tire or tube reclaim is of little value, as these reclaims are very nervy and consequently show much waviness. These reclaims then must be loaded to give a smooth surface. After a definite period of rest (1 hour is sufficient) the sample may be gaged and the percentage of swelling calculated. Thus a definite numerical rating of this quality is obtained. A control is desirable for this test.

TABLE I. PLASTICITY AND MILLING TESTS

| RECLAIM TYPE | YIELD ^a Mm. | RECOVERY ^b Mm. | MILLING TIME | |
|----------------------------|---------------------------|------------------------------|---------------------|-------------------------------------|
| | | | To smooth Mm. | To adhere to back roll Mm. |
| Boot and shoe, acid-alkali | 7.12 | 1.90 | 0.5 | 5.0+ |
| Whole tire, acid-alkali | 6.09 | 2.99 | 0.8 | 5.0+ |
| Whole tire, alkali | 5.14 | 3.11 | 0.85 | 4.4 |
| Solid tire, digester | 6.36 | 2.88 | 0.6 | 3.3 |
| Inner tube, digester | 3.98 | 3.73 | 1.6 ^c | 5.0+ |
| Inner tube, pan | 3.54 | 2.46 | 2.6 ^c | 5.0+ |

^a Williams (7) Y value.

^b After 10 minutes.

^c Difficult to interpret for tube reclaims.

Plasticity determinations on reclaimed rubber may be carried out on pieces cut directly from the slabs or by building up a laminated pellet from a calendered sheet as described by Winkelmann and Croakman (9). In this laboratory a great many tests have been run on reclaim slabs under various conditions, with the conclusion that the plasticity measurement as any sort of routine test is very variable for reclaimed rubber. Further, it measures only resistance to flow under load at a given temperature and load, and does not indicate much about processing qualities. The measurement of recovery, however, does indicate nerve very well, and in this respect coincides in order of magnitude with the smoothing time in the milling test. Table I shows typical figures on these tests for various types of reclaim. The boot and shoe reclaim, for example, has a very low plasticity (high numerical figure), and yet is the most inert, as is shown by the re-

covery and milling test. On the other hand, the plasticity and recovery tests on the compound in which the reclaim is used are very much more accurate, dependable, and useful.

The quantity of pigment which a reclaim will take up before crumbling is often important, and perhaps still more important is the speed of incorporation. The relative quantities of pigment which reclaims will absorb may be observed by incorporating first 100 per cent and then 25 per cent of its weight in whiting, continuing the addition of 25 per cent increments until the batch crumbles. Table II indicates how four typical reclaims behave under this test. The speed of incorporation may be recorded either by how much whiting or other pigment will be taken up in a given time or by how fast a given quantity is incorporated.

TABLE II. LOADING TESTS

| RECLAIM | WHITING LOAD % |
|---------------|-------------------|
| Whole tire I | 275 |
| Whole tire II | 225 |
| Solid tire | 175 |
| No. 2 tube | 275 |

The color of light grades of reclaimed rubber may be determined by matching the sample of reclaim against a control. In general it is necessary to dilute tube reclaims for a satisfactory color check. A simple recipe for this purpose is:

| | |
|------------|-----|
| Pale crepe | 50 |
| Lithopone | 25 |
| Reclaim | 25 |
| | 100 |

The crepe and lithopone are preferably master-batched for use. It is often desirable to use a mix of the specific color to be matched to achieve the most accurate comparisons.

RECLAIM CURED WITH SULFUR

It is now standard practice for all tests of reclaim, cured with sulfur only, to use a ratio of 100 parts of reclaim to 5 parts of sulfur.

The specific gravity determination is the only property for which this mixing is really worth while. In the actual determination of the specific gravity, the use of solutions as balancing media is recommended as the most accurate, most readily kept under control, and also the most rapid method for routine work. For calculating the true specific gravity of the reclaim, the following formula is applicable, where *A* equals specific gravity of reclaim plus sulfur mix.

$$\text{True specific gravity} = \frac{100 A}{105 - 2.41 A}$$

The tensile strength and elongation of reclaimed rubber, as determined from the reclaim-sulfur mix, has long been considered by many as a prime index of its quality. This is a very unfortunate assumption, as will be shown.

The cures are generally made at 141.7° C. (287° F.), the times usually being between 15 and 35 minutes. The rate of cure problem has been extensively studied (2, 5) and a reference to these papers will show the effect of time of cure. A cure of 25 minutes at 141.7° C. serves as a satisfactory standard of comparison for these tests.

For discussion of this test Table III is shown. One-half slab of each reclaim was cut into pieces and well blended on a mill. From this blend seven mixings with sulfur were made, two slabs from each mixing being cured 25 minutes at 141.7° C. Four strips from each slab were then tested, as described by Palmer (3). For both the alkali whole tire and neutral solid tire reclaim, a maximum deviation of 5 kg. per sq. cm. (70 lb. per sq. in.) in tensile strength and 35 and 25 per cent, respectively, in elongation is obtained.

TABLE III. ERROR IN PHYSICAL TESTS OF RECLAIM-SULFUR MIXES

| SLAB NUMBER | WHOLE TIRE | | SOLID TIRE | |
|-------------------------------|--------------|------------------------------|--------------|------------------------------|
| | Elongation % | Tensile strength Kg./sq. cm. | Elongation % | Tensile strength Kg./sq. cm. |
| 1 | 415 | 50 | 335 | 56 |
| 2 | 410 | 48 | 325 | 55 |
| 3 | 430 | 51 | 325 | 51 |
| 4 | 430 | 50 | 325 | 54 |
| 5 | 435 | 52 | 320 | 53 |
| 6 | 435 | 50 | 325 | 51 |
| 7 | 430 | 50 | 320 | 52 |
| 8 | 420 | 47 | 315 | 52 |
| 9 | 440 | 51 | 335 | 52 |
| 10 | 445 | 51 | 330 | 53 |
| 11 | 430 | 50 | 310 | 52 |
| 12 | 430 | 49 | 315 | 52 |
| 13 | 425 | 47 | 310 | 52 |
| 14 | 425 | 47 | 315 | 53 |
| Average | 429 | 49.5 | 322 | 52.7 |
| Maximum variation | 35 | 5 | 25 | 5 |
| Testing temperature, 22.5° C. | | | | |

If this numerical variation were based on a compound having a tensile strength of 211 kg. per sq. cm. (3000 lb. per sq. inch) and an elongation of 600 per cent, the percentage variation would be comparatively low, 2 to 3 per cent in tensile strength and 4 to 6 per cent in elongation. Based on the low tensile reclaim, however, the variation in tensile strength and elongation is approximately 10 per cent. These figures represent what is believed to be nearly a minimum variation in reclaim testing; therefore, one should not contract his critical judgment more than 10 per cent at most in examining reclaim-sulfur test figures. In many laboratories the general run of results will vary more than 10 per cent. If one desires to average the results from a sufficient number (minimum of 8) test strips (3), results of reproducible nature may be obtained. Assuming that such a test procedure is carried out, what meaning do the results have? Winkelmann (8) has stated, "There is a tendency to evaluate too much on tensile strength. The real significance of the tensile strength of a reclaim and its relation to the physical properties of the compound in which it is used have yet to be determined.... The reclaims which give a low tensile strength when cured with sulfur may, however, have the correct degree of disaggregation for yielding good results with rubber and other ingredients." In support of these statements, Winkelmann has shown the results of using three tube reclaims, three whole tire reclaims, and one carcass reclaim both in the reclaim-sulfur mix and in a friction compound containing 24 per cent of reclaim. While the reclaim-sulfur figures varied considerably, the stress-strain curves of the compounds were very close together. Specifically, two tube reclaims having tensile strengths, when cured with sulfur 25 minutes at 141.7° C., of (1) 1392 lb. per sq. in. and (2) 287 lb. per sq. in. showed, in his compound, maximum tensile strengths (from his curves) of (1) 2950 lb. per sq. in. and (2) 3000 lb. per sq. in.

Stafford (6) has further commented on reclaim testing: "The co-relation of tensile strengths and the compounding value of a particular reclaim is a very vexed one, and there is a large amount of evidence and experience indicating that the two are not directly proportional." Hurleston (1) has also suggested testing reclaimed rubber by admixture with crude rubber together with "curatives."

FORMULA I

| | |
|-----------------------|--------|
| Tube reclaim | 33.00 |
| Smoked sheets | 40.00 |
| Sulfur | 2.31 |
| Diorthotolylguanidine | 0.19 |
| Medium process oil | 1.00 |
| Zinc oxide | 4.00 |
| Whiting | 19.50 |
| | 100.00 |

Some results of tests in typical compounds using reclaims of quite different tensile strengths, as shown by reclaim-sulfur mixes, are shown in Tables IV and V. Two tube reclaims, A and B, were tested in a low-grade inner-tube compound as shown in formula I.

TABLE IV. TESTS ON TUBE RECLAIMS IN FORMULA I

| FORMULA | CURE Min. | NUMBER OF TEST STRIPS | TENSILE STRENGTH | | ELONGATION AT BREAK | |
|-----------------------------|-------------|-----------------------|------------------|---------------|---------------------|-----|
| | | | A Kg./sq. cm. | B Kg./sq. cm. | A % | B % |
| Reclaim 100 Sulfur 5 | (141.7° C.) | 4 | 47 | 142 | 640 | 660 |
| | 25 | | | | | |
| Formula I | (146.1° C.) | 3 | 181 | 184 | 710 | 715 |
| | 20 | | | | | |
| | 25 | | | | | |
| | | 3 | 190 | 189 | 695 | 700 |
| | | 3 | 184 | 190 | 670 | 680 |
| Temperature of test, 27° C. | | | | | | |

A was made by the digester process and B by the pan process, the former having about one-third the tensile strength of B in the reclaim-sulfur test. Table IV shows that the tensile strengths are comparable when either reclaim is used in formula I.

The results of the use of whole tire reclaim of quite different physical properties, as revealed by the reclaim-sulfur test, are shown in Table V. Samples of the same type of whole tire reclaim made on the same day were used. The difference in tensile strength of 15 kg. per sq. cm. represents the maximum observed in this reclaim, which is not as great as in the two tube reclaims, but is enough to cause intense argument upon occasion. The use of these reclaims in two different tread compounds, formulas II and III, shows comparable final results.

FORMULA II

| | |
|--------------------|---------|
| Whole tire reclaim | 25.000 |
| Smoked sheets | 42.500 |
| Diphenylguanidine | 0.375 |
| Sulfur | 1.625 |
| Carbon black | 19.500 |
| Zinc oxide | 8.000 |
| Pine tar | 3.000 |
| | 100.000 |

FORMULA III

| | |
|-----------------------|-------|
| Smoked sheets | 35.0 |
| Whole tire reclaim | 35.3 |
| Sulfur | 1.8 |
| Mercaptobenzothiazole | 0.4 |
| Stearic acid | 2.0 |
| Zinc oxide | 2.5 |
| Mineral rubber | 5.0 |
| Carbon black | 18.0 |
| | 100.0 |

TABLE V. TESTS ON WHOLE TIRE RECLAIM IN FORMULAS II AND III

| FORMULA | CURE Min. | NO. OF TEST STRIPS | ELONGATION AT BREAK | | STRESS AT 400 PER CENT ELONGATION | | TENSILE STRENGTH | | |
|-----------------------------|-------------|--------------------|---------------------|------------------|-----------------------------------|---------------|------------------|---------------|----|
| | | | L ^a % | H ^a % | L Kg./sq. cm. | H Kg./sq. cm. | L Kg./sq. cm. | H Kg./sq. cm. | |
| TEMPERATURE OF TEST, 22° C. | | | | | | | | | |
| Reclaim 100 Sulfur 5 | (141.7° C.) | 25 | 8 | 410 | 350 | 27 | 47 | 41 | 56 |
| | 25 | | | | | | | | |
| TEMPERATURE OF TEST, 30° C. | | | | | | | | | |
| Formula II | (143.3° C.) | 3 | 705 | 710 | 65 | 63 | 172 | 167 | |
| | 45 | | | | | | | | |
| | 3 | | | | | | | | |
| | 700 | | | | | | | | |
| | 690 | | | | | | | | |
| Formula III | (125.7° C.) | 3 | 695 | 665 | 83 | 87 | 192 | 194 | |
| | 45 | | | | | | | | |
| | 3 | | | | | | | | |
| Formula III | (125.7° C.) | 3 | 635 | 615 | 96 | 103 | 200 | 198 | |
| | 60 | | | | | | | | |
| | 3 | | | | | | | | |
| Formula III | (125.7° C.) | 3 | 600 | 610 | 109 | 107 | 199 | 200 | |
| | 60 | | | | | | | | |
| | 3 | | | | | | | | |
| Formula III | (125.7° C.) | 3 | 610 | 600 | 113 | 116 | 205 | 203 | |
| | 60 | | | | | | | | |
| | 3 | | | | | | | | |

^a L, whole tire reclaim, low tensile. H, whole tire reclaim, high tensile. Stress for reclaim-sulfur mixes is at 300 per cent elongation.

In compounds of the mechanical goods type, where often the reclaim is the major constituent of the compound, a definite average difference in reclaim-sulfur tensile strength may carry over to the compounds, showing a trend but not proportionally. Tests on formula IV, as recorded in Table VI, show a case where there is a small but essential difference in tensile and a definite difference in elongation in the compound. These differences are indicated in the reclaim-sulfur tests but not in the correct proportion, although the change in manufacture of the reclaim should assure the difference, as indicated by the results obtained when the reclaims are tested in formula IV.

FORMULA IV

| | |
|--------------------|-------|
| Blend reclaim | 70.0 |
| Sulfur | 1.6 |
| Diphenylguanidine | 0.5 |
| Lime | 3.5 |
| Zinc oxide | 1.0 |
| Whiting | 18.4 |
| Paraffin | 0.5 |
| Medium process oil | 4.5 |
| | 100.0 |

TABLE VI. TESTS ON BLEND RECLAIM IN FORMULA IV

| FORMULA | CURE Min. | NO. OF TEST STRIPS | TEMP. OF TEST ° C. | ELONGATION AT BREAK | | TENSILE STRENGTH | |
|-------------|------------------|--------------------------|-----------------------------|------------------------|-------------------|-----------------------------|--------------|
| | | | | Reclaim X % | Reclaim Y % | Reclaim X Kg./sq. cm. | Reclaim Y |
| Reclaim 100 | 141.7° C.) 25 | 16 | 19 | 370 | 390 | 55 | 65 |
| Sulfur 5 | | | | | | | |
| Formula IV | 157° C.) 8 | 16 | 29 | 185 | 215 | 36.5 | 38.3 |

The results of tensile-elongation testing on reclaim-sulfur mixes, therefore, force certain conclusions:

1. With the best testing conditions and with sufficient tests, reproducible results may be obtained.
2. Under routine testing conditions which do not allow sufficient tests, the results are accurate at best to 10 per cent, and will many times be less accurate than this.
3. Even the best results are not a criterion of the properties of the reclaim in the recipe in which it is to be used.

DISCUSSION

The manufacturer of reclaimed rubber must avail himself of any test which can be run in his factory or laboratory, inasmuch as he cannot have available all the typical processing equipment of his varied consumers. It is fortunate that physical tests on raw reclaim give results which indicate closely most processing conditions. The reclaim manufacturer may also run processing tests on type compounds in which the reclaim is being used, or through coöperation with the consumer he may run these tests in a specific test compound submitted by that particular consumer. In this way the manufacturer does the most he can in the way of control testing.

While the manufacturer is limited by not knowing each

specific compound in which his material is used and by not having available each specific set of equipment suitable for processing tests on this type of compound, the consumer on the other hand is in the position to carry out actual tests on his own equipment and in his own compound which will give the only accurate criterion for evaluating any raw material including reclaimed rubber.

Therefore, for the examination of reclaimed rubber by the consumer the following procedure is recommended:

1. On a sample shipment, a small sample from each slab, the whole being blended, should be used. On a carload shipment current practice is generally to take six to ten samples from the car, blending these for test.
2. Chemical tests should be run for any specific constituent.
3. Specific gravity on a reclaim-sulfur mix should be obtained.
4. Laboratory processing tests on the raw reclaim and in a test recipe, also physical tests on the cured test compound, may be made. Unless these tests are known to have a direct and accurate interpretation in reference to the actual processing and tests on the finished product, they should be omitted entirely.
5. An actual factory run of one or a few mixings of a typical compound should be made, wherein actual processing is noted and tests are made on the finished product.

Any manufacturer who will follow the above practice is performing his tests on reclaimed rubber recipes in the most practical and most satisfactory manner, and the results obtained in utilizing procedure 5 above are particularly satisfying from the standpoint of both consumer and manufacturer.

For many years the reclaimer has heard his product accused of being responsible, because of variation, for many of the multitudinous ills occurring in rubber manufacturing plants. As recently as 7 years ago many of these complaints were justifiable. Because of the progressive advances in control towards uniformity of production in the past 5 to 7 years, very few complaints of any kind are justifiable today. Every reclaimer has had experiences in which his product was held culpable, only to be able to prove that another factor was the cause of the difficulty. Further, every reclaimer will appreciate knowing the facts on which a just complaint is based, since they make available to him experience and knowledge through which he may profit. Reclaimed rubber should be considered only as an important compounding ingredient, and for the benefit of both consumer and manufacturer a rational, practical, and thorough testing procedure is indispensable.

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RECEIVED September 20, 1933. Presented before the Division of Rubber Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

GERMANY DEVELOPS IMPROVED PROCESS OF STERILIZING ARTIFICIAL ICE. A new process of sterilizing ice has been introduced in Germany, according to a report made public by the Commerce Department. Sterilized ice has up to now been produced throughout the world by freezing sterilized water, it is pointed out. This ice was always liable, however, to be infected during transfer from the factory to the user. There was, furthermore, the possibility of germs being transferred indirectly to the food-stuffs in ice-cooled rooms.

George Kaune, a Munich scientist, is reported to have succeeded in applying his Katadyn process, consisting of the sterilization of water by the use of metallic silver, to the production of

artificial ice. The use of this process has resulted in obtaining totally different results. Artificial ice made from water treated with this process not only is sterile, but in addition has bactericidal qualities. For this reason, it is being designated in Germany as "activated ice" to distinguish it from ordinary artificial or natural ice.

Careful bacteriological tests, carried out at the Hygienic Institute of the Dresden Technical University are said to have proved that germs introduced into the melting water of activated ice were killed after a few hours, so that the certain destruction of any bacteria that come in immediate contact with the ice may be safely relied upon.

New Type of Antimony Electrode for pH Measurements

T. R. BALL, WEBSTER B. SCHMIDT, AND KARL S. BERGSTRESSER, Washington University, St. Louis, Mo.

AN INVESTIGATION of the antimony-antimony oxide electrode for measuring pH was begun by Schmidt in this laboratory in the fall of 1931. The work was practically completed when the publication of Parks and Beard (3) appeared. Aside from the fact that these authors used a vacuum-tube potentiometer for their potential measurements, the two investigations were practically identical. Parks and Beard found that the electrode functions between a pH of 2 and 7, which is in perfect agreement with results in this laboratory. However, in calculating the pH Parks and Beard use the equation $E = -0.007 + 0.05195 \text{ pH}$ at 25° , while the present authors found that the equation $E = -0.020 + 0.05813 \text{ pH}$ at 20° gives the proper pH within about 0.02 unit when E is measured against a saturated calomel electrode with a Leeds and Northrup portable potentiometer. The difference in the value of the constant cannot be accounted for by the small difference in temperature unless the antimony electrode has a very large temperature coefficient, and probably lies in the apparatus used in making the measurements. Using 48 different electrodes prepared and annealed in various ways, very little difference was found in their performance, so that the discrepancy probably does not lie in the method of preparation or purity of the electrodes.

If it is assumed that the antimony-antimony oxide electrode functions by virtue of the changing antimony-ion activity in solutions of varying acidity, other antimony compounds should serve as a substitute for the oxide coating. The sulfide is immediately suggested. Mr. Schmidt prepared electrodes with sulfide coatings by suspending cast electrodes for 1 hour in hot 0.30 *N* nitric acid and then saturated the solution with hydrogen sulfide. The metal became coated with a thin yellowish film that was not removed with a stream of water from a wash bottle. These electrodes were found to function in the same manner as the ordinary antimony electrode and have the advantage of a greater range on the alkaline side. No claim is made that they are useful for precision measurements, but they will indicate the pH within ± 0.05 unit in the range from 2 to 10. They are slightly better than the oxide electrodes in the rapidity of establishing equilibrium and the difference between individual electrodes is usually not more than 2 or 3 millivolts.

Time did not permit of a thorough investigation of the antimony sulfide electrode by Mr. Schmidt, but the work was carried on by Mr. Bergstresser. The data hereafter presented are taken from the work of both.

EXPERIMENTAL

PREPARATION OF ELECTRODES. Five methods were used in preparing the sulfide coated electrodes.

1. Polished stick electrodes were immersed in 0.30 *N* nitric acid which was kept on the steam bath for 1 hour. The hot solution was then saturated with hydrogen sulfide while it cooled to room temperature. When not in use the electrodes were kept in this saturated hydrogen sulfide solution.

2. The procedure was identical with that of the first method, except that 0.50 *N* nitric acid was used.

3. Polished electrodes were placed in a long Pyrex tube which was sealed at one end and connected to a vacuum pump at the other. A small amount of sulfur was placed in the sealed end of the tube. The tube was evacuated and the portion containing

the electrodes was heated to 400°C . in an electric tube furnace. In a second run a temperature of 490°C . was used. The sulfur was then distilled onto the electrodes by applying heat to the sealed end. The tube was allowed to attain room temperature before the vacuum was released.

4. Polished electrodes were heated to 400°C . in a stream of dry hydrogen sulfide.

5. A heavy coating of oxide was formed on the electrodes by heating them to 500°C . in a stream of air. The cooled electrodes were then treated with hydrogen sulfide while suspended in 0.30 *N* nitric acid.

A complete study of these various electrodes showed that those prepared by the first method gave more nearly reproducible results and all the data in this paper were obtained from electrodes so prepared.

RESULTS. Table I contains typical sets of data obtained with buffers which were standardized with quinhydrone up to a pH of 7 and with a hydrogen electrode in the more alkaline range.

TABLE I. CALCULATION OF CONSTANT E_0 OF EQUATION 1

| BUFFER | pH | E. M. F. | | E_{0sb} | pH CALCULATED | pH ERROR |
|---------------|-------|----------|---------------------|-------------|---------------|------------|
| | | ps. | SAT. CAL. t° | | | |
| HCl-KCl | 1.12 | 0.0540 | 20 | (-0.2406) | 1.21 | +0.09 |
| Phthalate-HCl | 2.20 | 0.1100 | 20 | -0.2339 | 2.18 | -0.02 |
| Phthalate | 3.92 | 0.2125 | 24 | -0.2358 | 3.93 | +0.01 |
| Phthalate | 3.97 | 0.2135 | 20 | -0.2345 | 3.96 | -0.01 |
| Phosphate | 5.29 | 0.2930 | 20 | -0.2377 | 5.33 | +0.04 |
| Phosphate | 5.54 | 0.3074 | 24 | -0.2353 | 5.54 | ± 0.00 |
| Phosphate | 5.91 | 0.2370 | 20 | -0.2355 | 5.92 | +0.01 |
| Phosphate | 6.66 | 0.3739 | 24 | -0.2358 | 6.67 | +0.01 |
| Phosphate | 6.97 | 0.3870 | 20 | -0.2337 | 6.95 | -0.02 |
| Borate | 8.01 | 0.4480 | 20 | -0.2347 | 8.00 | -0.01 |
| Borate | 9.20 | 0.5160 | 20 | -0.2331 | 9.17 | -0.03 |
| Phosphate | 10.00 | 0.5615 | 20 | -0.2324 | 9.96 | -0.04 |
| | | | | Av. -0.2348 | | |
| Phosphate | 10.28 | 0.5935 | 23 | -0.2437 | 10.43 | +0.15 |
| Phosphate | 10.82 | 0.5966 | 22 | -0.2166 | 10.51 | -0.21 |
| Phosphate | 11.41 | 0.6438 | 23 | -0.2472 | 11.60 | +0.19 |
| Phosphate | 11.77 | 0.6714 | 22 | -0.2359 | 11.79 | +0.02 |
| Phosphate | 12.11 | 0.7046 | 23 | -0.2473 | 12.40 | +0.19 |

The e. m. f. values of column 3 are the averages obtained from four or more electrodes measured against the saturated calomel electrode. The E_0 values of column 5 are calculated from the equation

$$E_0 = \text{pH} [0.0577 + 0.0002(t - 18)] - \text{e. m. f.} - E_{\text{cal.}} \quad (1)$$

The value of $E_{\text{cal.}}$ at any given temperature was computed from the equation (2)

$$E_{\text{sat. cal.}} = 0.2504 + 0.00065(t - 18) \quad (2)$$

The average value of E_0 is computed over the pH range of 2.2 to 10 only, since in the more acid and alkaline ranges the electrodes behave erratically. Having established the value of the constant E_0 as -0.2348 volt, the pH of each solution was calculated to the closest 0.01 unit from Equation 3.

$$\text{pH} = \frac{E. \text{ m. f.} + E_{\text{cal.}} - 0.2348}{0.0577(t - 18)} \quad (3)$$

This equation would, of course, apply to any type of calomel electrode. The last two columns show the calculated pH and the deviation from the correct value of column two. Over the range of 2.2 to 10 the pH may be relied upon to about 0.05 unit. Individual electrodes rarely differed from others in the same solution by more than 2 or 3 millivolts if the pH was 10 or less. This is somewhat better than the oxide electrodes of Parks and Beard (3). A study of their data shows a variation between electrodes of from 3.2 to 5.2 millivolts, even in the

most favorable range. In solutions of pH above 10, the sulfide electrodes showed a maximum variation among themselves of 11.5 millivolts. Table I shows that the sulfide electrode is not reliable in this range even when average values of several electrodes are taken.

Sugar, starch, and nitrates have no deleterious effect upon the electrodes between pH 2.2 and 10. However, hydroxy acids, such as tartaric, citric, and lactic, render the electrode useless. This has been found to be true of the antimony oxide electrode as well (1). The sulfide electrodes were used in the back-titration of alcoholic potassium hydroxide in determining the saponification number of oils. As would be expected, the strongly alkaline solution quickly removes the sulfide film, but the electrode still functions. The end point as determined by finding the maximum value of $\Delta E/\Delta V$ agrees with the phenolphthalein end point. In this respect the sulfide electrode offers no advantage over the ordinary antimony-antimony oxide electrode.

SUMMARY

1. Antimony electrodes coated with antimony sulfide have been prepared by five different methods.

2. Electrodes prepared by suspension in hot 0.30 *N* nitric acid for 1 hour, followed by saturation with hydrogen sulfide, may be used to determine the pH of solutions in the range from 2 to 10.

3. Electrodes so prepared agree among themselves within about 3 millivolts if the pH is 10 or less, but may differ by as much as 11.5 millivolts in more alkaline solutions.

4. Starch, sugar, and nitrates have no deleterious effect in the range over which the electrode functions in their absence.

5. The electrode, like the oxide electrode, is useless in the presence of hydroxy acids.

6. The electrode should be useful in determining the saponification of highly colored oils, but offers no advantage over the ordinary antimony electrode.

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Colorimetric Determination of Fluorine

O. M. SMITH AND HARRIS A. DUTCHER, Oklahoma Agricultural and Mechanical College, Stillwater, Okla.

THE fluoride content of natural water has taken on new significance, since the researches of Smith, Lantz, and Smith (4), Churchill (2), and Kehr (3) have shown that it may be the cause of the tooth defect known as mottled enamel. Of the numerous methods which have been devised for the detection and determination of fluorides, few find satisfactory application in the field of water analysis, where a very sensitive method is required.

In the modified Casares-DeBoer method used by Thompson and Taylor (5), the fluorides are determined by the degree of fading of a zirconium-alizarin lake. Willard and Winter (6) suggest the use of quinalizarin (1, 2, 5, 8-tetrahydroxyanthraquinone) as an indicator in their method. Quinalizarin seems to the writers to have advantages over alizarin when used as in the Casares-DeBoer method, in that it is more sensitive to small changes in fluoride content and the change in color is easier to distinguish. For example, a difference in color between samples containing 0.2 and 0.4 part per million is greater in the case of zirconium-quinalizarin than zirconium-alizarin reagent. The best range of the colorimetric standards is from 0 to 2 p. p. m. or 0.0 to 0.1 mg. of fluoride per 50 ml. Above this concentration the fading is too great, and comparisons are not easily made.

RECOMMENDED METHOD

The zirconium-quinalizarin reagent is prepared by mixing equal parts of a 0.14 per cent solution of quinalizarin (1, 2, 5, 8-tetrahydroxyanthraquinone) and an 0.87 per cent solution of zirconium nitrate, and diluting the mixture 1 to 40. The quinalizarin is dissolved in a 0.30 per cent sodium hydroxide solution, as it is insoluble in water.

METHOD OF ANALYSIS. Precipitate the sulfates by the addition of 5 ml. of 2 per cent barium chloride solution to 100 ml. of the sample. After settling several hours, draw off a 50-ml. portion for the test. The barium sulfate may be filtered off if desired. Add 3 ml. of 1 to 1 hydrochloric acid and 5 ml. of the zirconium nitrate-quinalizarin reagent and mix thoroughly. After 20 minutes compare with standards made at the same time and in the same manner. Comparisons are easily made in

American Public Health Association tubes with standard fluoride solution containing from 0 to 2 p. p. m. in steps of 0.2 part.

The fading of the color of the zirconium-quinalizarin or zirconium-alizarin lake is a function of time, temperature, and acidity. After 15 minutes at room temperature the change is very slow and the color remains sufficiently constant for comparisons. Care must be taken that exact amounts of indicator (zirconium-quinalizarin reagent) and acid are added to the sample and to the standards and that the time of fading is the same for unknown and standard.

Of the commonly occurring ions, none in the quantities occurring in natural or treated water affect the results except aluminum, iron, sulfates, and phosphates. Less than 20 p. p. m. of sulfates have no effect and may easily be removed by barium chloride, since the Ba^{++} ion has no effect. Iron above 10 p. p. m. changes the color, making comparisons impossible. Aluminum has no effect up to 0.2 p. p. m. as Al; above this amount and up to 0.6 p. p. m. as Al the results will be low by 0.1 p. p. m. of fluorine. Aluminum is rarely present in water in amounts greater than 1 p. p. m. expressed as Al_2O_3 or 0.5 p. p. m. as Al, and may thereby be neglected in most cases. This is further confirmed in the comparative results between those obtained by direct colorimetric and distillation methods. Phosphates affect the color when from 0.3 to 0.4 p. p. m. or more are present. The color is different and is easily recognized by one experienced in the determination. Fortunately these two substances rarely occur in water in amounts greater than 0.5 p. p. m. except in certain localities. When they do occur the distillation method seems to be the reliable procedure.

In case phosphates and aluminum are present, distillation with perchloric acid as recommended by Boruff and Abbott (1) will be necessary.

Place the sample containing approximately 0.2 ml. of fluoride in a 125-ml. distilling flask, and add a few glass beads and sufficient dilute sodium hydroxide to make it just alkaline to litmus. Reduce the volume to 10 to 15 ml. by distilling off the water, and obtain a 50-cc. distillate according to the procedure outlined by Boruff and Abbott (1).

In carrying out the distillation, care must be exercised to avoid bumping, as the presence of much perchloric acid in the distillate will seriously interfere with the colorimetric test. Its presence can be readily detected by the off color of the sample when the reagents are added. The temperature should not be allowed to rise above 150° C., in order to avoid decomposition of the perchloric acid. Sulfuric acid cannot be used, as sufficient passes over into the distillate to affect the color developed on adding the quinalizarin reagent. In routine water analysis the distillation method is time-consuming and it becomes desirable to determine how necessary is this precaution.

In a study of 201 Oklahoma waters, 177 samples had a fluoride content of 1 or less. Of these, 59 gave the same value when determined by both methods; in 88 samples the results obtained by the direct colorimetric method were below those obtained by distillation by an average of 0.13 p. p. m. of fluorine, and in 30 cases they were above by an average of 0.11 p. p. m. The 15 samples containing 1.1 to 2.0 p. p. m. and 9 containing 2.1 and above were too few in number to draw definite conclusions. These 201 cases indicate that the

direct colorimetric method may give results which are about 10 per cent lower than that obtained by distillation.

The authors' experience confirms that of previous investigators that fluorine is usually found in natural waters in quantities less than 2 p. p. m., 95 per cent of the samples containing less than 2.0 p. p. m.; hence a method that is accurate to within 10 per cent of the numerical value, when the fluoride content is from 1 to 2 p. p. m., and that is rapid and reliable should be a valuable acquisition to water analysis and worthy of trial by other investigators.

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Determination of Potash in Fertilizers

F. B. CARPENTER AND R. O. POWELL, Virginia-Carolina Chemical Corporation, Richmond, Va.

MUCH work has been done by the Association of Official Agricultural Chemists to overcome the inaccuracies in the present method, which specifies the determination of only the water-soluble potash, but no attempt has been made to determine the available potash, as in the case of other fertilizer constituents. This method has been in use for a long time and is incorporated in practically all state laws, but there is no logical reason why it should be continued if it does not show the correct results in available potash.

A series of tests was made on a number of mixed fertilizers, including the five samples sent out by the Chemical Control Committee of the National Fertilizer Association, to determine the effect on the percentage of potash produced by washing with larger quantities of water than are specified by the official method. Four successive leachings were made on each sample with approximately 225 cc. of water, and the potash was determined in the separate solutions and in the final residue. Potash was also determined in solutions made with 1 per cent hydrochloric acid. Blank tests were made on all reagents, and the same method was employed in all analyses. The results are shown in Table I.

TABLE I. POTASH DETERMINATIONS IN SOLUTIONS FROM SUCCESSIVE LEACHINGS WITH WATER, FROM RESIDUE, AND FROM HYDROCHLORIC ACID SOLUTIONS

| SAMPLE | LEACHINGS ^a | | | | IN RESIDUE | TOTAL | BOILED* 1 PER CENT HCl SOLUTION |
|--------|------------------------|--------|-------|--------|------------|-------|--|
| | First | Second | Third | Fourth | | | |
| 1 | 17.24 | 0.10 | 0.04 | 0.02 | 0.18 | 17.56 | 17.50 |
| 2 | 3.90 | 0.11 | 0.04 | 0.02 | 0.40 | 4.47 | 4.40 |
| 3 | 3.88 | 0.12 | 0.05 | 0.02 | 0.40 | 4.47 | 4.20 |
| 4 | 4.04 | 0.07 | 0.03 | 0.03 | 0.07 | 4.24 | 4.22 |
| 5 | 3.96 | 0.10 | 0.02 | 0.02 | 0.04 | 4.14 | 4.17 |
| 6 | 5.32 | 0.06 | 0.05 | 0.04 | 0.09 | 5.56 | 5.65 |
| 7 | 4.18 | 0.04 | 0.05 | 0.03 | 0.14 | 4.44 | 4.48 |
| 8 | 3.10 | 0.03 | 0.04 | 0.03 | 0.17 | 3.37 | 3.27 |
| 9 | 3.92 | 0.09 | 0.05 | 0.03 | 0.13 | 4.22 | 4.24 |
| 10 | 5.38 | 0.10 | 0.05 | 0.03 | 0.13 | 5.69 | 5.66 |
| 11 | 6.15 | 0.02 | 0.02 | 0.01 | 0.14 | 6.34 | 6.36 |

* 225 cc. each.

These analyses show that potash is being recovered in small amounts in the fourth washing, after approximately

900 cc. of water have passed through the material, and there still remains from 0.04 to 0.40 per cent in the residues. If the washings had been continued, it is probable that most of the potash would finally have been recovered. If the sum of potash obtained in the different leachings, plus that in the residues, is compared with that obtained in the acid solutions, the results are in close agreement.

The two samples showing the largest amount in the residue, 0.40 per cent, were also tested by washing with water and digesting in ammonium citrate, as in the determination of insoluble phosphoric acid. The results showed 0.06 per cent of insoluble potash in each case.

Solutions made with 1 per cent hydrochloric acid give very good results, especially if neutralized with caustic soda instead of ammonia. There should be no objection to this procedure, as insoluble silicates are not decomposed in acid solutions of this strength.

In all samples the potash was supplied from a soluble source, and the results indicated that some of the potash is slightly fixed, so as to yield slowly to solution in water, but is in a form which is assumed to be readily available as a plant food. This is supported by the fact that the insoluble portion is soluble in ammonium citrate, the standard test for available phosphoric acid. As these tests were made on regular grades of mixed fertilizers, no data are available concerning the amount of potash in the different components, but in previous work similar losses have been confirmed on carefully formulated theoretical mixtures.

CONCLUSION

Much work has been done to perfect the official method so as to obtain theoretical results, but it would appear that the only remedy for correcting the inaccuracies is to change the method so as to determine available instead of water-soluble potash.

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Use of Aëration in Kjeldahl Distillations

W. B. MELDRUM, R. MELAMPY, AND W. D. MYERS, Haverford College, Haverford, Pa.

THE extremely useful method for the determination of nitrogen in organic substances, brought forward by Kjeldahl in 1883 (5) as an extension of a method first applied to urea in 1875 by Heintz and Ragsby (4), has undergone a number of modifications to widen the scope of its application and to facilitate the analysis. One has been the aëration of the alkalinized solution to expedite the sweeping over of the ammonia into the standard acid solution. Suggested by Folin in 1903 (3) in connection with urine analysis,

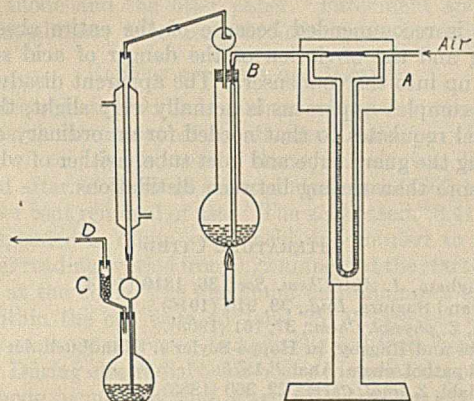


FIGURE 1. DIAGRAM OF APPARATUS

it was proposed as a general procedure in Kjeldahl distillations by Kober in 1908 (6) and by Sebelien in 1909 (7). Dillingham in 1914 (1) and Falk and Sugiura in 1916 (2) demonstrated that complete recovery of the nitrogen by aëration alone was not practicable but that heat was also necessary; aëration alone, even when carried on for several hours, resulted in the recovery of less than 95 per cent of the nitrogen.

Although aëration with simultaneous heating has been used by many analysts with satisfactory results, no critical examination of the method seems to have been made. The authors of this paper failed to find any data in the literature on nitrogen recovery under various experimental conditions or any information as to the most desirable procedure. Accordingly a critical examination was carried through, some of the results of which are summarized in this communication.

PROCEDURE

The substance selected for analysis was *N*-butyramide, procured from the Eastman Kodak Co., and found to give satisfactorily reproducible analyses from a large batch in close agreement with the theoretical nitrogen content of 16.09 per cent. A sample of about 0.2 gram was oxidized with 40 grams of concentrated sulfuric acid, to which were added 10 grams potassium sulfate and 0.5 gram of mercury. The digestion was continued for 30 minutes after the contents of the Kjeldahl flask became colorless.

The ammonia distillation was carried out using the apparatus shown in Figure 1. By the application of suction at *D*, air from outside the laboratory was drawn in through the flowmeter *A* and the inlet tube *B*, passed over together with steam and ammonia, bubbled through the standard acid solution, and drawn out through the guard tube *C*. The guard tube *C* contained glass beads without perforations, and through it the acid solution and the methyl orange indicator were introduced into the receiving flask. The beads, remain-

ing wet with the colored acid solution, served to show whether or not the ammonia was being completely absorbed and to absorb any such that came through; change to the alkaline color at the base of the tube usually did occur, more markedly in the case of high aëration rates. The sodium sulfide solution to precipitate the mercury and the excess sodium hydroxide solution were admitted through a funnel temporarily attached to the inlet tube, *B*. The temperature of distillation was read from a thermometer attached to the inlet tube inside the flask. To this temperature the solution was raised as rapidly as practicable before aëration was begun.

The effects of varying the conditions upon which the rate of distillation might depend were in turn examined. The more important conclusions so far as this investigation was concerned are brought out by the data given in Tables I and II and plotted in Figures 2 and 3.

TABLE I. NITROGEN RECOVERY FOR VARIOUS AÉRATION RATES AT VARIOUS TEMPERATURES

| TEMPERATURE ° C. | AÉRATION RATE L./min. | NITROGEN RECOVERED | |
|---------------------|-----------------------------|--------------------|----------------------|
| | | % | PER CENT RECOVERY |
| 25 | 0.2 | 0.36 | 2.24 |
| | 0.4 | 0.54 | 3.36 |
| | 0.6 | 0.64 | 3.98 |
| | 0.8 | 1.00 | 6.22 |
| 50 | 0.2 | 0.62 | 3.85 |
| | 0.4 | 1.28 | 7.96 |
| | 0.6 | 1.63 | 10.13 |
| | 0.8 | 1.87 | 11.62 |
| 75 | 0.2 | 1.91 | 11.88 |
| | 0.4 | 3.74 | 23.24 |
| | 0.6 | 5.40 | 33.56 |
| | 0.8 | 7.01 | 43.57 |
| 90 | 0.2 | 6.05 | 37.60 |
| | 0.4 | 9.21 | 57.21 |
| | 0.6 | 11.21 | 69.67 |
| | 0.8 | 12.33 | 76.63 |
| 100 | 0.2 | 13.56 | 84.27 |
| | 0.4 | 15.26 | 94.84 |
| | 0.6 | 16.00 | 99.44 |
| | 0.8 | 16.06 | 99.81 |

Data obtained using a sample of 0.2 gram, a total volume for distillation of 250 ml., and with 20-minute distillation. Complete recovery equals 16.09 per cent nitrogen.

It was found that increasing the dilution of the solution greatly slowed up the rate of ammonia distillation. With a solution temperature of 90° C. and an aëration rate of 0.8 liter per minute, the recovery for 15 minutes' distillation

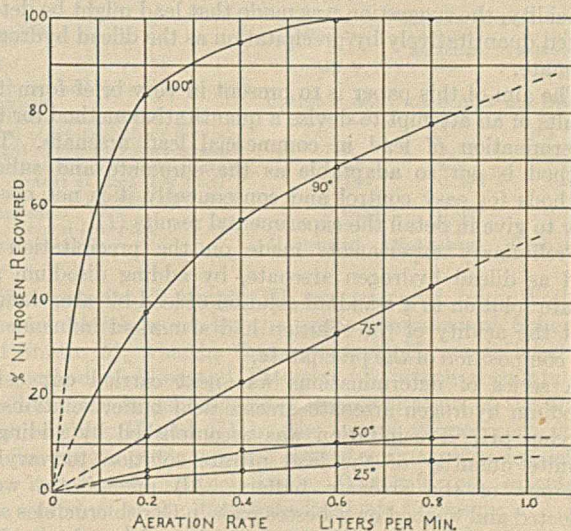


FIGURE 2. RELATION OF NITROGEN RECOVERY TO AÉRATION RATE

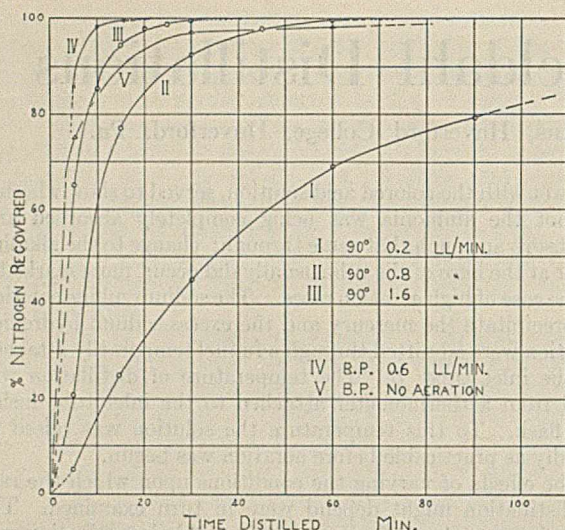


FIGURE 3. VARIATION OF NITROGEN RECOVERY WITH TIME OF DISTILLATION

was 95.93, 79.86, and 58.67 per cent, from total volumes of 100, 300, and 500 ml., respectively.

It was also found that it makes little difference whether the inlet tube delivers the air in large bubbles or in small bubbles distributed more widely through the solution.

SUMMARY

1. The conditions favorable for carrying out Kjeldahl distillation using aëration are indicated. With fairly rapid aëration at the boiling point of the solution distillation is complete in less than 15 minutes.

2. In addition to the saving of time involved, the use of

TABLE II. NITROGEN RECOVERY FOR VARIOUS TIMES OF DISTILLATION

| AERATION RATE L./min. | TIME OF DISTILLATION Min. | NITROGEN RECOVERED % | PER CENT RECOVERY |
|--------------------------|------------------------------|-------------------------|-------------------|
| 0.2 | 5 | 0.95 | 5.90 |
| | 15 | 3.93 | 24.42 |
| | 30 | 7.20 | 44.74 |
| | 60 | 11.08 | 68.89 |
| | 90 | 12.78 | 79.43 |
| 0.8 | 5 | 3.41 | 21.19 |
| | 15 | 12.32 | 76.57 |
| | 30 | 14.89 | 92.54 |
| | 45 | 15.59 | 96.88 |
| | 60 | 16.11 | 100 |
| 1.6 | 5 | 10.51 | 65.32 |
| | 10 | 13.72 | 85.27 |
| | 15 | 15.27 | 94.94 |
| | 20 | 15.75 | 97.89 |
| | 25 | 15.95 | 99.12 |
| | 30 | 16.10 | 100 |

Data obtained using a sample of 0.2 gram, a total volume of solution of 250 ml., and a distillation temperature of 90° C. Complete recovery equals 16.09 per cent nitrogen.

aëration is recommended because of the entire absence of bumping and the obviation of the danger of acid solution backing up into the condenser. The apparent disadvantage of more complex apparatus is actually very slight, the only additional requisites to that needed for an ordinary distillation being the guard tube and inlet tube, neither of which requires more than rinsing between distillations.

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Determination of Lead as Dilead Hydrogen Arsenate

C. L. DUNN AND H. V. TARTAR, Chemistry Department, University of Washington, Seattle, Wash.

AN INVESTIGATION in this laboratory (2) on the system $PbO-As_2O_5-H_2O$ showed that dilead hydrogen arsenate, Pb_2HAsO_4 , is very insoluble; the results indicated that its solubility is comparable to that of the chromate and sulfate. Since this compound exists over such a wide range of acidity, the suggestion was made that lead might be determined quantitatively by precipitation as the dilead hydrogen arsenate.

The aim of this paper is to present in very brief form the results of an attempt to devise a quantitative method for the determination of lead in commercial lead arsenate. The method is not so adaptable as the chromate and sulfate methods for easy control and consequently it is not necessary to give in detail the experimental results (1).

Preliminary experiments made on the precipitation of lead as dilead hydrogen arsenate, by adding disodium arsenate solution to a standard solution of lead nitrate, showed that the acidity of the solution had a marked influence on the composition of the precipitate.

A series of determinations was next carried out using disodium hydrogen arsenate-arsenic acid buffer solutions of varying pH. Precipitation was accomplished by adding a definite quantity of the lead nitrate solution to varying amounts of the arsenate buffers. All precipitates were collected and washed on asbestos pads in Gooch crucibles and dried at 120° C. The pH of the solutions changed considerably during the precipitations, becoming more acid. The

data afforded evidence that a still greater control of the hydrogen-ion concentration would be necessary to obtain precipitates corresponding in composition to dilead hydrogen arsenate.

Further experiments showed that lead can be precipitated quantitatively from a solution of lead nitrate as dilead hydrogen arsenate by the use of a disodium hydrogen arsenate-arsenic acid buffer solution. The proper acidity necessary for precipitation is pH 4.6—that is, just alkaline to methyl orange. Any marked change in the acidity due to the liberation of nitric acid will materially change the composition of the precipitate obtained. The acidity can be kept sufficiently constant during the precipitation by the gradual addition of a dilute solution of sodium hydroxide using methyl orange indicator. The arsenate solution should be subjected to mechanical stirring during the precipitation.

Attempts were also made to precipitate as dilead hydrogen arsenate the lead in samples of commercial lead arsenate. The samples were dissolved in 0.5 N nitric acid. The results indicated that fairly accurate results can be obtained. The procedure is laborious and necessitates too close control to rival the present accurate sulfate and chromate methods.

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RECEIVED October 12, 1932. Resubmitted September 26, 1933.

Purification of Substances by Electrodialysis

ALBERT L. ELDER, RUSSELL P. EASTON, HAROLD E. PLETCHER, Syracuse University, AND FLOYD C. PETERSON, New York State College of Forestry, Syracuse, N. Y.

MANY references are to be found on the subject of electrodialysis, and new applications and uses are numerous. Most of the data reported in the present paper have resulted from research necessary to obtain a substance of a certain purity for use in some other investigation.

The apparatus used in the electrodialysis experiments was essentially that described by Holmes and Elder (4). In all experiments a piece of platinum foil was placed between the carbon anode and the filter paper. Parchment and Cellophane membranes were used throughout the investigation.

ELECTRODIALYSIS OF CASEIN

Samples of both acid and rennin casein were obtained from the research laboratory of the Borden Company. The ash content of acid casein before electrodialysis was 3.69 per cent and after 56 hours of electrodialysis was 0.067 per cent, a 98.4 per cent removal of ash. The acid casein (8.41 grams) was suspended in dilute acetic acid and diluted to 850 cc. Ammeter readings varied from 0.22 ampere at the start to 0.027 ampere at the end. The maximum and minimum temperatures within the cell were 45° and 25° C., respectively. A sliding resistance was used to keep the cell from heating too much. During electrodialysis a horny material deposited on the cathode membrane, and, when dried, had an ash content of 0.069 per cent.

In two other electrodialysis experiments no acetic acid was added, but the acid casein was kept in suspension by vigorous mechanical stirring. Ash removals of 95.2 and 97.3 per cent were obtained after 42.2 and 28 hours, respectively. In the first of these two runs the ammeter readings were 0.130 maximum and 0.0091 minimum, and in the second 0.425 and 0.0108. Temperature variations were from 25° to 51° C. Of the 11.35-gram sample of acid casein used in the second run, 8.81 grams were recovered by filtering the electrodialyzed solution.

Removal of the ash from rennin casein was not as satisfactory. The original ash content was 7.98 per cent and the final 2.17 per cent, an average ash removal of 72.9 per cent. Considerable difficulty was encountered with casein sticking to the mechanical stirrer.

ELECTRODIALYSIS OF GRAPE JUICE

It appeared likely that the ash content of unfermented grape juice could be lowered by electrodialyzing out the tartrates present. Cellophane membranes were mounted wet on the cell and held in place by rubber bands. The potential current was held at 120 volts. The drip water was collected through funnels supported below the filter papers which were between the carbon blocks and the Cellophane membranes.

In preliminary experiments Kahlbaum's c. p. potassium acid tartrate was added to water and electrodialyzed, using Sutton's method (6) to determine the tartaric acid in the positive drip. Ninety-six per cent of the potassium acid tartrate was recovered in the drip waters and in the cell; 40 per cent of the 4.08-gram sample placed in the electrodialysis cell was removed in 12 hours by electrodialysis. As a further check on the acid collected in the positive drip, carbon and hydrogen analyses were made, and the excellent checks obtained indicated that nearly pure tartaric acid was obtained in the positive drip water.

Samples of commercial grape juice were diluted 1 to 1 and placed in the electrodialysis cell. The average of several determinations gave 18 to 20 per cent removal of the tartrate radical present in the grape juice in 3 hours. The flavor of the grape juice was unchanged by electrodialysis. The main pigments, anthocyanins or enins (1, 2), in grape juice did not come through the membranes during the electrodialysis.

ELECTRODIALYSIS OF SUGARS

One difficulty encountered by workers in sugar chemistry is that of preparing the sugar in an ash-free condition. The isolation and purification of arabogalactan by the lead-tannate method of Schorger and Smith (5) result in a product which even under very careful purification contains an appreciable amount of ash, only a portion of which under normal conditions is removable by repeated solution and precipitation.

This procedure results in a great loss of the purified sugar. The ash content of material purified by such methods is never so low that the sugar may be considered ash-free. Englis and others (3) found that electrodialysis of samples of artichoke sirup, from which levulose is obtained, produced part of the necessary acidification which resulted in a final lower ash content of the levulose. They found that the colloid content of the extract was also reduced.

Table I shows typical results in further purification of sugars by electrodialysis. The amorphous powder, sample III, before electrodialysis was straw-colored and had an ash content of 1.39 per cent. After electrodialysis and subsequent precipitation the sugar was snow-white and contained 0.063 per cent of ash. Aqueous solutions before electrodialysis were slightly turbid, while the dialyzed solutions were perfectly clear, making possible accurate polariscopic readings. The reducing value of the sugar was unchanged by electrodialysis, indicating that no hydrolysis took place during the purification. The maximum temperature during the electrodialysis was 55° C.

TABLE I. PURIFICATION OF SUGARS BY ELECTRODIALYSIS

| Sugar | SAMPLE I Galactose | SAMPLE II Arabo- galactan 120 | SAMPLE III Arabo- galactan 120 |
|---|-----------------------|--|---|
| Volts | 120 | | |
| Maximum and minimum ammeter readings | 0.0128-0.004 | 0.05-0.0129 | 0.2-0.006 |
| Maximum temperature | 46° C. | 26° C. | 55° C. |
| Period of electrodialysis (hours) | 48 | 43 | 72 |
| Weight of sugar at start (grams) | 7.6 | 10.31 | 10 |
| Weight of sugar recovered (grams) | 5.02 | 9.0 | 7.64 |
| Ash content at start (per cent) | 0.156 | 0.278 | 1.39 |
| Ash content purified product (per cent) | 0.0135 | 0.027 | 0.063 |
| Ash removal (per cent) | 91.3 | 90.3 | 95.6 |
| Specific rotation | Unchanged | Not taken | Unchanged |

The material of sample III was prepared from Western American larch wood by the original method of Schorger and Smith (5), whereas that in sample II was isolated by the method of Wise and Peterson (7), which accounts for the difference in ash content. Reprecipitation of the sugar from samples II and III by the use of 95 per cent ethyl alcohol gave a product which settled very rapidly and left a clear supernatant mother liquor. The galactose, sample I, was a product of the Pfanstiehl Products Company.

Further studies are being made on other simple sugars, polysaccharides, and hemicelluloses.

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New Apparatus for Determination of Size Distribution of Particles in Fine Powders

ROBERT T. KNAPP, California Institute of Technology, Pasadena, Calif.

EVERY year a greater need for accurate analysis of the size distribution of subsieve material is being felt by the engineer, because of the increasingly vital part it plays in the manufacture of cement, pigments, and other powdered products. Sieves are a satisfactory means of obtaining this information as long as the material is relatively coarse, but when from 70 to 95 per cent of the sample passes the 200-mesh screen (the finest one giving consistent reading), some new scheme of analysis must be used.

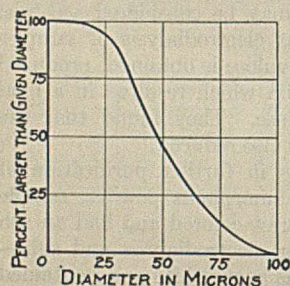


FIGURE 1. CUMULATIVE DISTRIBUTION CURVE

Several methods of analyzing this fine fraction have been developed. For example, Professor Work at Columbia has perfected an excellent microscope technic. Elutriation and sedimentation methods employing various fluid media have been shown to be feasible, and additional methods are constantly being developed, but most of them are slow and tedious.

Some time ago the Riverside Cement Company inaugurated a comprehensive research program. A consideration of its scope quickly showed that to carry on the program it was absolutely necessary to have some reliable method of making large numbers of subsieve analyses. After considerable study it was concluded that none of the existing instruments were satisfactory for the purpose; therefore, the development about to be described was undertaken.

Before starting the design of the instrument a careful analysis of the needs of the research program was made, which resulted in setting up the following five specifications:

1. High accuracy.
2. Ability to determine complete size distribution as distinguished from a fineness modulus or a value of total surface.
3. Capacity for analyzing a large number of samples per day.
4. Ability to use relatively large samples to reduce sampling errors.
5. Freedom from personal equation of the operator.

The principle upon which the new instrument was to operate was then chosen by comparing the above specifica-

tions with the operating characteristics of existing instruments.

The microscopic method was eliminated because it was too slow and employed too small a sample. Elutriators appeared unsuitable because of their doubtful accuracy and the length of time required to separate the sample into a large number of fractions. Methods involving light-scattering appeared to show promise for the determination of total surface but not for size distribution. In spite of the fact that existing instruments required prohibitive amounts of attention and their results were largely qualitative, the sedimentation method appeared to be the most promising; consequently this principle was adopted as the basis of the new design.

THEORY

STOKES' LAW. When a small body is allowed to fall freely in a viscous fluid, it soon reaches a velocity where the downward acceleration is balanced by the friction. Therefore, the velocity ceases to increase. This limiting velocity is expressed by the equation known as Stokes' law

$$V = \frac{2g(\sigma - \sigma_m)r^2}{9\eta} \quad (1)$$

where V = velocity of fall
 g = acceleration of gravity
 σ = density of falling substance
 σ_m = density of fluid medium
 η = viscosity of fluid medium
 r = radius of the particle

For the present purpose, the time required for a particle to fall a given distance is more interesting than the velocity. Therefore, the equation becomes

$$T = \frac{H}{V} = \frac{9H\eta}{2g(\sigma - \sigma_m)r^2} \quad (2)$$

where T = time of fall
 H = height of fall

If the height, viscosity, and densities are held constant, this becomes

$$T = \frac{K}{r^2} \text{ or } r = \frac{K_1}{\sqrt{T}} \quad (3)$$

K and K_1 being constants.

If a known weight of material composed of different sized particles is allowed to settle a distance H through a column of liquid, the relation between the weight of the material reaching the bottom and the time can be determined. By means of Equation 3, values of the radius, r , or diameter, d , can be substituted for the corresponding times, T , and the curve similar to Figure 1 constructed.

This curve supplies the desired information about the size distribution of the particles in the sample. Unfortunately,

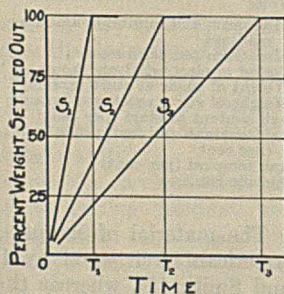


FIGURE 2. SETTLING CURVE

there are great difficulties in the experimental determination of this curve. The most serious one is encountered when an attempt is made to start a sample settling from the top of the column of liquid. Since the layer of sample (dry or mixed with a small quantity of liquid) is considerably more dense than the underlying liquid, the condition is very unstable and the sample tends to go en masse to the bottom, forming strong eddy currents on the way. This is a fundamental difficulty, and one for which as yet no remedy has been found.

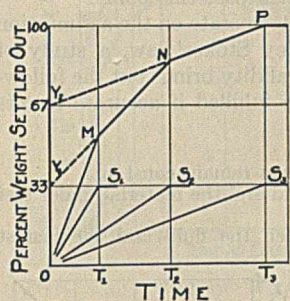


FIGURE 3. SETTLING CURVE

OPERATION OF SEDIMENTATION APPARATUS (3). The simplest method of starting sedimentation is to stir the sample thoroughly into the liquid until a homogeneous mixture is obtained, and then allow it to settle. However, this entirely changes the relation between the time of settling and the amount of material reaching the bottom, because the height is no longer the same for each particle. Nevertheless, there is a definite relation between the rate of settling in this latter case and that of the hypothetical sample which is all started from one definite height. Therefore, if the time settling rate relation is determined for the homogeneous mixture, the size distribution of the particles in the sample is readily obtainable. This relation is unique and interesting and is best illustrated by the consideration of a hypothetical example.

A sedimentation column of height H is available. Three samples of known uniform size are to be used: The first sample, s_1 , consists of particles, all of which have a radius r_1 ; the second, s_2 , of radius r_2 ; and the third, s_3 , of radius r_3 . All the constants of Equations 2 and 3 are known. Substituting in the numerical values, it is determined that the particles of s_1 will settle distance H in T_1 minutes, s_2 in T_2 , and s_3 in T_3 .

First s_1 is placed in the sedimentation column, mixed thoroughly, and allowed to settle. Since the particles are all of the same size, they will all settle with the same velocity. As they are distributed uniformly throughout the column, the amount collected on the bottom will be a linear function of the time, being 0 per cent at time 0, and 100 per cent at the time T_1 , as shown in Figure 2, curve s_1 . Likewise, if sample s_2 is tested in the same manner the result will be represented by curve s_2 , and in the same way s_3 is obtained. All these relations are straight lines, because all the samples consisted of uniform sized particles, which were uniformly distributed in the sedimentation chamber.

Now, a sample consisting of one-third s_1 , one-third s_2 , and one-third s_3 is placed in the sedimentation column. If s_1 were settling out alone it is obvious that the curve would be the one labeled s_1 in Figure 3, since there is only $33\frac{1}{3}$ per cent of s_1 . Likewise s_2 and s_3 would be as shown, if either were the only one present.

Since they are all settling together, in the time T_1 , all of s_1 will be out, together with a per cent of s_2 and b per cent of s_3 ; therefore, the total per cent out will be:

$$M = 33\frac{1}{3} + a + b$$

but $a = 33\frac{1}{3} \times \frac{T_1}{T_2}$ and $b = 33\frac{1}{3} \times \frac{T_1}{T_3}$

Therefore $M = 33\frac{1}{3} \left(1 + \frac{T_1}{T_2} + \frac{T_1}{T_3} \right)$

Likewise at time T_2 all of s_1 and s_2 will be out, together with

$$c = 33\frac{1}{3} T_2 / T_3 \text{ from } s_3$$

That is, $N = 33\frac{1}{3} (1 + 1 + T_2/T_3)$

At time T_3 , all the sample will have settled out, so point $P = 100$ per cent. Since the individual settling curves are straight lines, the composite curve will be the broken straight line $O-M-N-P$. It is instructive to investigate where $N-M$ produced crosses the y axis—i. e. the point Y_1 . By inspection this simple geometric relation is obtained:

$$Y_1 = M - T_1 \left(\frac{N - M}{T_2 - T_1} \right)$$

Substituting in the previously determined values for M and N and simplifying, this becomes $Y_1 = 33\frac{1}{3}$.

Likewise, $P - N$ produced intersect the y axis at Y_2

$$Y_2 = N - T_2 \left(\frac{P - N}{T_3 - T_2} \right) = 66\frac{2}{3}$$

This is significant, since $33\frac{1}{3}$ is the per cent of s_1 in the total sample, and $66\frac{2}{3}$ is the sum of the percentages of s_1 and s_2 .

ODEN'S INTERPRETATION OF SETTLING CURVES. The above hypothetical example serves to illustrate the method used by Oden to interpret settling curves. He proved that the above relations hold in any suspension of different sized particles of the same substance where the sizes are such that they follow Stokes' law. A general statement of the method is as follows:

If the sedimentation curve is plotted with the time of the settling as abscissa and the weight of the material as ordinate, then the intercept on the y axis of a tangent to the curve at a point T will give the per cent of the sample whose particles have diameters equal to or larger than that of a particle which would just settle a distance equal to the height of the sedimentation column in the time T .

A more mathematical derivation of this relation is given below.

PROOF OF INTERCEPT METHOD OF INTERPRETING SETTLING CURVES. The derivation postulates (a) that particles of a given diameter have a constant and characteristic rate of fall in a given liquid; (b) that the particles are uniformly distributed throughout the liquid at the instant settling commences; and (c) that the particle concentration is sufficiently low so that there is no interference.

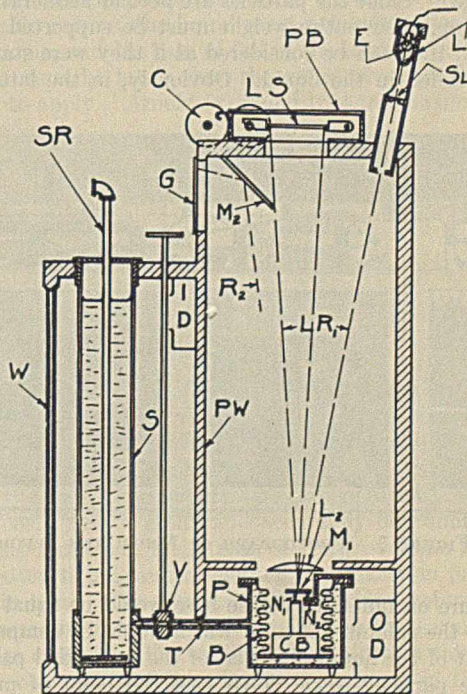


FIGURE 4. SECTIONAL DIAGRAM OF MICRONE-TER UNIT

Given a settling curve of weight settled out, W , plotted as a function of time t , let W_t equal the weight of the fraction whose particles have a fall time t for the height of the liquid column.

Therefore $\frac{dW}{dt}$ equals the rate of settling out of this fraction and $\tau \frac{W_t}{t}$ equals the weight of this fraction settled out in time τ .

Now $\frac{dW}{dt} = \int_0^\infty \frac{W_t}{t} dt$, since all fractions with settling times of t or less are all settled out and therefore do not contribute to $\frac{dW}{dt}$.

Consider time τ :

$$\begin{aligned} W_\tau &= \int_0^\tau W_t dt + \int_\tau^\infty \tau \frac{W_t}{t} dt \\ &= \int_0^\tau W_t dt + \tau \int_\tau^\infty \frac{W_t}{t} dt \end{aligned} \quad (4)$$

That is, total weight settled out at time τ = the sum of all fractions having settling times of τ or less + proportional amounts of all fractions having settling times greater than τ .

$$\text{Now} \quad \left[\frac{dW}{dt} \right]_\tau = \int_\tau^\infty \frac{W_t}{t} dt \quad (5)$$

Substituting in Equation 4

$$W_\tau = \int_0^\tau W_t dt + \tau \left[\frac{dW}{dt} \right]_\tau$$

$$\text{or} \quad \int_0^\tau W_t dt = W_\tau - \tau \left[\frac{dW}{dt} \right]_\tau = I_\tau \quad (6)$$

since $\int_0^\tau W_t dt$ is the total weight of all fractions having settling times of τ or less.

It should be noted that this derivation assumes no specific law of settling beyond the three postulates; therefore this method of analysis may be used under any settling conditions for which the relation between particle diameter and settling time can be experimentally determined, whether or not Stokes' law is applicable.

MEASURING AMOUNT OF MATERIAL SETTLING OUT. The next question to be answered is: How can the amount of material reaching the bottom of the sedimentation column in a given time be measured? There are several ways of doing this, but one of the simplest is to measure the hydrostatic pressure just above the bottom of the column. This is the method used by Wiegner in his instrument for silt analysis (4). Since the particles are neither accelerating nor decelerating, their entire weight must be supported by the liquid and they can be considered as if they were stationary and suspended in the liquid. Obviously, in the latter case

the liquid because a volume of liquid equal to the volume of the settled-out material flows into the column. Thus it can be stated that the change in pressure at the point on the wall of the sedimentation column is directly proportional to the amount of material that has settled past this point.

Since sedimentation instruments operate on the assumption that the suspended particles obey Stokes' law, a study of Equation 1 and the range of its validity brings out the following as conditions which must be fulfilled if accurate results are to be obtained:

1. The viscosity of the fluid must remain constant.
2. The densities of both the fluid and the material under test must not vary.
3. The relative velocity between the fluid and the fastest moving particles must not be over a certain critical maximum—i. e., the velocity above which local turbulence is set up.
4. There must be no thermal convection currents to upset equilibrium.

Conditions 1, 2, and 4 all point to one conclusion—namely, that temperature must be very carefully controlled.

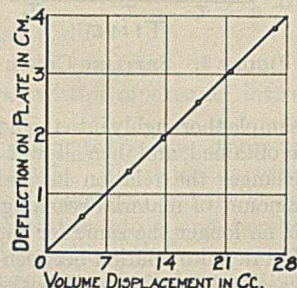


FIGURE 6. CALIBRATION CURVE FOR PRESSURE UNIT

DESCRIPTION OF APPARATUS

The apparatus (1) finally constructed depends upon the principles just discussed. It consists of six sedimentation units, each equipped to measure and record the change in pressure at the bottom of the column. These units are in one housing, using a common source of time axis movement, a common liquid supply and removal system, and a common system of temperature control. A schematic diagram of the arrangement is seen in Figure 4.

Each unit consists of a glass-walled sedimentation tube S , which contains a stirring rod SR . The tube is closed at the bottom by a brass casting, containing a small pressure-measuring orifice. This is connected to the pressure cell P by means of the tube T . The connection can be opened or closed by means of the valve V , whose operating handle projects out through the top of the case. The pressure cell P is composed of a rigid outer case containing a metal bellows B . The change of pressure acting on the closed bottom of the bellows causes it to move. The pressure due to the normal column of liquid is counterbalanced by the mass CB which is fastened to the bottom of the bellows. The movement of the bellows is indicated by the tilting of the mirror M_1 , to which are fastened three needle-point supports. One, N_1 , bears on a glass surface on the top of a pedestal fastened to CB and therefore to the bottom of the bellows. The other two, N_2 , rest on a bracket which is fastened rigidly to the case of P , and therefore has no movement. The tilting of the mirror is recorded by a beam of light, whose source is a small globe E . This is focused on the slit SL by means of the lens L_1 . The beam passes through the lens L_2 , to the mirror M_1 , then back through L_2 which brings it to a sharp focus on the lantern slide plate LS , housed in a light-tight plate box PB . The plate rests in a carriage which is given a motion perpendicular to the plane of the paper through the medium of the clock shaft C and a train of gears. The operating range of the beam of light is shown by the dotted lines LR_1 . For lower pressures the ray travels forward toward the settling tube S . As it leaves the front edge of the photographic plate it passes onto the mirror M_2 , which reflects it onto a small strip of ground glass G visible from the front of the apparatus. The position of the ray in this state is shown by the dotted line R_2 . The intensity of the light

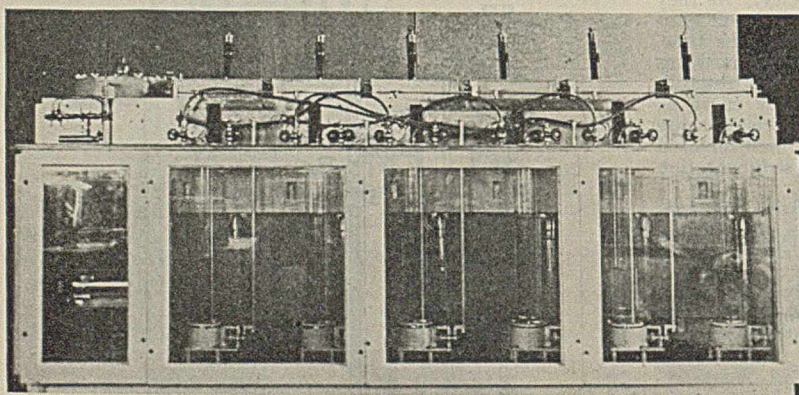


FIGURE 5. PHOTOGRAPH OF APPARATUS BEFORE INSTALLATION

the pressure on unit area at the base would be equal to the weight of the column above it, which would be composed of the weight of the liquid plus that of the suspended particles. When the particles settle down past the point of pressure measurement, the pressure decreases. The decrease is only equal to the apparent weight of the particles suspended in

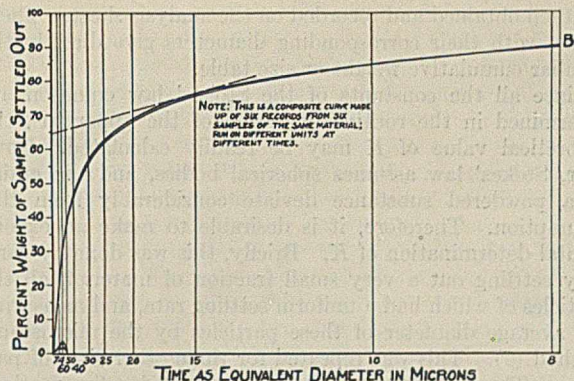


FIGURE 7. ANALYZING SCREEN

is controlled by a small rheostat and millimeter located near the ground-glass window *G*. A stationary mirror is also provided which projects a fixed light spot on the plate. This spot traces a reference line which defines both the zero value and the direction of the abscissa independent of the rough edge of the photographic plate.

Six of these units are housed in one case which has a set of windows *W* running along the entire front, so that the settling chambers can be inspected at all times. The case is divided into two parts by a partition wall *PW*, which comes down low enough to protect the optical system from too much stray light. At the upper part of the sedimentation compartment there is an air inlet *ID* running the entire length of the case, with numerous ports to supply air. The corresponding outlet duct *OD* is in the lower right-hand corner of the case. These ducts are connected with a blower and a heater box outside the case. The electric heater units are controlled by a sensitive thermoelement located inside close to the sedimentation tubes. Thus the entire case is operated as an air-bath thermostat. Figure 5 is a photograph of the apparatus as it appeared before installation.

The clock shaft *C* runs along the entire length of the case and drives the carriages of all the units. The power is supplied by a small synchronous motor which furnishes a reliable as well as a convenient means of obtaining the movement of the time axis.

LIQUID SYSTEM. In the operation of the apparatus it is necessary to have a supply of the liquid at the correct temperature and also a removal system to take care of the liquid

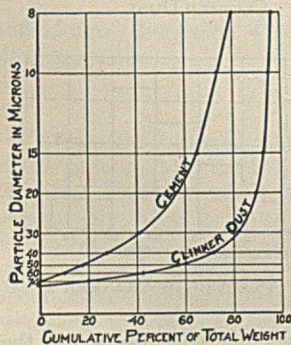


FIGURE 8. METHOD OF PLOTTING SIZE DISTRIBUTION DATA

Particle diameter vs. cumulative per cent of total weight

in the sedimentation chambers after analyses are completed. To meet this first requirement a thermostated storage tank is provided. The tank is arranged so that air pressure can be supplied to it and a system of piping carries the liquid to each sedimentation chamber. Thus by opening a valve the desired unit can be filled with fresh liquid. The used liquid is removed by applying suction to the hollow stirring rod. It is then stored in settling tanks for several days, after which the nearly clear liquid passes through a filtering system and is returned to the thermostated tank for further use. Care is taken to remove any traces of moisture introduced by the sample. A careful watch is maintained to see that no trace of flocculation appears in any of the units, and a suitable deflocculator is added as necessary to maintain the concentration well above the limit of safety.

ACCESSORIES. The necessary instruments for standardizing the liquid and for determining the density of the samples are located inside the case because of the desirability of

making these determinations at the working temperature. They are so arranged that the measurements can be made from the outside. The viscosity is measured with a capillary tube pipet. The densities of the liquid and of the samples are determined with the help of an analytical balance mounted on the left end of the case. A fine wire is carried down from one pan into the inside of the apparatus. Liquid densities are obtained by means of an Invar plummet suspended from the wire and immersed in a beaker of the liquid. Sample densities are obtained by hanging a small bucket from the wire. A small amount of the material is placed in the bucket and weighed. The bucket is then immersed in the beaker of the fluid, the density of which has just been determined, and weighed again. Obviously, the sample density can be calculated from these two weights. A very necessary precaution in this procedure is to insure that no air is trapped in the sample when it is weighed in the liquid.

In order to facilitate operation, the apparatus is located in a dark room. This makes the changing of the plates a very simple matter, and facilitates temperature control because

the entire room is used as a secondary thermostat and its temperature is held constant within $\pm 0.5^\circ \text{F.}$ ($\pm 0.3^\circ \text{C.}$)

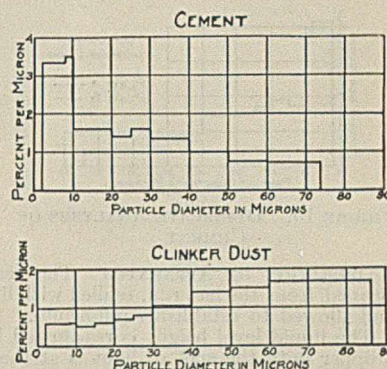


FIGURE 9. METHOD OF PLOTTING SIZE DISTRIBUTION DATA

Method most employed in representing Microneter data

CALIBRATION AND OPERATION

Several factors govern the choice of the liquid to be used in the sedimentation. Most of these depend upon the sample itself; therefore a suitable liquid must be selected for each class of material. The sample and the liquid must have no chemical reaction, the liquid must not induce flocculation of the sample, and the rate of fall of the larger particles of the sample must be lower than the value at which Stokes' law ceases to apply. Arnold (2) found that the maximum allowable radius is

$$r_{\text{max.}} = \frac{0.6\eta}{v\sigma_m} \tag{7}$$

Combining this with

$$V = \frac{2g(\sigma - \sigma_m)r^2}{9\eta} \tag{1}$$

and solving for viscosity

$$\eta_{\text{min.}} = \sqrt{0.37r_{\text{max.}}^2 g \sigma_m (\sigma - \sigma_m)} \tag{8}$$

This is the minimum allowable viscosity for the liquid to be used with a sample whose largest particles have a radius $r_{\text{max.}}$ Care must be taken to stay well over this limit.

It is necessary to know how much the beam of light deflects because of a given pressure change in the sedimentation chamber. This is easily and accurately determined by suspending a series of metal rods of known volume in the sedimentation liquid, and measuring the deflection produced by each in turn. The displacement of a given volume of liquid increases the head, or pressure, at the measuring orifice a definite amount. The calibration obtained in this manner is an over-all one, and thus includes all errors in the pressure element, optical system, etc. Figure 6 is an actual calibration curve for a unit. The deviations are so small that a

straight-line calibration may be assumed. With this value determined it requires simply routine calculation to secure the sample weight for each unit so that the pressure ordinate on the plate will have the desired scale. Likewise the position of the initial liquid level is calculated so that when the sample is added the recording spot will fall on the plate. When this initial level is known the corresponding position of the point of light, which under these conditions appears

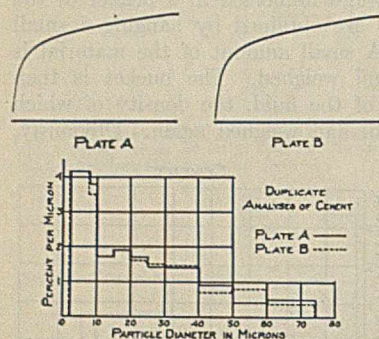


FIGURE 10. DUPLICATE ANALYSES OF CEMENT

OPERATION OF APPARATUS. The sedimentation chamber is cleaned from the last run, refilled with liquid to the correct level, and allowed to establish equilibrium.

The liquid level height is readjusted by means of a medicine dropper until the spot of light is at the correct position on the front ground glass. The light is then turned off.

The room is darkened and the plate carriage is loaded with the correctly labeled plate. The plate box cover is replaced and the rest of the operation is carried on with normal illumination in the room.

The valve between the sedimentation chamber and the pressure unit is closed and the sample is emptied into the chamber.

The sample is stirred vigorously.

The plate carriage gear train is then thrown into mesh and the light in the optical bench turned on.

A few more strokes are made with the stirring rod and the valve is opened immediately after the completion of the last stroke. The stirring rod remains in position throughout the run.

Nothing is disturbed for 3.25 hours. At the end of this time the recording light is turned off, the valve is closed, the photographic plate is removed, and the unit is ready to be cleaned for the next run.

The position of the movable spot on the ground-glass window before the sample is added is determined so that the addition of the calculated weight of sample causes this spot to coincide in position with the stationary reference spot at the instant the run commences. The reference line, therefore, locates the origin of the curve, and is used for that purpose during the analyzing process.

ANALYSIS OF PLATES. After development, the plates are analyzed by the tangent method previously discussed. To increase the speed of this work a projector is employed which projects the image of the curve, magnified about 4 diameters, upon the under side of the opal-glass screen. The plate may be moved in directions parallel to the two axes by means of the adjusting rods seen projecting up through the top. The screen is ruled as shown in Figure 7. The y axis is graduated to show per cent settled out, since this is directly proportional to change in pressure. The x axis is of course the time axis, but is graduated as diameter in microns, using the relation of Equation 3, $r = K/\sqrt{T}$.

The technic of analysis is as follows: A plate is placed in the projector, its image appearing on the screen as in A-B (Figure 7). The position of the plate is then adjusted until the zero reference line is parallel to the abscissa and the upper edge of this reference line passes through the origin on the screen. The y intercepts of the tangents to the top edge of the curve at the points of intersection of the micron lines

are then obtained and recorded on the analysis sheet. These values with their corresponding diameters give directly the familiar cumulative weight or size table.

Since all the constants of the Stokes' law equation are determined in the routine operation of the apparatus, the theoretical value of K may be readily calculated. However, Stokes' law assumes spherical bodies, and the grains in a powdered substance deviate considerably from this assumption. Therefore, it is desirable to make an experimental determination of K . Briefly, this was done by carefully settling out a very small fraction of material, all the particles of which had a uniform settling rate, and measuring the average diameter of these particles by the microscopic method (5). This was repeated for three other sizes of particles. The separation was made by repeated sedimentations in one of the tubes of the apparatus with standard conditions of viscosity and density. The results are shown in Table I.

TABLE I. EXPERIMENTAL DETERMINATION OF K

| SAMPLE | SETTLING TIME OF PARTICLES | | STATISTICAL DIAMETER MICRONS | PREDICTED DIAMETER, STOKES' LAW | SHAPE FACTOR |
|--------|----------------------------|----------------------|---------------------------------|------------------------------------|--------------|
| | Minimum Min. Sec. | Maximum Min. Sec. | | | |
| A | 5 | 15 | 56.6 | 44.2 | 1.28 |
| B | 18 | 0 | 45 | 23.9 | 1.22 |
| C | 70 | 0 | 72 | 12.2 | 1.32 |
| D | 315 | 0 | 330 | 7.3 | 1.28 |

It is interesting to note the agreement between A and D, the largest and the smallest fractions, and also that the average of the four is 1.275. An additional factor was considered before finally determining K . The results from the apparatus were to be correlated with the regular standard sieve analysis of the larger particles in order to obtain the complete size distribution of the sample. Screen sizes are given as the dimension of the square opening between the wires. Therefore, the microscopic determination was also made of the average size of particle just passing a standard sieve. It was found that the ratio of the microscopic diameter to the screen opening gave an average value of 1.22. Since sieve sizes are so well established, it was decided to reduce the results from the sedimentation analysis to the sieve size basis. Thus Equation 3 has the following forms:

- (a) Calculated from the physical constants $D = \frac{105}{\sqrt{T}}$
 (b) Determined by experiment $D = \frac{134}{\sqrt{T}}$
 (c) The latter reduced to sieve size basis $D = \frac{110}{\sqrt{T}}$

(c) is the form of the equation used in final analysis. Note the small difference between (a) and (c).

SAMPLE ANALYSES. There are many graphical methods of plotting size distribution data. Figures 8 and 9 show two alternative schemes. Figure 8 is the familiar cumulation per cent vs. diameter curve, which is convenient for many

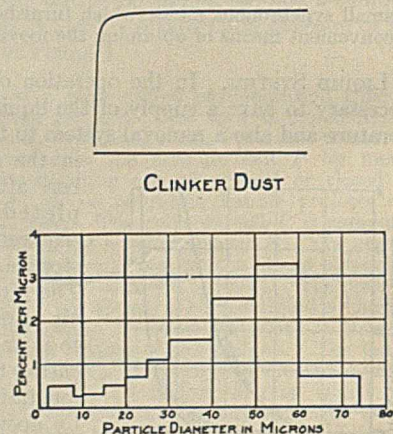
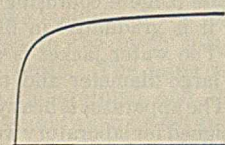


FIGURE 11. ANALYSIS OF CLINKER DUST

purposes but is not very suitable for studying the amount of material of given size present. Figure 9 illustrates a more useful diagram, and is the one most employed in representing the Microneter data. In constructing this form of curve one precaution must be taken: the size increment must be kept the same over the entire range of diameters. If this is not done the curve shape is very misleading. It will be noted from Figure 9 that apparently the minimum diameter is 2 microns. This is a statistical minimum—i. e., a study of some special 30-hour plates showed that there was no significant fraction of this particular material that had a diameter less than 2 microns. Figure 10 shows duplicate analyses of portions of the same cement, and demonstrates the consistency of the results obtained with the Microneter.

Figures 11 to 13 illustrate the great variation in size distribution found in fine powders. Each represents the analysis of a different sample of material. However, all the samples passed 100 per cent through the 200-mesh sieve and thus with normal technic there would have been no further way to determine their relative fineness. Each figure consists of the reproduction of the original plate and the per cent per micron curve calculated from it. If the



LOW SURFACE
EXPERIMENTAL GRIND

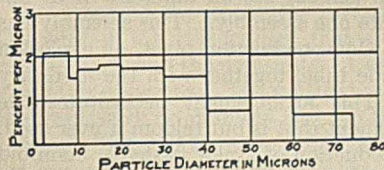


FIGURE 12. LOW SURFACE EXPERIMENTAL GRIND

and in many properties of interest to the producer or user of such products.

CONCLUSIONS

The apparatus described has been in operation for several years, during which time it has been used to analyze more than five thousand samples. The capacity, 36 samples a 24-hour day, is great enough for work where more than the occasional sample has to be analyzed. Where the maximum capacity is not necessary, it has been found that one skilled operator can complete 18 analyses per 8-hour day, including preparing the sample, operating the machine, developing the plates, analyzing them, and calculating the results. The accuracy of these determinations of subsieve sizes is at least comparable to, if not considerably better than, that obtained with standard sieves of 200-mesh and coarser which are universally employed to analyze materials of larger particle diameters.

The apparatus has demonstrated its adaptability for use with a wide range of substances. Although designed pri-

marily to analyze cement samples, it has been successfully employed for materials ranging in specific gravity from 2.7 to 3.7, including cement clinker, cement rock, diorite, limestone, silica, sand, and slag.

Experience has demonstrated that the optimum size range for one plate is about 10—i. e., the largest particles in the sample are about 10 times the diameter of the smallest size for which a reading is desired (but not necessarily the smallest particles present). There is no reason, however, why the position of this range cannot be varied over wide limits by proper control of the viscosity of the liquid and the density difference. The practical upper limit of size is controlled by the possibility of securing a uniform mixture, which becomes increasingly difficult as the viscosity is raised. The lower limit is governed by the allowable length of time for a run, and by the entrance of colloidal effects, such as Brownian movements.

The Microneter has satisfactorily met the five specifications originally set up as the prerequisite qualities needed for a successful instrument.

ACKNOWLEDGMENT

The writer wishes to acknowledge the whole-hearted support given by John Treanor, president of the Riverside Cement Company, and by Hubert Woods, director of the Research Department of the same company, for which this work was undertaken.

Albert E. Myers assisted greatly during the early stages of development. Emory L. Ellis operated the instrument for many months, completing several thousand analyses, and put it on a producing basis. Howard Starke, who has had complete charge of the instrument for the past three years, has contributed many improvements in construction and operating technic which have decreased the labor required while increasing the speed and reliability.

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JAPAN'S CHEMICAL INDUSTRY FORGES AHEAD. That the organized effort of Japan to make itself self-sufficient in chemical products for which it formerly depended on outside sources is meeting with success is indicated in a report to the Commerce

Department. As a result of the increase in plant capacities and the devaluation of the yen, Japan is now able to compete with other chemical manufacturing countries in world markets, particularly in the Far East.

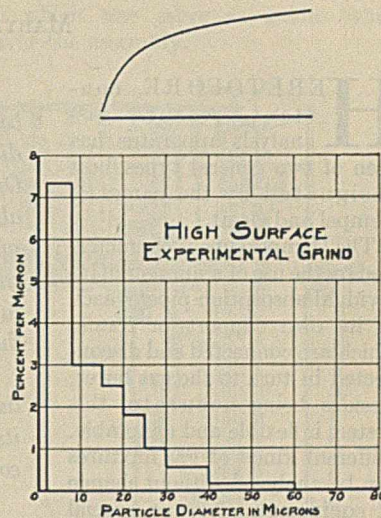


FIGURE 13. HIGH SURFACE EXPERIMENTAL GRIND

Unitized Gas-Analysis Apparatus¹

MARYAN P. MATUSZAK, 709 Forbes St., Pittsburgh, Pa.

HERETOFORE, constant-pressure gas-analysis apparatus has been of two general types, best designated by the names of Hempel and Orsat.

The Hempel type is characterized by the use of a number of individual absorption pipets, each in its own support or frame, which are connected and disconnected in turn to the gas buret. Besides being accurate, this system is flexible and adaptable. Different kinds of gas mixtures can be analyzed without change of equipment. New or special absorbents can be employed in additional pipets without any limitation as to number. New and better devices can be added to the equipment without discarding the old. The apparatus, however, is bulky and not readily made portable, in spite of changes in the direction of more compact pipets, such as described by Augustin (1). Moreover, it is inconvenient and time-consuming because of the many connections and disconnections.

The familiar Orsat type is characterized by having a fixed frame, a fixed number of pipets, and a fixed manifold. This combination overcomes the disadvantages of the Hempel type, but only at the sacrifice of almost all flexibility and adaptability and frequently of considerable accuracy.

The unitized gas-analysis equipment described in this paper combines the advantages of both the Hempel and Orsat types and eliminates their disadvantages. It is the result of an effort to eliminate the objectionable features of traditional gas-analysis apparatus and to develop a more satisfactory analytical tool. No less than a fundamental re-designing of apparatus has been found necessary to meet the needs of modern gas analytical work. The changes introduced have increased simplicity, accuracy, convenience, or usefulness.

RECENT LITERATURE

Aside from descriptions of minor changes or improvements, the recent literature contains but few articles that deal with the fundamental design of gas-analysis equipment, perhaps the best known of these, especially in America, being Shepherd's (13).

The apparatus described by Shepherd is an improvement over the usual Orsat apparatus in such details as a metal framework that permits greater accessibility to the various parts, a buret illuminator, a more efficient bubbling pipet for the removal of oxygen, and a special stopcock for controlling the flow of mercury. It is, however, subject to a number of criticisms that have undoubtedly militated against its adoption. It is somewhat complicated in construction and operation. Its range is limited by the absence of a copper oxide tube. The large number of stopcocks—two for every pipet—necessitates much extra handling, increases the cost of the apparatus, and multiplies the danger of leakage. Furthermore, it increases the amount of dead capillary space, which must be corrected for by time-consuming "simple

Constant-pressure gas-analysis equipment has been devised which utilizes the advantages and discards the disadvantages of the Hempel and Orsat systems, combining the flexibility and adaptability of the one with the convenience, compactness, and rapidity of the other. The apparatus consists of complete self-contained units that fasten together to form any desired assemblies of the Orsat type.

A number of improvements have been devised that have simplified gas-analysis equipment and its manipulation, and increased its accuracy, convenience, and usefulness.

arithmetic" or additional operations. The manifold is built up of T-bore stopcocks after the manner suggested by Pfeifer (12), who devised this arrangement for the purpose of making the manifold flushable. It is not, however, flushable in the modern sense, as are manifolds built up of 120° three-way stopcocks (2, 11) or of three-way stopcocks having special L- or V-bores (5, 7). The short length of the buret, if not accompanied by any loss of accuracy, has made it more confusing to read, as it is graduated in fifths of a

milliliter instead of in tenths. The water jacket is unnecessarily expensive because of its large diameter and the additional glass-blowing involved. The apparatus is heavy and not readily made portable, being designed for laboratory work only.

Another apparatus developed in this country is that designed for use in the laboratories of the subsidiary companies of the U. S. Steel Corporation (5). To eliminate the need for more than one apparatus for different kinds of gas mixtures, all the devices in general use on different Orsat apparatus are combined into one assembly. This assembly has six absorption pipets, a slow-combustion pipet, an explosion pipet, and a copper oxide tube, together with the necessary electrical equipment. This arrangement necessitates the purchase of much equipment that is but seldom if ever used, and aside from the introduction of a new flushable manifold (7), presents no improvement of fundamental design.

A greater divergence from the traditional Orsat apparatus is that developed abroad by Bahr (2). The apparatus is made in two parts, one for the absorption operations and one for the combustion analysis. Each is provided with its own buret, so that a second sample can be undergoing absorption while the first is undergoing combustion. Combustion is effected with two copper oxide tubes, one being heated to 300° C. for oxidation of hydrogen and carbon monoxide and the other to 900° C. for oxidation of methane and ethane. The accessory apparatus for flushing and heating the two copper oxide tubes makes this apparatus too bulky and the operations too involved.

A more compact arrangement described by Vossieck and Schmitz (15) contains two burets but only one copper oxide tube, which is used for hydrogen and carbon monoxide. Methane, mixed with air or oxygen, is oxidized over a hot platinum wire in a quartz capillary. In the absence of ethane, the reduced copper oxide may be simultaneously reoxidized. Another apparatus containing two burets is described by Burkhardt, Fischer, and Frank (3). One buret is of smaller volume than the other and is used for the combustion work.

An interesting article by Neumann and Sträuber (10), which deals with the design of gas-analysis apparatus of the Orsat type, presents complete details of the apparatus used by the Warmestelle at Düsseldorf, including scale drawings of the different parts. It also gives an unusually thorough consideration of capillary error, but presents no important changes in fundamental design.

No successful effort apparently has been made heretofore

¹ Patents applied for.

to combine the flexibility and adaptability of the Hempel system with the compactness, convenience, and rapidity of the Orsat system. A start in the proper direction, however, has been made by discarding the fragile, inflexible, one-piece manifold. For example, Bahr (2), Vossieck and Schmitz (15), and Ott (11) have adopted pipets terminating at the top in three-way stopcocks of the 120° type and have shifted the rubber connections from the vertical branches to the main line of the manifold.

ADVANTAGES OF UNITIZED APPARATUS

Both precision and technical assemblies of the unitized gas-analysis equipment are shown in the illustrations. Precision assemblies are capable of the most exact work that can be performed with assemblies of the Orsat type. Technical assemblies are limited to a lower degree of accuracy by the shorter length of the buret and the absence of a compensator. A technical assembly is made portable by simply being provided with a carrying case.

The chief departure from the traditional Orsat design is the division into individual self-contained units, each including its share of the framework and manifold. This change permits the building of any assembly, from the simplest one-pipet type to the more complex several-pipet types, from standard units. The same reaction units are used in both precision (laboratory) and technical (portable) assemblies, and an assembly can be expanded at any time by the addition of more units. For example, a fractional-combustion or copper oxide unit can be added without expensive alterations in manifold or framework. Devices embodying future improvements in apparatus or technic can be added when developed without discarding an expensive piece of equipment.

Referring to the apparatus designed for the U. S. Steel Corporation (5), it is evident that a corresponding assembly can be built from the new units. Certain advantages are immediately apparent. The unitized assembly is not limited by the framework or manifold and can therefore be expanded or contracted at will to meet special requirements. The operator can arrange the units in whatever order he considers best—for example, the buret can be placed at either the right or the left end of the assembly, or two burets can be incorporated. These can be of different designs to deal more adequately with different kinds of gas mixtures or to conduct the combustion operations more accurately; or, they can be used to permit taking in a new sample and subjecting it to the absorption procedure while the old is undergoing the combustion analysis. Other incidental advantages, such as an all-metal framework, greater accessibility of parts, greater ease of removal and cleaning of glassware, elimination of the unnecessarily large size of the instrument panel and safety-glass shield, greater flexibility, smaller fragility of glass parts, elimination of dead capillary space, etc., will be apparent from the description of the equipment.

FRAMEWORK

The framework is entirely of metal, employing aluminum alloys wherever possible. Sturdiness, durability, and full accessibility to all parts have been achieved. All parts are symmetrically designed to permit standardization and interchangeability.

The framework allotted to each reaction unit consists of two parts. One is a back piece, bolted to identical pieces in other units or to a clamp on a frame support, from which extends a vertical rod carrying a phosphor-bronze clip for securing the top of the reaction vessel. The other is a vertically adjustable shelf piece, cup-shaped and lined with felt for protection of the absorption pipets.

The two vertical frame supports for technical assemblies

consist simply of half-inch (12.7-mm.) aluminum rods about 50 cm. long, imbedded in cast-aluminum feet. They can be screwed or bolted to any appropriate base, such as the bottom of a carrying case, and are provided at the top with removable bottle-rests which also serve as guides when slipping a case down over the assembly.

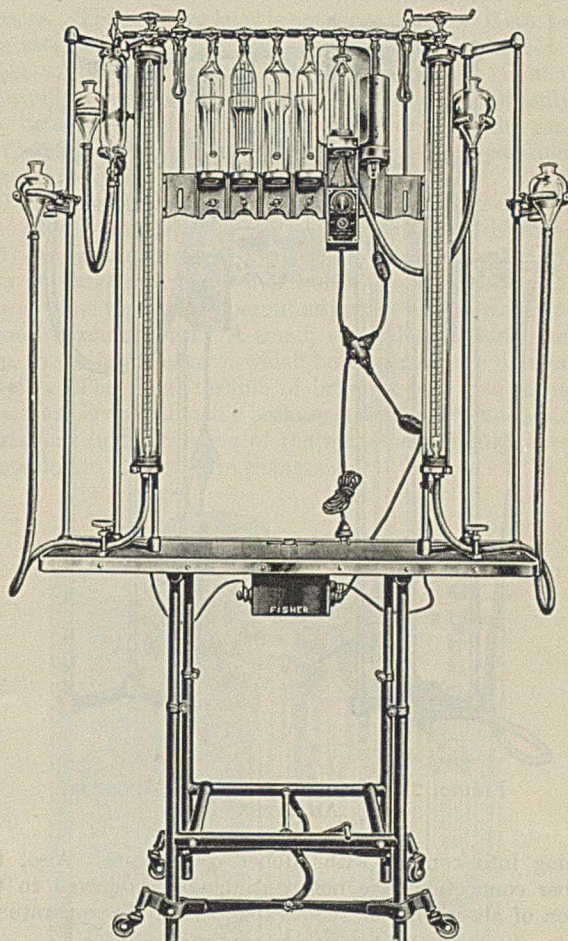


FIGURE 1. UNITIZED PRECISION TIME-SAVER GAS ANALYZER

Each support for precision assemblies consists of three parallel stainless-steel rods, about a meter long, in a staggered or V-formation with two rods in the line of the reaction train and the third or middle rod set back about 75 mm. They are held together by a light removable aluminum top piece, and by brass feet which are bolted or screwed to a table or other appropriate base. The three rods at each end of the assembly support the train of reaction units, the measuring unit, the sampling bulb, and the various leveling bulbs.

MANIFOLD

The manifold is built up of stopcocks which are integral with the various pipets or other reaction vessels, joined together by horizontal rubber connections. This permits a maximum of flexibility and adaptability with a minimum of fragility.

The number of rubber connections has been decreased. For example, in the well-known Bureau of Mines assembly (4, 6) there are ten rubber connections, one of which has been eliminated in later models; in the corresponding unitized assembly the number has been reduced to seven. In general, the number of rubber connections with which the sample can come into contact during the analysis proper has been reduced

by one in all models not having a copper oxide tube, and by two in all that do include such a device.

Dead capillary space in the vertical branches is practically nonexistent. The reagents can be drawn up almost to the stopcock. Unlike the U. S. Steel Corporation apparatus referred to above, this can be done without the absorbents

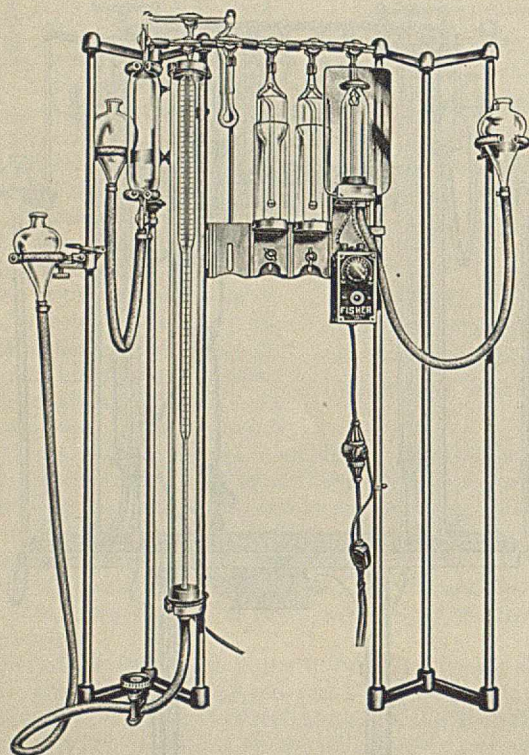


FIGURE 2. UNITIZED PRECISION MINE-AIR ANALYZER

coming into contact with rubber connections. Also, the rubber connections are not continuously subjected to the action of absorbents or their vapors when the apparatus is idle.

For elimination of capillary error the manifold should be filled with nitrogen at the beginning of an analysis. A more awkward and time-consuming procedure is to fill the horizontal capillary with acidulated water or mercury from the slow combustion pipet or from an auxiliary pipet. Since such devices as manometers and copper oxide tubes can be flushed only with inert gas, the use of liquids to eliminate capillary error is not to be recommended. On the other hand, it is desirable to be able to use acidulated water for washing out any absorbent drawn into or beyond the bore of a stopcock, without dismantling the assembly and without loss of the sample.

The new manifold is more perfectly flushable and more easily cleaned than any other known to the author. This has been achieved by its straight-line design and the use of straight-bore three-way stopcocks.

The principle of operation of the straight-bore three-way stopcock is the same as that of the 120° stopcock, but the construction is different. Two of the arms are in the same straight line, with the third at right angles. The plug has a single, straight, eccentric bore. This construction makes it possible to pass a length of cotton-covered wire completely through the manifold from one end to the other without removing any plugs. Other flushable manifolds have three-way stopcocks with bores of an L- or V-shape (5, 7).

All stopcocks used in the unitized manifold are identical

in construction and operation. The four-way stopcock on the fractional combustion unit is but an adaptation of the straight-bore three-way stopcock, and is manipulated exactly like the others. Every stopcock has the same relative position, with two arms horizontal, the third downward, and the handle to the front. This simplification aids the operator to manipulate the stopcocks without examining them to determine the position of the plug. The usual precision Orsat apparatus has three or more different kinds of stopcocks—the Shepherd apparatus has five, not including the control stopcock at the lower end of the buret—and these are sometimes placed with handles to the side instead of to the front.

BURETS

All burets are provided with one stopcock at the top. Their symmetrical construction permits an unusual flexibility of adaptation.

PRECISION BURETS. Reducing the number of stopcocks on the precision buret to one permits it to be raised relative to the reaction train, and to be read with greater ease and comfort. It also permits increasing the length of the graduated section, thus making the spacing of the graduation marks somewhat greater and contributing to the accuracy and ease of reading.

The change has also decreased the fragility of the buret, and lowered maintenance cost. Fewer rubber connections result in a gain in flexibility and in freedom from strains.

Precision burets have an over-all length of 87 cm., a graduated section of about 70 cm., and a capacity of 100 ml. The graduations are black, more permanent than the usual white ones, and standing out in sharper contrast against the background afforded by the water jacket. The graduations include the bore of the stopcock.

The latest style of graduations is used. Whole milliliter marks extend completely around the buret, for elimination of parallax, and even milliliter marks are numbered. The other marks extend around a portion of the buret but not halfway. This style of graduations is as accurate as the so-called "U. S. Bureau of Standards style of engraving" and is more rapid and easier to read, because immersion of the buret in water causes magnification or even the appearance of additional images or reflections of each graduation mark. If half-circles are present the resulting maze of marks and their images is distracting and tiresome to the eye, particularly as the marks are usually placed much closer together than recommended by the Bureau of Standards (14). However excellent half-circles may be on other pieces of laboratory glassware, they constitute a decided handicap on gas burets.

Precision burets are of two principal models. The universal model is of uniform bore, graduated in 0.1 ml., and is suited for the analysis of any kind of gas mixture. The other model is designed for use with mine air and similar gases that have small percentages of some components. It is made in three sections of different diameters, conforming in this respect to the specifications of the U. S. Steel Corporation (5). The top section has a capacity of 72 ml., graduated in 0.2 ml.; the middle section, 22 ml. in 0.1 ml.; and the bottom section, 6 ml. in 0.05 ml. A third model, with a narrow 50-ml. upper part and a 50-ml. bulb at the bottom, is sometimes advantageous in conducting combustions.

TECHNICAL BURETS. Technical or portable burets are about 45 cm. long, of 100 ml. capacity, and of three different designs. The universal model is of uniform-bore Schellbach tubing, graduated in 0.2 ml. The flue-gas model has a 50-ml. bulb at the top and a lower portion of Schellbach tubing graduated in 0.1 ml. The purity model is of clear glass with a 94-ml. bulb in the middle, the top and bottom 3-ml. sections being graduated in 0.05 ml. It is designed for determining

the impurities in cylinder gases, either directly or by difference.

Placing the intake stopcock of earlier portable Orsat apparatus at the top of the technical buret increases the accuracy of the assembly, as the sample can be drawn directly into the buret instead of first traversing the manifold. Hence, all the sample is successively treated in the absorption pipets, as none is trapped in the manifold beyond the particular pipet in use. The graduations include all of the capillary stem and the bore of the stopcock.

LEVELING BULB SUPPORT. The leveling bulb of a precision buret is supported by a movable split-ring support with an automatic locking device which replaces the thumbscrew on earlier supports. A slight pressure with the thumb releases the support, which can then be moved up or down. Releasing the pressure automatically locks it securely in place. It is provided with a simple screw device for fine adjustment of the mercury level in the buret. This gives excellent control when balancing the pressure and when drawing the reagents up to the mark. The leveling bulb support will doubtless find acceptance in many laboratory set-ups other than gas-analysis apparatus.

An oversize screw clamp, with large knurled handle, controls the flow of mercury during combustions and can also be used to draw reagents up at a slow controlled rate. It is screwed permanently in place on the base of the apparatus.

FROSTED-BACK WATER JACKET. The back of the water jacket in precision assemblies is etched. It provides a frosted background against which the black buret marks stand out in sharp contrast. It also diffuses the light and eliminates distracting images and distortions.

The buret is located in a central position in front of the axis of the water jacket, where it can be viewed without side-wise distortions caused by different depths of water.

The combination of the frosted back of the water jacket, the front-central position of the buret, and the back-central position of the compensator tube causes the formation of longitudinal light-images which give the back of the buret an appearance resembling that of Schellbach tubing. When the illuminator described below is used three colored vertical lines are formed: a central ribbon of about the same size as that in Schellbach tubing, which quickly centers the eye, and two narrow side lines which break sharply with their reflections on the mercury meniscus. These sharp breaks can be used to determine the position of the top of the meniscus, as they are more readily perceived and are lower than it by a small constant distance corresponding to about 0.02 ml. An alternative method that may be preferred is to interpose a shield between the light and the water jacket with its lower edge slightly above the level of the mercury meniscus. This causes the meniscus to stand out in very sharp contrast against the background. Both methods are easy, accurate, and rapid.

COMPENSATOR

A compensator of the Petterson type is employed with precision burets. It is simple, accurate, and easily used.

COMPENSATOR TUBE. The compensator tube is held firmly in place directly behind the buret by a glass rod that projects from its lower end into an opening in the rubber stopper of the water jacket. It terminates at the top in a straight-bore three-way stopcock, which may be replaced with a T-bore stopcock, since it never requires flushing with a liquid. Unlike the stopcocks of the unitized straight-line manifold, it is placed behind and above that of the buret. Its lateral arms are longer than those of the other stopcocks, extending to the center of the adjoining "unit space." One arm is connected to the manometer and the other is left free for communication with the atmosphere.

MANOMETER. The manometer is of a new symmetrical design that permits placing it always between the buret and the train of reaction units, irrespective of the position of the buret. It is supported by a clip in the same manner as the tops of the reaction vessels. Its rubber connections are fully accessible, as none is encased within the water jacket.

It is more compact and has less dead space than its predecessors. The mercury level is not more than 2 or 3 cm. below the stopcock, which is itself a part of the manifold. In other words, it automatically approximates the elimination of capillary error that can be achieved with others only by the time-consuming technic (13, 16) of drawing the gas out of the manometer and subjecting it to the same operations as the sample itself.

The arms of the manometer are of 1.5- to 2-mm. bore. The effect of impurities on the surface tension of the mercury (13) can be minimized by keeping the menisci covered with a film of water acidulated with sulfuric acid. The arms are placed close together to permit adjusting both menisci to the same horizontal level. A small, vertically adjustable metal clip, to the lower edge of which both menisci are brought, is helpful. The usual technic of bringing only one meniscus to a mark is objectionable because it does not compensate for variations in the volume of the manometer liquid, such as those due to temperature changes.

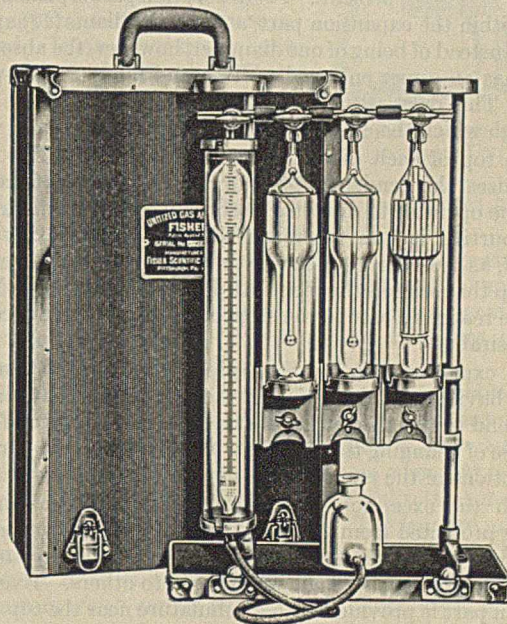


FIGURE 3. UNITIZED TECHNICAL FLUE-GAS ANALYZER

The manometer is provided with a simple check valve consisting of a spherically-true glass ball, that prevents accidental forcing of mercury and sample into the compensator tube.

When using the manometer, its stopcock should be turned once, after the buret has been roughly compensated to within 1 or 2 mm., so that the manifold can attain the same pressure as the buret. Close balancing can then be made. Contrary to a generally accepted idea, repeated turning is unnecessary. For example, should the manifold pressure be 2 mm. too high, the error introduced amounts to only 0.0026 ml. for every milliliter of uncompensated space. A milliliter corresponds to 56.6 cm. of 1.5-mm. bore capillary, or to 31.8 cm. of 2-mm. bore, and is therefore the approximate volume of a several-unit manifold; hence the error introduced would not be detectable on the buret. It is obvious that such turning of the

stopcock is unnecessary if the buret pressure, when communication to the manometer is first made, balances that in the compensator tube to within a few millimeters.

Turning of the manometer stopcock when balancing can be eliminated by substituting a T-bore stopcock for the straight-bore three-way stopcock. The buret, manifold, and manometer can then be simultaneously connected (13), and if desired can be kept so connected throughout the analysis, as ordinary manipulations do not cause the mercury in the manometer to escape into the manifold. Should, however, the volume of mercury be inadvertently changed, it is automatically compensated for by the technic of adjusting both menisci to the same horizontal level. Use of a T-bore stopcock can thus be used to expedite operations at only a slight sacrifice of flushability.

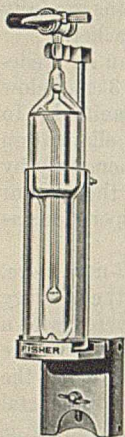


FIGURE 4.
VALVE BUBBLER ABSORPTION UNIT

ABSORPTION PIPETS

The absorption pipets are free from the fragility inherent in the familiar Orsat pipets. No easily broken U-tube connection is present. The absorption part is placed above

and within the expansion part, as in the Williams (17) apparatus. Instead of being of one diameter, however, the absorption part has an upper enlarged portion and a lower narrow portion. This decreases the height of the pipet and the range through which the absorbent level must move.

The top of each pipet is essentially conical. This shape minimizes the tendency to trap small bubbles of gas and aids the operator to draw the absorbent up to the mark without spurring it into the manifold. No etched mark is required, as the absorbent can be drawn up to the lower edge of the clip that secures the pipet just below its stopcock. Drawing the reagent closer to the stopcock is usually not necessary nor desirable.

The expansion part of each pipet is a simple cylindrical vessel having an indentation in the bottom for centering the lower end of the absorption part. It can be removed for the purpose of changing the reagent without removing any rubber connections in the manifold.

With the exception of fuming sulfuric acid, absorbents can be protected from the atmosphere by a layer of paraffin or mineral oil. This technic has long been in use by analysts of respiratory air but is not well known to others. Every expansion part is provided with a tubulature near the top which permits attaching a rubber expansion bag or a liquid seal. If this is used the junction between the absorption and expansion parts is closed with a short length of Gooch rubber tubing.

VALVE BUBBLER ABSORPTION PIPET. The valve bubbler absorption pipet contains a nonfloating automatic glass valve. It has both the valve chamber and the bubbling or gas conducting tube completely enclosed within itself. The construction is thus sturdier and less fragile than that described by La Condamine (9) and Francis (8). It is also neater and more pleasing in appearance, because of the general symmetry of its design.

The valve consists of a solid spherically-true glass ball. The fragile construction of other valves, which are made hollow in order to float, is not present; in fact, the valve is the least fragile part of the entire pipet. Likewise, the fragile projections previously necessary to guide the valves into their seats have been eliminated, as the ball can seat itself in any position.

Previous pipets have had an essentially cupshaped valve seat. This design, combined with the inverted cone- or pear-shape of the effective portion of the valves, has offered considerable resistance to free movement and has tended to cause sticking or freezing.

The valve seat in the new pipet consists simply of the upper end of a short vertical tube. The valve makes contact with it in such a narrow and but slightly inclined zone that there is no tendency to stick or freeze, although sticking might occur under unusual conditions, as, for example, under long-continued evaporation and caking of an alkaline solution around the valve. In such case, the ball valve could be liberated with the aid of a wire inserted from below, a feat impossible with older pipets.

On passing gas into the pipet the ball valve remains on its seat, making a gas-tight seal. The gas perforce is conducted by the bubbling tube into the absorbent, through which it ascends in the form of bubbles, which collect in the upper part of the absorption chamber, below the valve. A plug of liquid usually remains in the short tube whose end forms the valve seat.

On the return passage of the gas, the first portion kicks over the ball valve, together with the plug of liquid beneath it, to the adjacent wall of the valve chamber. It adheres to the wall because of the surface tension exerted by the liquid. The valve is now open and the gas comes up through it. As soon as the ascending liquid surrounds the ball the surface tension effect is eliminated, the ball falls back into its seat, and the pipet is ready for the next pass.

The end of the bubbling tube ends in a small bulb having several pinholes that break the issuing gas up into small bubbles.

The initial length of the column of liquid through which the bubbles pass is about 150 mm. It is decreased to about 80 mm. by the passage of 100 ml. of gas. These figures are larger than those for standard pipets of the usual design, indicating a longer time of contact between gas bubbles and absorbent. The time of contact is also somewhat increased by the fact that the narrowness of the lower part of the absorption chamber causes the downward flow of the absorbent to retard the upward rise of the bubbles.

CONTACT ABSORPTION PIPET. The contact pipet is filled with thin-walled glass contact tubes of different lengths which are staggered or cascaded to conform with the conical top of the absorption compartment, minimizing the usual unfilled space at the top. The tubes are held in place by a perforated porcelain disk. It is impossible to force a bubble of gas down any of them into the expansion part.

A modification of the contact absorption pipet contains some twisted copper strips among the glass contact tubes. It is used with cuprous solutions for the absorption of carbon monoxide.

FRACTIONAL-COMBUSTION UNIT

The fractional-combustion or copper oxide unit is a self-contained unit in exactly the same sense as are the absorption units. It is standard equipment that can be incorporated in any unitized assembly, without a special manifold or expensive changes in the framework. It occupies a "unit space" of the size allotted to an absorption pipet and is located in the same relative position. This position decreases the over-all height of the assembly and makes it as easily accessible and observed as any other unit. No troublesome heating of the stopcock or adjacent glass parts occurs.

The copper oxide tube is built integral with a single in-and-out four-way stopcock that replaces the two stopcocks used in other apparatus. This simplification has a number of obvious advantages.

It reduces the amount of stopcock handling required during the analysis. A single turn of 120° of the stopcock handle changes it from the by-passing position, with the copper oxide tube completely shut off from the manifold, to the in-and-out position, with the gas entering the tube through one bore and emerging through the other.

It eliminates completely the dead space in the manifold between the two stopcocks previously used, as there is no dead space whatever in the new stopcock. It also reduces the number of possible sources of leakage by eliminating both a stopcock and a rubber connection.

The small closed loop of the new tube makes it sturdier, more compact, and less fragile than the extended open loop of its predecessors. Its free space is smaller, because of reduction of capillary space and the use of small glass balls instead of glass wool for keeping the copper oxide out of the capillaries.

The electric furnace for the fractional combustion tube is small and compact. A short thermometer with a graduated range from 250° to 325° C. is inserted alongside the copper oxide tube and is held in place with a small metal clip that also indicates the proper position for the top of the furnace. The thermometer is easily read, as it is located at the eye-level of the operator.

SLOW-COMBUSTION UNIT

All electrical accessories for the slow-combustion unit are enclosed in a small aluminum box, built integral with the shelf piece, which replaces large electrical panels present in earlier apparatus. It contains a specially wound transformer for stepping down the usual lighting current, a toggle switch, and a rheostat, and fits snugly into a unit space. A shield of safety glass is clamped in front of the pipet.

Aside from the integral stopcock, the pipet itself differs from the traditional design only in having its upper part terminating in a cone instead of a half-sphere. The traditional design has been retained as being most simple and reasonably free from faults. A single glass support carries the insulated leads to the coil.

Instead of the usual desultory loop, the coil forms a clearly defined inverted V, whose middle point is supported by a small extension of the central glass support. The small glass support keeps the platinum coil always in position without the disadvantages inherent in ceramic supports, such as those of uneven heating, insufficient heating, and absorption of gas (13).

The shape of the coil permits it to be inserted well up into the apex of the conical top of the pipet. This decreases the danger of an explosion because of delayed ignition or too rapid passage of gas.

ACCESSORIES

SAMPLING BULB. The sampling bulb or sample container is provided with a straight-bore three-way stopcock at each end. Like the best of its predecessors, these stopcocks permit flushing and filling of the capillary connections at both ends without losing any of the sample or contaminating it with air. In addition they can be connected to any apparatus by either vertical or horizontal connections. They are arranged so that the sampling bulb can be connected to either end of a unitized manifold. It can be inverted so that the stopcock handles will always be in front, as the leveling bulb can be connected to either end.

The sampling bulb, when used with a precision assembly, is held by a split-ring support placed on the back rod of one of the upright frame supports. It can then be connected directly to the end of the unitized straight-line manifold—i. e., directly to the stopcock on the buret. The sampling bulb

can be left in position during an analysis, as the stopcock at its top permits communication to the atmosphere, if desired. A second sample can be withdrawn without the necessity of reconnecting the sampling bulb.

NEON BURET ILLUMINATOR. The buret illuminator for precision assemblies consists of a straight neon-filled tube of the same length as the water jacket. A suitable standard transformer is used for stepping up the ordinary lighting current. The illuminator affords a soft, restful, uniform orange-tinted illumination, and used in conjunction with the frosted-back water jacket, which properly diffuses the light, it forms an efficient accessory for any precision assembly. It is considered superior to the recently available incandescent bulbs with filaments about 30 inches (76 cm.) long in that its light is cold and does not waver because of vibrations of the filament.

CARRYING CASE. The carrying case for portable assemblies is lowered over the assembly and clamps to the base to which the assembly is bolted. This design permits full accessibility to all parts of the apparatus when the case is removed. It is built of strong light plywood covered with black fiber, with edges bound in aluminum, and is provided with chromium-plated corners, catches, and hardware for the leather handle.

The slip-proof, draw-bolt construction of the catches insures them against slipping and dropping the apparatus.

The carrying case is made in two sizes. The large size can hold an assembly of two burets and five reaction units or one buret and six reaction units. The smaller size can hold a buret and three pipets. Limitation to two sizes effects important economies in production.

GAS-ANALYSIS TABLE. The adjustable and movable table shown in Figure 1 presents certain advantages for gas analytical work. The top is made of heavy plywood, covered with black linoleum, provided with an aluminum edge that extends above the surface for 0.25 inch (0.6 cm.) and retains mercury spilled or expelled from the apparatus. The legs are made of telescoping steel tubing which make it adjustable in height from about 20 to 31 inches (50 to 79 cm.) and are provided with castors which can be put in or out of operation in an instant by a simple lever device.

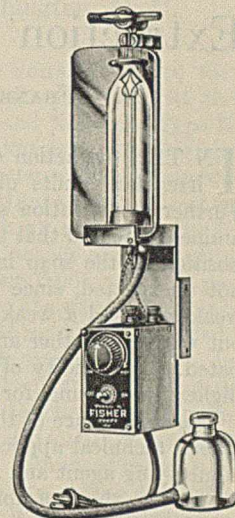


FIGURE 5. SLOW-COMBUSTION UNIT

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to the management and personnel of the Fisher Scientific Company for the opportunity and cooperation that have made possible the conception and development of the unitized gas-analysis apparatus.

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Extraction of Triethanolamine Oleate from Aqueous Solution

FRANK M. BIFFEN AND FOSTER DEE SNELL, Foster D. Snell, Inc., Brooklyn, N. Y.

IN THE extraction of oil from a soap and oil emulsion, irregular results obtained indicated some abnormality. Further investigation showed that the soap was triethanolamine oleate and that the variable results were due to decomposition of the soap in extraction. Such decomposition is not unexpected, since triethanolamine oleate is a salt of a weak acid and a weak base. The extractions were carried out with ethyl ether and all results were higher than anticipated. The acidity of the extracted material proved to be higher than normal for the type of oil being extracted.

The importance of this behavior is increased by the widespread technical application of triethanolamine oleate as an emulsifying agent and for other purposes. Normally, soaps other than those of abietic acid are not decomposed by extraction of an aqueous solution with ethyl ether. This method of separation of oils, etc., from soap solutions is therefore widely used.

A 200-cc. portion of the soap solution was extracted with 3 successive 50-cc. portions of ethyl ether. In each case shaking was carried out for approximately 2 minutes under similar conditions by the same chemist. The composite ether extractions were washed 3 times with 20-cc. portions of water. The ether was then evaporated, and the extract weighed, dissolved in alcohol, and titrated with 0.5 N sodium hydroxide. From this titration the amount of oleic acid extracted from the triethanolamine oleate was calculated to terms of percentage. In the case of experiments 3 and 6 the excess of oleic acid was allowed for before this calculation.

The results are summarized in Table I. The original commercial oleic acid contained 97.25 per cent of oleic acid as oleic acid. The acidity of the extract varies from 95.0 to 97.0 per cent by weight, and is highest in the experiments where recovery of the oleic acid was most complete.

More dilute solutions give a more nearly quantitative extraction. A determination of nitrogen on the extract from

TABLE I. OLEIC ACID EXTRACTED FROM TRIETHANOLAMINE OLEATE SOLUTIONS

| EXPERIMENT | CONCENTRATION OF TRIETHANOLAMINE OLEATE | | EXCESS OLEIC ACID | COMBINED OLEIC ACID PRESENT | WEIGHT OF EXTRACT | PURE OLEIC ACID BY TITRATION, CORRECTED FOR FREE OLEIC ACID | | OLEIC ACID EXTRACTED, CORRECTED FOR FREE OLEIC ACID | | COMMERCIAL OLEIC ACID RECOVERED |
|------------|---|------------------------|-------------------|-----------------------------|-------------------|---|-------|---|---|---------------------------------|
| | M | EXCESS TRIETHANOLAMINE | | | | M | Grams | Grams | % | |
| 1 | 0.1 | .. | .. | 5.808 | 3.4702 | 3.3050 | 95.2 | 58.5 | | |
| 2 | 0.1 | 0.05 | .. | 5.808 | 2.4746 | 2.3500 | 95.0 | 41.7 | | |
| 3 | 0.1 | .. | 0.05 | 5.808 | 6.1986 | 2.8910 | 95.4 | 54.7 | | |
| 4 | 0.01 | .. | .. | 0.5808 | 0.4265 | 0.4135 | 97.0 | 73.2 | | |
| 5 | 0.01 | 0.05 | .. | 0.5808 | 0.4916 | 0.4746 | 96.6 | 84.0 | | |
| 6 | 0.01 | .. | 0.05 | 0.5808 | 0.6900 | 0.2660 | 97.0 | 68.5 | | |

The tentative explanation reached was that triethanolamine oleate was giving up oleic acid because of its instability. To verify this, a 10 per cent neutral triethanolamine oleate solution was extracted with ethyl ether under conditions normal for extraction of soap. A recovery of 85 per cent of the oleic acid present was obtained and the composition of the extract confirmed by titration.

To express this phenomenon quantitatively, a series of experiments was carried out in which triethanolamine oleate was produced in solution alone, in the presence of excess triethanolamine, and in the presence of excess oleic acid. In preparing these solutions, commercial triethanolamine and commercial oleic acid (olive elaine) were titrated and then combined in proportions to give the solutions outlined in Table I.

The extractions were carried out as follows:

experiment 1 showed that less than 0.1 per cent of the triethanolamine had been extracted with the oleic acid. Table I indicates the possibility that all of the oleic acid could be recovered by further extractions. The results of 6 extractions instead of 3 showed recoveries as follows: Experiment 1, 76.32 per cent; experiment 4, 93.73 per cent; experiment 6, 81.84 per cent. This indicates that further extraction may approach 100 per cent of the oleic acid present, particularly in dilute solution.

It is to be concluded that normal conditions of separation of oils from soap solutions, in which the soap is triethanolamine oleate, will not apply and that either prolonged extraction with correction for the free fatty acid content is necessary, or that, preferably, a method other than extraction from aqueous solution without acidifying should be used.

RECEIVED August 26, 1933

CONDITIONS TO PRESERVE PUBLICATIONS. Light, adverse temperature and humidity, acid pollution of the air, and low-grade paper appear to be the main deteriorative agents to be guarded against in libraries and other book depositories, according to a report prepared by the Bureau of Standards.

Sulfur dioxide gas is a potential destroyer of all classes of paper, but tests demonstrated that this condition can be com-

pletely removed by washing the air with alkaline wash water. The destructive effect of light is emphasized. The removal of dust and the maintenance of a medium degree of temperature and humidity are recommended. Extensive tests of old newspapers showed that many made from crude fibers such as ground wood were badly deteriorated, whereas papers composed of chemically purified fibers were found to be in good condition.

Glass and Other Electrodes for Measuring pH Values of Very Dilute Buffers and of Distilled Water

JOHN O. BURTON, HARRY MATHESON, AND S. F. ACREE, Bureau of Standards, Washington, D. C.

IN THE electrometric measurement of the pH values of buffered solutions more dilute than 0.0001 M by means of quinhydrone and hydrogen electrodes the resistance of the solution, escape of carbon dioxide, acid properties of the quinhydrone, and polarization of the electrodes are so disturbing that the e. m. f. readings may vary as much as 5 to 30 millivolts or 0.1 to 0.5 pH unit. The isohydric indicator technic (1) is apparently applicable within 0.1 pH to such solutions and distilled water, but has not heretofore been compared with a reliable e. m. f. method. By adding Varley shunts to a modification of the vacuum tube potentiometer used by Partridge (5), keeping the grid attached to the circuit when balancing it, and using a Thompson (2, 3, 4, 7) glass electrode, e. m. f. readings can be made within 0.1 to 2.0 millivolts on weakly buffered solutions and distilled water, and the pH values agree with those obtained by the isohydric indicator method. This combination is also suitable for measuring the pH of solutions containing active oxidizing or reducing agents, such as chlorine or tannins (6, 8) where the hydrogen and quinhydrone electrodes and indicator methods might fail.

Figure 1 shows a diagram of the circuit used with a special Duovac triode tube. Recent work by the authors shows that the F. P. 54 G. E. tube is especially good with this circuit.

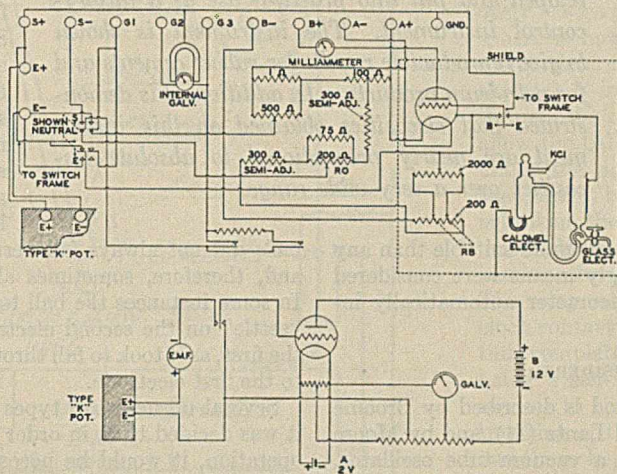


FIGURE 1. WIRING DIAGRAM OF GLASS ELECTRODE-POTENTIOMETER SYSTEM

Upper, circuit as modified in this work
Lower, schematic Partridge circuit

TABLE I. pH VALUES OF SOLUTIONS OF VARIOUS CONCENTRATIONS OBTAINED BY DIFFERENT METHODS

| | HYDROGEN ELECTRODE | QUINHYDRONE ELECTRODE | GLASS ELECTRODE | ISOHYDRIC INDICATOR METHOD |
|---|--------------------|-----------------------|-----------------|----------------------------|
| 0.1 M NaHPh | 3.93 | 3.93 | 3.92 | 3.90 |
| 0.01 M NaHPh | 4.05 | 4.06 | 4.04 | 4.05 |
| 0.001 M NaHPh | 4.34 | 4.37 to 4.33 | 4.35 | 4.30 |
| 0.0001 M NaHPh | 4.85 | 4.82 to 4.72 | 4.84 | 4.90 |
| 0.00001 M NaHPh | 5.68 to 5.95 | 5.34 to 5.20 | 5.61 | 5.70 |
| Tap water | 8.42 to 8.98 | 7.11 | 7.58 | 7.70 |
| Boiler water | 11.74 | .. ^a | 11.52 | 11.70 |
| Double-distilled water | 6.18 to 7.66 | 6.05 to 5.71 | 6.57 | 6.50 |
| Leather extract | 5.28 | 5.40 | 5.25 | .. ^b |
| 0.01 M buffer containing 0.07 gram of chlorine per liter ^c | 4.59 | 4.66 | 4.72 | .. ^d |
| 0.01 M buffer containing 1 gram of chlorine per liter ^e | .. ^f | 0.20 | 1.90 | .. ^d |

^a Solution too alkaline for quinhydrone electrode.
^b Solution too deeply colored for indicator method.
^c Solution prepared by diluting 50 ml. of 0.05 M KHPH-NaOH solution (pH = 4.80) and 5 ml. of saturated chlorine water (pH = 1.71) to 250 ml.
^d Indicator faded quickly.
^e Solution prepared by passing chlorine gas into 0.01 M KHPH-NaOH solution (pH = 4.80).
^f Solution removed palladium sponge from electrode.

The sensitivity of this modified equipment with the Leeds and Northrup Type K potentiometer and 2500-e galvanometer and the Thompson glass electrode of about 60 megohms resistance, made from Corning No. 015 glass is about 0.004 millivolt per mm. scale division with 0.001 M sodium, acid phthalate (designated NaHPh in Table I), 0.007 millivolt with 0.0001 M solution and 1 millivolt for double-distilled water. Standard cells can be checked to within 0.1 millivolt. With the Thompson glass electrode the readings are easily made to within 0.1 millivolt, are reproducible with double-distilled water to within 2 or 3 millivolts, and

become better as the buffer concentration increases.

Table I gives some illustrative pH data on dilute solutions. The results show that the hydrogen electrode (1 × 1 cm. gold covered with palladium sponge) gives drifting readings in very dilute solutions, especially tap water and distilled water containing traces of carbon dioxide. The quinhydrone electrode (1 × 1 cm. gold) gives e. m. f. values which decrease steadily for 20 to 30 minutes as the weakly acid solid quinhydrone dissolves. Chlorine attacks the quinhydrone and alters the e. m. f. values. The glass electrode and isohydric indicator methods give approximately the same pH values in very dilute buffers and distilled water. In general, either method is satisfactory for such solutions. For other samples which are colored, turbid, or possess oxidizing or reducing properties a glass electrode is, of course, to be preferred.

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An Automatic, Modified Falling-Sphere Viscometer

B. A. JONES, Research Laboratory, Physics Division, Firestone Tire & Rubber Company, Akron, Ohio

AN INSTRUMENT, suitable for factory use, was needed for the measurement of the consistency of rubber cements. The principal requirements were that it should indicate the consistency of a cement automatically, yield results fairly rapidly, be convenient to operate, and be of rugged construction. It was thought that the falling-sphere type of viscometer was more suitable than any of the other types, and accordingly means were considered for making the falling-sphere viscometer automatically indicating.

METHODS CONSIDERED

HIGH FREQUENCY. This method is described by Broome and Thomas (1), by Symmes and Lantz (11), and by Moore and Cuthbertson (8), who used a vacuum-tube oscillator, in an appropriate circuit. The presence of a steel ball at a point is determined by the operator by the change of a beat-frequency note heard in headphones. The disadvantage of this method is that the rate of change of the beat-frequency note is a function of the velocity of the ball. Thus the precise time at which the note becomes inaudible is a matter of the personal judgment of the operator.

PHOTOELECTRIC. An excellent apparatus of this type is described by Jones and Talley (4). Photoelectric methods are inconveniently complicated when the sample is itself opaque, as is often the case with rubber cements.

ELECTROMAGNETIC. Consideration was given to a method of electromagnetically detecting the presence of a steel ball at a point in the liquid. Laboratory experiments, not described herein, showed that the method was impractical.

CONTACTS. If the viscous liquid is an electrical insulator (as is nearly always the case with rubber cement), and a metallic sphere is used, the timing of the fall of the sphere may be accomplished by allowing it to come into contact with a pair of mutually insulated electrodes at the upper end of the column of liquid, and into contact with another pair of electrodes at the lower end. The short-circuiting of the electrodes by the sphere may be utilized to operate some external timing device. This apparatus is very much simpler than any of the others considered and, in addition, can be more ruggedly constructed. For these reasons it was decided to develop this type of automatic instrument. The method is not new. Robinson (9), in 1929, patented a viscometer for nontransparent liquids. The patent describes a falling-sphere method in which the arrival of the sphere at the bottom of the column of liquid is indicated by an electric light, the circuit to which is closed by connections operated by the sphere. The patent does not cover automatic timing.

DEVELOPMENT OF APPARATUS

Great difficulty was experienced in obtaining a type of electrode that would make a definite electrical contact with a

An automatic, modified falling-sphere type of viscometer for very viscous liquids has been developed and put into practical use as a factory-control instrument. The instrument is shown to give reproducible results for rubber cements and for petroleum products. In addition, it is demonstrated that viscosities obtained on this instrument are nearly proportional to absolute viscosities over a very wide range.

hardened steel ball when both were immersed in rubber cement. Steel balls were chosen for the reasons listed by Sheppard (10), and Gibson and Jacobs (2). Obviously the contact area between a smooth, hardened sphere and a metal electrode is very small, and consequently of high resistance. The difficulty was enhanced by the fact that the steel

balls did not always fall vertically in very viscous cements and, therefore, sometimes alighted on only one electrode. In some instances the ball took as long a period of time to "settle" on the second electrode after making contact with the first, as it took to fall through the entire column of cement to the first electrode.

Several unsuccessful types of electrodes were tried before it was decided that, in order to attain absolute reliability of operation, it would be necessary to guide the ball along a definite path towards a pair of definite points on the two electrodes. It was realized that if the fall of the ball was restricted or constrained by guides it would be impossible to express the velocity of the ball by Stokes' law, and that Ladenburg's correction factor for wall effect would not apply. For routine factory-control use, however, it was considered more important for the automatic instrument to be reliable in operation, than for the velocity of the ball to be expressible according to a known law.

APPARATUS AND METHOD OF USE

The apparatus finally adopted may be described briefly as an inclined guide immersed in the liquid to be tested. The ball is released from an electromagnetic member immersed a short distance beneath the surface of the sample, and at the same instant an electric clock is automatically started. The ball moves down the guide for a fixed distance in the liquid until it comes into contact with a sharp-edged electrode (the guide itself being the other electrode). When the ball strikes the lower electrode, the electric clock is automatically stopped, and the reading of the clock is a measure of the viscosity of the liquid.

The complete apparatus, as built and put into use in the factory, and the method of operation, will be understood most easily by reference to the schematic diagram (Figure 1).

A glass or metal tube, sealed at the lower end by any suitable means, is filled with about 350 cc. of the cement to be tested. Into this tube of cement is inserted a rigid steel guide, a cross section of which is shown in Figure 2, which is firmly held in a clamp at an angle of 75° to the horizontal. Integral with the guide at its upper end is an iron-core electromagnet to which is attached a steel pole-piece. The electromagnet and pole-piece are electrically insulated from the guide. A steel ball (9.525 mm., 0.375 inch, diameter) is allowed to fall into the liquid through a hole (11.1 mm., 0.44 inch, diameter) in the steel pole-piece. The ball rolls into the starting position (1), at the tip of the pole-piece, about 25 mm. (1 inch) beneath the surface of the rubber cement, and is held there by the alternating magnetic flux passing

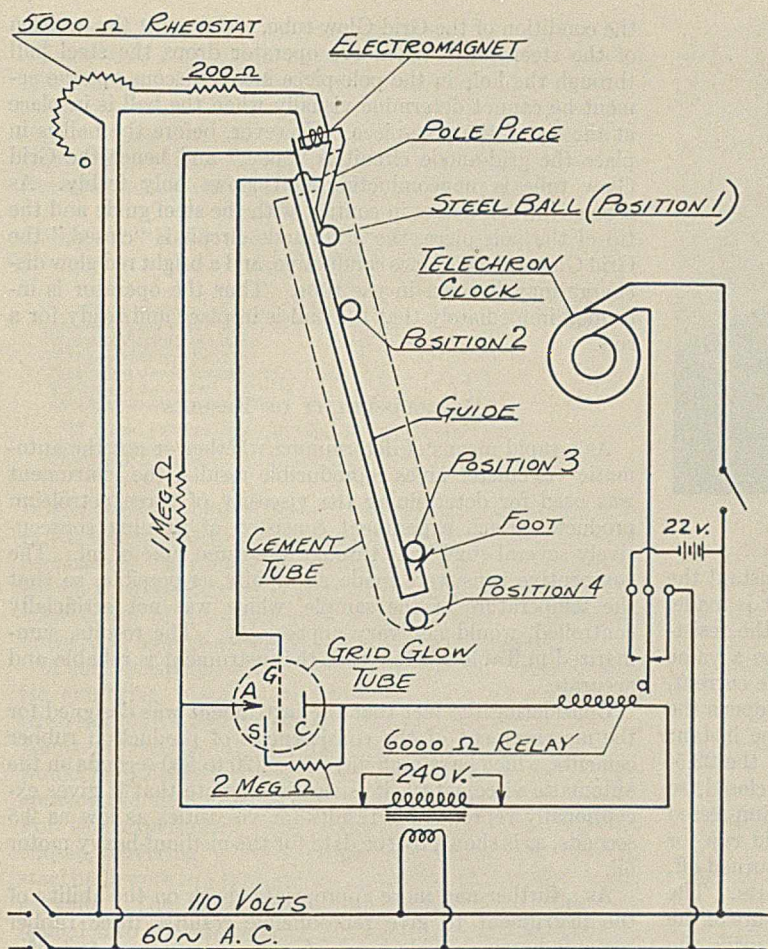


FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS

between the pole-piece and the steel guide. This magnetic flux is induced by the electromagnet which is excited by alternating current from the 110-volt line.

The pole-piece is grooved on its inner surface, so that the ball is always guided to the same relative position between the pole-piece and the guide. The inner surface of the tip of the pole-piece is of semicircular cross section, so that the ball is always held in the same lateral position relative to the pole-piece and the guide. The level of the ball (at position 1) is determined by the location of the greatest flux density between the pole-piece and the guide. This position does not vary by an amount sufficient to be detected, either by observation or by its effect on the results obtained.

When held in this position, the ball is in electrical contact with both the pole-piece and the guide, and forms part of the circuit between the anode and the grid of a glow-discharge tube. [For a complete theoretical and practical discussion of this tube, known commercially as a Grid Glow tube, type DKU-618, the reader is referred to articles by Knowles and Sashoff (6) and Knowles (5).] When connected as shown in Figure 1, the anode-cathode circuit is nonconducting if the combined resistance of the parallel paths between the guide and the foot and the guide and the pole-piece is more than 8 megohms. This condition obtains when the surrounding medium is an ordinary commercial rubber cement, or a petroleum lubricating oil. When either of the two parallel paths referred to above has a resistance less than 8 megohms, as when the steel ball connects the guide and the pole-piece, the tube is in a state of discharge—that is, the anode-cathode circuit will pass a uni-directional, pulsating current (15 milliamperes maximum average). This current may be used to

energize a relay. The current passing through the grid-anode circuit is at all times very small, the high limiting resistance (1 megohm) always being in the circuit, so that the making and breaking of the grid-anode circuit by the sphere is accompanied by the minimum of sparking.

Referring again to Figure 1, it will be seen that when the ball is in position 1, touching both the guide and the pole-piece, the Grid Glow tube is in a state of discharge, the relay coil is energized and the Telechron clock is prevented from starting. The clock switch, which previously has been open, is now closed. The steel sphere is now ready to be released for a viscosity determination. The resistance of the rheostat is increased until the current passing through the electromagnet is sufficiently low to allow the ball to fall away from the pole-piece under the action of gravity. At the instant the contact between the ball and the pole-piece is broken, the resistance of the grid-anode circuit is increased by several megohms and the anode-cathode circuit becomes nonconducting. The relay is thus deenergized, and allows the clock contact to close. The 110-volt circuit is thus completed to the Telechron clock, which, being a self-starting synchronous motor, commences to time the fall of the steel ball. The breaking of the contact between the steel ball and the pole-piece, and the starting of the clock occur practically simultaneously. The steel ball now moves down the guide (position 2). This guide (Figure 2) is inclined at an angle of 75° from the horizontal. This particular angle was chosen because it is large enough to be quite positive in its guiding effect upon the ball. The surfaces of the steel guide, down which the ball moves, are highly polished, so that the

velocity of the ball will be mainly dependent upon the consistency of the rubber cement being tested.

The distance along the guide from the pole-piece to the foot is approximately 305 mm. (12 inches). This distance was chosen for practical reasons. It was found to be long enough to give a suitable spread in results when used with a

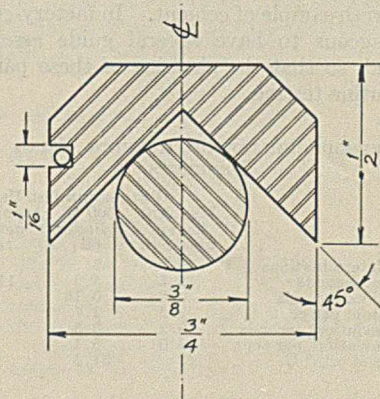


FIGURE 2. CROSS SECTION THROUGH STEEL GUIDE AND SPHERE

ball of 9.525 mm. (0.375 inch) diameter, which is a convenient size to handle. The steel foot is rigidly connected to, but electrically insulated from, the guide. The foot is electrically connected to the pole-piece by means of an insulated wire laid in a groove in the side of the guide. The wire insulation is impregnated with Bakelite varnish, and

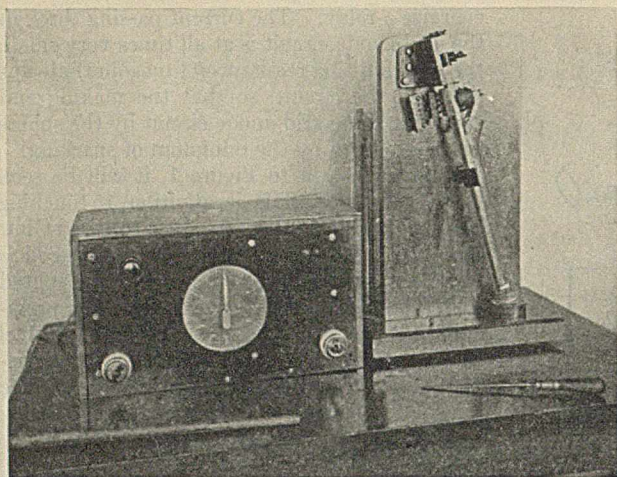


FIGURE 3. APPARATUS READY FOR USE

the whole is baked solidly in the groove. At the instant the ball touches the foot (position 3) electrical contact is made, and since the ball is already touching the guide, the resistance of the grid-anode circuit is again decreased to a value less than 8 megohms. The resulting anode-cathode current, or glow discharge, energizes the relay, which then opens the 110-volt line to the Telechron clock. At the same instant as the 110-volt alternating current line is opened, the 22.5-volt direct current line to the Telechron clock is closed, so that the clock is instantly stopped. Without this impressed direct current voltage, the hand of the clock would run for approximately half a second after the current was turned off, on account of the momentum of the moving parts. The reading of the clock in seconds is recorded as a measure of the consistency of the cement. To make a check run using the same sample of cement, it is necessary only to allow the ball to fall off the foot (by tipping the guide sideways), and to proceed as before, using another ball. In order to determine the consistency of another sample of cement, it is necessary to clean both the tube and the guide. After the guide is removed from the tube, the cement adhering to the slide is allowed to dry until it can be peeled off, or else it is washed off with solvent before drying. The tube holding the cement must also be cleaned in a similar manner before it is again filled with a fresh sample of cement. In factory-control work it is advantageous to have several guide assemblies and tubes on hand, so that the cleaning of these parts will not retard the routine testing.

TABLE I. REPRODUCIBILITY OF RESULTS USING PETROLEUM PRODUCTS

| | PETROLEUM OIL USED | | |
|-----------------------------|------------------------|--------------------|----------------------------------|
| | Medium-heavy motor oil | 600 W cylinder oil | Asphaltic base petroleum residue |
| Number of determinations | 15 | 7 | 3 |
| Average time, seconds | 2.5 | 5.9 | 1110 |
| Mean deviation, seconds | 0.03 | 0.16 | 12 |
| Mean deviation, per cent | 1.3 | 2.7 | 1.08 |
| Maximum deviation, seconds | 0.2 | 0.3 | 17 |
| Maximum deviation, per cent | 8.0 | 5.1 | 1.5 |
| Temperature of oil, °C. | 27 | 31.5 | 31.5 |

Figures 3 and 4 are photographs of the actual apparatus. For convenience in operation, the apparatus is divided into two parts; on the right is shown the wooden stand supporting the clamp, guide, and cement tube. In the cabinet on the left is the auxiliary electrical apparatus including the Telechron clock, relay, and Grid Glow tube. In the top of the cabinet may be seen a small window. Immediately beneath this window is the glow-discharge tube (Figure 4). This window is furnished to enable the operator to see at a glance

the condition of the Grid Glow tube, and from it the position of the steel ball. When the operator drops the steel ball through the hole in the pole-piece into a viscous opaque cement he cannot determine visually when the ball is in place at the tip of the pole-piece. However, before the ball is in place the grid-anode circuit is "open," and hence the Grid Glow tube is nonconducting and glows only feebly. As soon as the ball comes in contact with the steel guide and the tip of the pole-piece, the grid-anode circuit is "closed," the Grid Glow tube becomes conductive, and a bright red glow discharge may be seen in the tube. Thus the operator is informed immediately that the ball is in place and ready for a run.

REPRODUCIBILITY OF RESULTS

As a rapid means of determining whether or not the automatic viscometer gives reproducible results, the instrument was used for determining the viscosity of three petroleum products. Each experiment consisted of running consecutively several steel balls through the same tube of oil. The consecutive runs were made as rapidly as possible, so that the temperature of the sample, which was not artificially controlled, would not vary appreciably. The results, summarized in Table I, show that the instrument is reliable and accurate.

Considering the fact that the instrument was designed for the measurement of the consistencies of production rubber cements, which have high viscosities (20 to 500 seconds on the automatic viscometer), it is worthy of note that it gives exceptionally reproducible results for viscosities as low as 2.5 seconds, as is shown by the data for the medium-heavy motor oil.

As a further and more appropriate check on the ability of the instrument to give reproducible results, three rubber cements having a wide range of consistencies were tested in the automatic instrument. One 5-gallon sample of each cement was taken from a large factory batch. From each 5-gallon sample the viscometer tube was filled several times, and only one test was made on each tube of cement. The

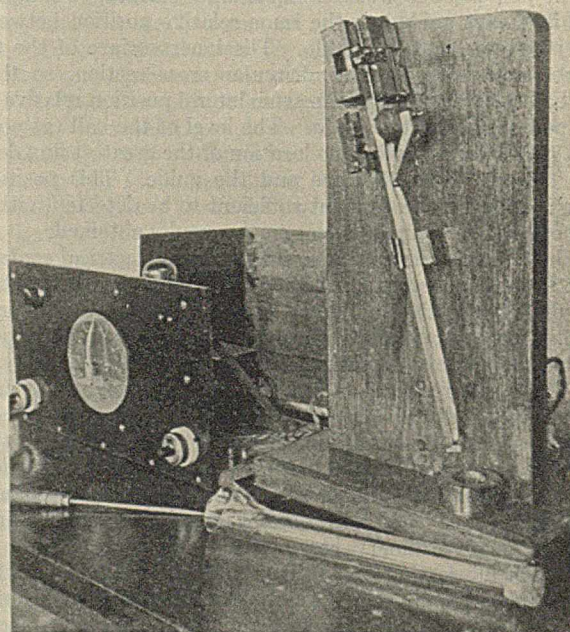


FIGURE 4. APPARATUS

Cover of cabinet removed, cement tube removed to show steel guide and steel ball at tip of pole-piece.

tests were made at room temperatures. The 5-gallon containers were kept tightly sealed during the intervals between the withdrawal of consecutive samples, so that there would be no unnecessary loss of solvent by evaporation. In order to demonstrate that the accuracy of the results obtained on this instrument does not depend upon the skill of the operator, the tests on cement K were run by two operators.

TABLE II. REPRODUCIBILITY OF RESULTS USING RUBBER CEMENTS

| | CEMENT K ^a | CEMENT L ^b | CEMENT M ^c |
|-----------------------------|-----------------------|-----------------------|-----------------------|
| Number of determinations | 19 | 6 | 5 |
| Average time, seconds | 26 | 64.2 | 291 |
| Mean deviation, seconds | 0.7 | 1.15 | 19 |
| Mean deviation, per cent | 2.7 | 1.8 | 6.5 |
| Maximum deviation, seconds | 2.0 | 2.8 | 34 |
| Maximum deviation, per cent | 7.7 | 4.35 | 11.7 |
| Average temperature, ° C. | 28.5 | 26.5 | 30 |

^a 5% milled smoked sheet, gasoline, iron oxide, zinc oxide.

^b 8% first latex crepe in gasoline.

^c 10% first latex crepe in gasoline.

The results shown in Table II are indicative of the reliability of the instrument in giving reproducible measurements of the consistency of rubber cements. The maximum deviation shown is believed to be within the limits of variability of the consistency of a rubber cement occasioned by evaporation of solvent, change of temperature, and nonhomogeneity.

A considerable amount of time (5 to 10 minutes) is required for emptying, cleaning, and refilling the apparatus with a fresh sample for the purpose of making a check determination. Hence an experiment was run to ascertain whether or not it would be possible to make check determinations by running consecutive steel balls in the same tube of rubber cement. For this experiment, eight different rubber cements were chosen, covering a wide range of consistencies. Several steel balls were run through the same tube of each of the eight cements. The balls for the consecutive tests were each loaded into the instrument as rapidly as possible after the preceding ball had been removed from the foot, so that the consistency of the rubber cement in the tube would have very little chance to change, between runs, by evaporation of the solvent.

The results obtained in this experiment are shown graphically in Figure 5. Three of the rubber cements gave reasonably constant values of consistency as succeeding balls were used. The other five cements, however, yielded remarkably variable results, the general tendency being for the apparent consistency to increase steadily up to some maximum, then to decrease suddenly, only to increase again to some still higher maximum consistency as succeeding balls were allowed to fall through the cement. It will be noticed that the three rubber cements of low consistency gave constant results and that the five of higher consistency gave variable results. No investigation was carried out for the purpose of determining the cause of the increase in consistency. It is thought, however, that the increase is evidence of a grain effect in the rubber cement brought about by the mechanical working of the cement by the successive steel balls as they fall along the same path. Obviously, it is impossible, with cements showing this effect, to obtain check results by using successive balls in the same tube of rubber cement.

RELATIONSHIP BETWEEN AUTOMATIC VISCOMETER SECONDS AND ABSOLUTE VISCOSITIES

Some question arose as to whether the automatic instrument would yield values of relative viscosity which are proportional to absolute viscosities. To settle this debatable point, three true liquids, having a wide range of viscosities, were chosen for test. These were run both in a viscometer of the usual falling-ball type, and in the automatic instrument. The three liquids chosen were castor oil, corn sirup, and

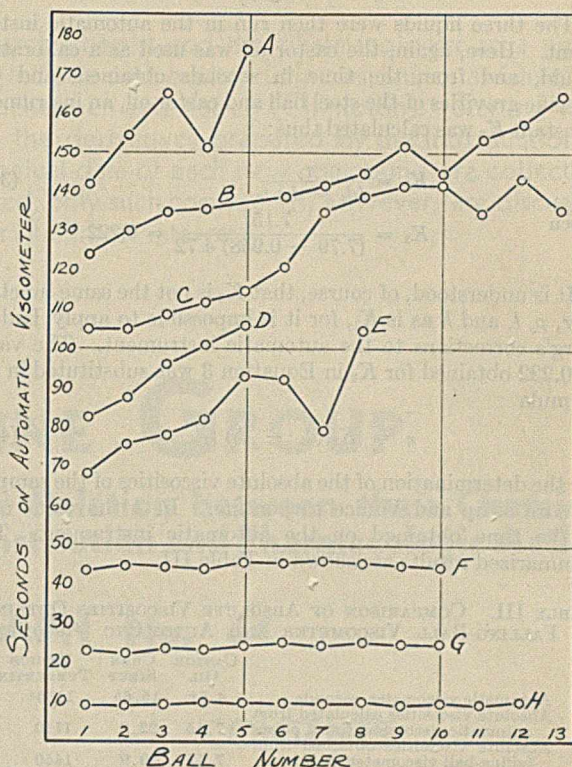


FIGURE 5. EFFECT OF REPEATED TESTS ON APPARENT CONSISTENCY OF SAME SAMPLES OF RUBBER CEMENT

- A. 8 per cent first latex crepe in gasoline
 B, C, E. 7 per cent first latex crepe in gasoline
 D. 10 per cent first latex crepe in gasoline
 F. 5 per cent milled smoked sheet in gasoline; iron oxide, zinc oxide
 G. 5 per cent milled smoked sheet in benzene and gasoline
 H. 4 per cent milled smoked sheet in benzene and gasoline
 The seven batches of rubber used in these cements were not necessarily milled for the same length of time.

Venice turpentine. All the measurements in this experiment were made at room temperatures, 24° to 25.5° C. The absolute viscosity of the castor oil was determined as 7.15 poises, by calculation from the Saybolt viscosity and the specific gravity, using the formula given by Herschel (3).

The same sample of castor oil was then used as a calibrating liquid for the usual type of falling-ball viscometer—that is, the castor oil was used for the purpose of obtaining the instrument constant, K_1 in the formula:

$$\eta = K_1 (d_1 - d_2) t_1 \quad (1)$$

where η = absolute viscosity in poises

$$K_1 = \frac{2gr^2}{9l \left(1 + 2.4 \frac{r}{\rho}\right) \left(1 + 3.3 \frac{r}{h}\right)} \quad (2)$$

d_1 = density of falling sphere

d_2 = density of the liquid

t_1 = time of fall in seconds in falling-ball viscometer

r = radius of the sphere in cm.

ρ = radius of the cylinder in cm.

l = distance in cm. through which the sphere falls vertically in the liquid

h = height of the liquid in cm.

The value of K_1 is a constant for constant values of r , ρ , l , and h . It is, of course, merely a convenient grouping of various constants of Stokes' law and Ladenburg's correction formula (7). The value of K_1 for the particular falling-ball viscometer used was 0.455. Substituting this in Equation 1, and using the values of t_1 and d_2 obtained for the samples of corn sirup and Venice turpentine, the absolute viscosities of these two liquids were found to be 19.9 poises and 1450 poises, respectively.

The three liquids were then run in the automatic instrument. Here, again, the castor oil was used as a calibrating liquid, and from the time in seconds obtained, and the specific gravities of the steel ball and castor oil, an instrument constant K_2 was calculated thus:

$$K_2 = \frac{\eta}{(d_1 - d_2) t_2} \quad (3)$$

Then
$$K_2 = \frac{7.15}{(7.79 - 0.958) 4.72} = 0.222$$

It is understood, of course, that K_2 is not the same function of r , ρ , l , and h as is K_1 , for it is impossible to apply Ladenburg's corrections to the automatic instrument. The value of 0.222 obtained for K_2 in Equation 3 was substituted in the formula

$$\eta = K_2 (d_1 - d_2) t_2 \quad (4)$$

for the determination of the absolute viscosities of the samples of corn sirup and Venice turpentine. In 4 the value of t_2 is the time obtained on the automatic instrument. The summarized results are shown in Table III.

TABLE III. COMPARISON OF ABSOLUTE VISCOSITIES OBTAINED ON FALLING-BALL VISCOMETER AND AUTOMATIC VISCOMETER

| | CASTOR OIL | CORN SIRUP | VENICE TURPENTINE |
|---|------------------|-------------------|-------------------|
| 1 Automatic viscometer, seconds | 4.7 ^a | 15.6 ^b | 1135 ^c |
| 2 Absolute viscosities calculated from automatic viscometer times, poises | 7.15 | 22.2 | 1710 |
| 3 Absolute viscosities obtained from falling-ball viscometer, poises | 7.15 | 19.9 | 1450 |
| 4 Ratio between 2 and 3 | 1 | 1.115 | 1.180 |

^a Mean of 9 determinations.
^b Mean of 5 determinations.
^c Mean of 3 determinations.

The results in Table III show that over a wide range of viscosities the automatic viscometer gives values of relative viscosity which, when corrected for the specific gravity of the liquid, are nearly proportional to absolute viscosity. The 18 per cent error in the absolute viscosity of Venice turpentine and the 11.5 per cent error in the viscosity of corn sirup are no greater than should be expected when it is considered that Equation 3 applies strictly to only true falling-sphere viscometers, in which r is small with respect to ρ , and does not apply to the more complicated case of a ball rolling down an inclined V-shaped guide, as was assumed in Equations 3 and 4.

TEMPERATURE CORRECTIONS

For factory-control work, where rapidity in obtaining results is an important factor in the use of any instrument, it is not practical to measure the consistency of a rubber cement at a standard temperature, because of the difficulty of bringing the cement to that standard temperature within a reasonable time. For this reason, the automatic viscometer, instead of being equipped with an elaborate temperature control, was furnished to the factory operators with a temperature-correction table applicable to rubber cements of all consistencies actually met with in practice, and covering a range of temperatures greater than that normally encountered in the cement-house.

CONCLUSION

The automatic viscometer described in this paper is a simple, rugged instrument suitable for factory-control work where reliability of operation is of prime importance. It is not claimed that the instrument will give results with as high a degree of accuracy as certain other automatic viscometers, such as the one described by Jones and Talley (4), or as the manually operated Saybolt, Ostwald, or straight falling-sphere viscometers provided with thermostatically controlled con-

stant-temperature baths. However, it is better suited than other viscometers to the automatic measurement of the consistency of very viscous rubber cements, whether they are transparent or opaque. The instrument will yield results which are within the limits of variability encountered in rubber cement itself, as the data in Table II show. It will yield results quickly, actual times in seconds on the instrument being approximately equivalent to poises when the specific gravity of the liquid is about 1 and steel balls of 9.525 mm. (0.375 inch) diameter are used. The instrument requires only a small amount (350 cc.) of cement for one determination, and its operation requires no greater skill than the ability to turn three switches in correct sequence. The particular apparatus shown in Figures 3 and 4 has been used by factory operators over a period of 6 months at the time of writing.

ACKNOWLEDGMENT

The author thanks Norris Johnston and N. A. Shepard for their many valuable criticisms and suggestions throughout the course of this work.

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Cleaning Platinum Wire for Flame Tests

WESLEY G. LEIGHTON

Pomona College, Claremont, Calif.

THE usefulness of potassium acid sulfate for removing persistent deposits from a platinum test wire seems to have been overlooked in textbooks on qualitative analysis, in spite of the fact that this very effective flux is commonly recommended for cleaning platinum vessels. In the hands of a student in qualitative analysis a platinum wire occasionally acquires a deposit which volatilizes sufficiently to contaminate flame tests, but which is removed with difficulty by hydrochloric acid and heat. In such cases it is more effective to use potassium acid sulfate. A coating of potassium acid sulfate is picked up by drawing the hot wire across a piece of the solid salt. On passing the wire slowly through a flame, the bead of potassium pyrosulfate which forms travels along the wire, dissolving the contaminating deposits. When cool, the bead is readily dislodged. Any small residue of pyrosulfate dissolves at once in water, while the last traces are usually removed by a single moistening with concentrated hydrochloric acid, followed by heating. The clean, bright platinum resulting imparts no color to the flame.

RECEIVED October 14, 1933.

THIS monograph is planned for the use of the research chemist and the pharmacologist as a guide through the literature of the quinoline derivatives. These include such outstanding compounds as Quinine, the Hydrocupreines, the Acridine Dyes, Plasmoquine, Cinchophen and Yatren (Chiniofon). Starting with quinoline, the nucleus common to all these compounds, the derivatives prepared by the introduction of certain groups are discussed, and the available pharmacological data of each new compound are collected. Among the great number of quinoline derivatives synthesized, only such compounds, however, are discussed which have been studied pharmacologically, or which are of clinical interest.

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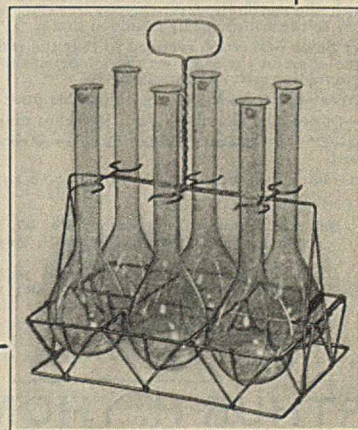
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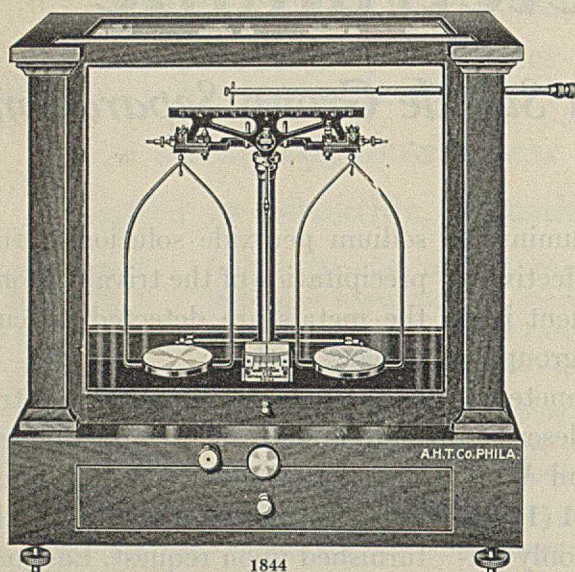
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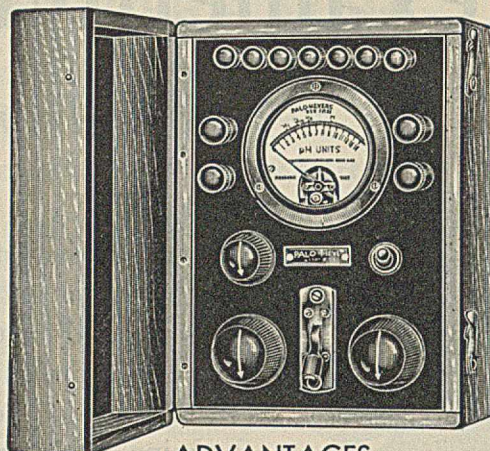
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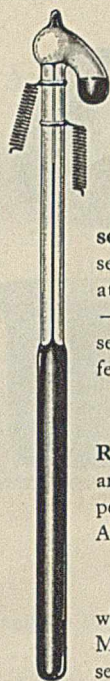
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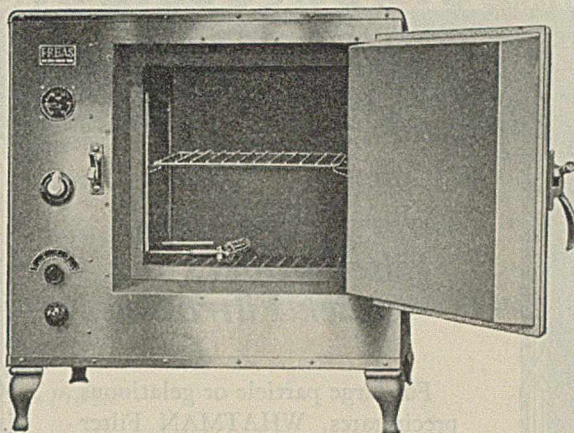


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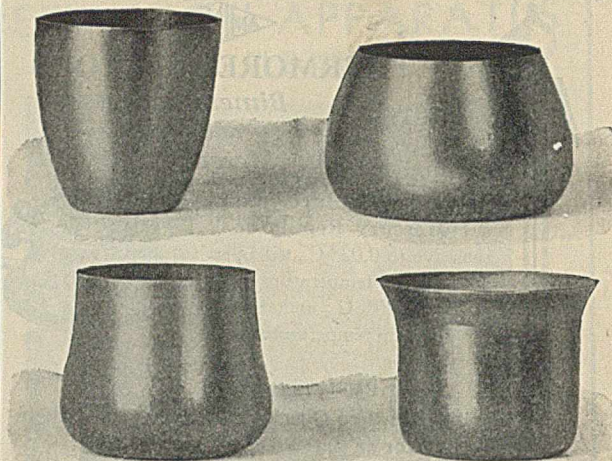
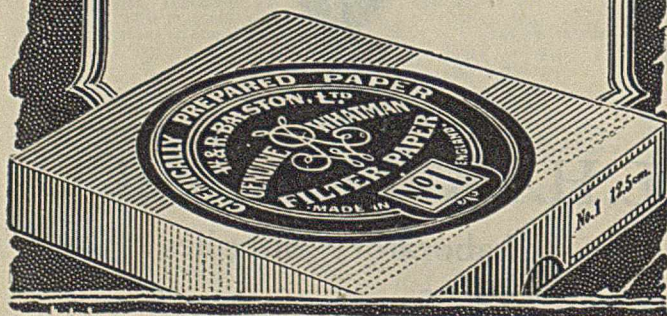
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