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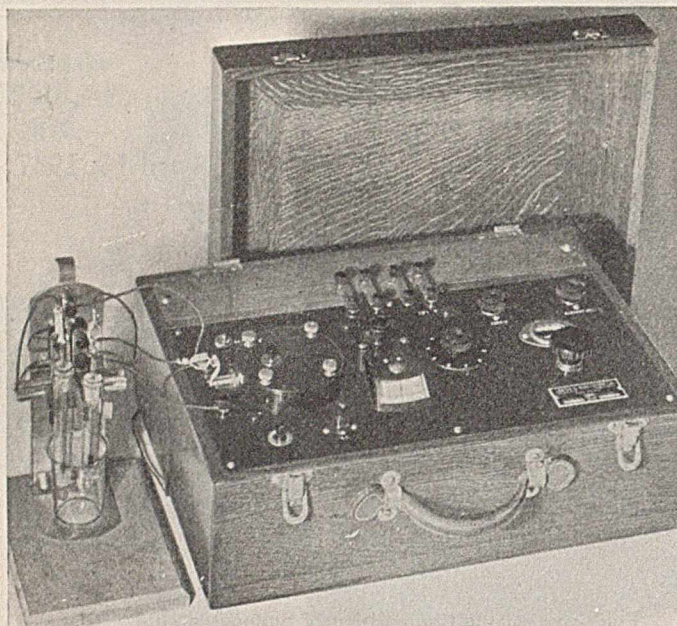
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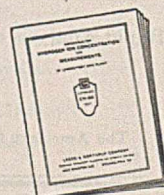
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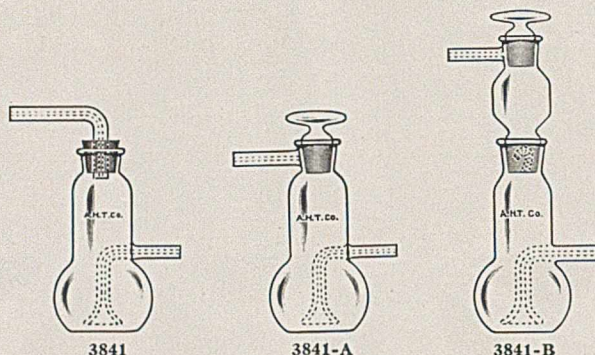
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INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Determination of Carbon Monoxide in Air

ADAM A. CHRISTMAN, WALTER D. BLOCK, AND JULIUS SCHULTZ

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THE most commonly accepted methods for the determination of carbon monoxide in air are so well described elsewhere (1, 5, 8, 11) that only a brief mention of them will be made in this paper. The iodine pentoxide method, which depends upon the liberation of iodine when the dried gas mixture containing carbon monoxide is passed over heated iodine pentoxide, is probably one of the most accurate and sensitive. Accurate results, however, can be obtained by this method only by skilled analysts, who appreciate the many sources of error in each step of the method, from the preparation of a suitable sample of iodine pentoxide to the final iodine titration. Moreover, because of the time required to season the iodine pentoxide and establish reliable blank determinations, this method is not convenient if only an occasional determination of carbon monoxide is to be made.

Because of the toxicity of carbon monoxide in relatively low concentrations, a simple method, which may be used for the detection and quantitative determination of from 1 to 10 parts per 10,000 parts of air, should be of great value. The authors believe that analysis by the method described can be made with a minimum of special apparatus, without undue technical difficulties, and with an accuracy approaching that of the iodine pentoxide method. The time required for the laboratory manipulations for check determinations is less than 1 hour, and concentrations of carbon monoxide which would prove toxic if breathed for a period of 1 hour, may be detected qualitatively in a few minutes. A rough quantitative measure of the carbon monoxide, based on the time required for the qualitative test, is also obtained in the same procedure.

Principle of Present Method

The air under examination is brought in contact with palladium chloride and if carbon monoxide is present, the following reaction occurs: $\text{CO} + \text{PdCl}_2 + \text{H}_2\text{O} = \text{Pd} + \text{CO}_2 + 2\text{HCl}$. Böttger (3) was the first to use palladium chloride for the detection of carbon monoxide, and it has since been used by various workers, notably C. Winkler (12) and Brunck (4), for the quantitative determination of carbon monoxide. These latter authors were interested in the measurement of relatively high concentrations of carbon monoxide and calculated their results from the weight of metallic palladium formed in the above reaction. More recently, however, L. Winkler (13) has utilized this reaction for the determination of carbon monoxide in concentrations comparable to those given in the present work. By his procedure, the metallic palladium formed in the reaction is treated with bromine in excess of that required to form palladium bromide

and the excess bromine is determined by titration. A recent Bureau of Mines publication (2) has reviewed the detection and semiquantitative determination of carbon monoxide by ampoules containing palladium salt solution.

In the present method, a definite volume of palladium chloride solution is exposed to the air containing carbon monoxide and after the reaction of carbon monoxide and palladium chloride is completed, the excess of the chloride is separated from the metallic palladium by filtration, and the palladium chloride is determined colorimetrically. The addition of potassium iodide, in excess of that required to precipitate the palladium chloride as palladous iodide, dissolves the latter salt to give a red solution, which, in the presence of a protective colloid such as gum ghatti, remains perfectly clear for at least 24 hours. This procedure for the colorimetric determination of palladium chloride was employed by Christman (6) for the determination of carbon monoxide in blood.

Reagents

GUM GHATTI SOLUTION. Five grams of gum ghatti are added to 500 cc. of distilled water and allowed to stand for 24 to 48 hours with occasional shaking. After filtration, a clear solution results which appears to keep indefinitely, although it becomes slightly turbid on standing and must be re-filtered from time to time.

ALUMINUM SULFATE. A 10 per cent solution.

POTASSIUM IODIDE. A solution containing 15 grams of this salt per 100 cc. of solution. Since this solution develops a yellow tinge on standing, only enough for immediate use is prepared.

PALLADIUM CHLORIDE SOLUTION. Five hundred milligrams of palladium chloride (Baker and Company) dried at 100° C. for 1 hour are placed in a 400-cc. beaker and covered with 150 cc. of distilled water, 2.5 cc. of concentrated hydrochloric acid are added, and the mixture is heated until complete solution of the palladium chloride results. After cooling, this solution is transferred to a 500-cc. volumetric flask and made up to volume. Analysis of the resulting solution by the standard gravimetric procedure, which consists of the precipitation of palladium in acid solution as the salt of dimethylglyoxime (9), indicated that the palladium chlo-

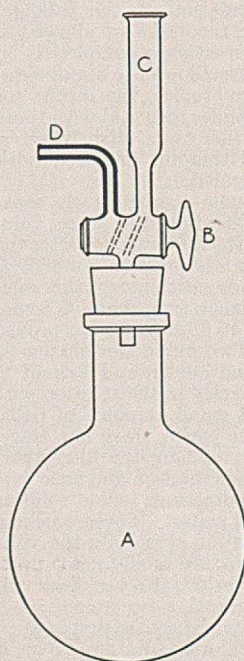


FIGURE 1. APPARATUS

ride was 99.5 per cent pure. It is advisable, if large volumes of this solution are made, to store it in a number of well-stoppered, small bottles rather than in one large bottle, to minimize the deterioration due to exposure to air and dust when samples are removed for use.

Procedure

The apparatus required for this determination is shown in Figure 1. Flask *A* is a 500-cc., round-bottomed, short-necked Pyrex flask, fitted through a one-hole rubber stopper with a two-way stopcock, *B*. The volumes of these flasks with the stopcocks in position must be determined, and for convenience in calculation, it is desirable that these flasks be of approximately the same volume. The flasks used in the present work varied in volume from 528 to 532 cc. One of the upper outlets of the stopcock is fitted with a small reservoir, *C*, which has a capacity of approximately 7 cc. The second upper outlet of the stopcock, *D*, extends upward for 2 to 3 cm. and is then bent at right angles away from the reservoir for another 2 to 3 cm. The lower outlet of the stopcock is cut off at approximately 4.5 cm. and protrudes through the lower surface of the stopper far enough (0.5 to 1.0 cm.) to ensure the passage of palladium chloride into the flask without contact with the stopper. The inside diameter of tube *D* should be less than 1.5 mm.

The flasks are attached to a vacuum pump, connected with a manometer evacuated to less than 1 mm. of pressure, and the stopcocks are closed. There is no appreciable change in the pressure within these flasks at the end of 24 hours, provided the stopcocks are properly ground and greased and all rubber connections are tightly fitted. Stopcocks that do not meet these requirements should not be used. Lubricants which contain ingredients that react with palladium chloride must not be used. Lubriseal (Arthur H. Thomas Company) has proved satisfactory. The samples of gas for analyses are obtained by opening the stopcocks of several of these evacuated flasks until equilibrium with the air to be analyzed is attained. Tube *D* of the flask containing the sample to be analyzed is connected by pressure tubing with tube *D* of an evacuated sample flask of approximately the same volume. The stopcocks are now turned so that the contents of the two flasks are brought into equilibrium. After a few seconds, the stopcocks are closed and the flasks are disconnected.

Three cubic centimeters of the palladium chloride solution and 0.2 cc. of the aluminum sulfate solution are introduced into reservoir *C* and quantitatively transferred to the flask by three 1-cc. washings of distilled water. Care is taken at all times to prevent the access of air into the flask. The flask is now shaken gently at various intervals for the next 2 hours, particularly during the period when the major part of the metallic palladium is forming, to prevent the formation of a layer of metallic palladium on the surface of the liquid which will prevent the free access of the carbon monoxide to the palladium chloride. The presence of aluminum sulfate facilitates the flocculation of the colloidal palladium. After the period of shaking, the flasks are allowed to stand at least 4 hours before the determination is completed; in most of the authors' work, the flasks were allowed to stand overnight or for 24 hours. In comparative studies, the results for the 6-hour period of reaction were sometimes identical with those obtained for the longer period, and in other cases, slightly lower. The differences, however, are so small that for practical work the shorter period of reaction is recommended.

The excess of palladium chloride is now quantitatively separated from the metallic palladium by filtration into 50-cc. volumetric flasks. The volume of liquid in the 50-cc. flasks, after the apparatus and filter paper have been thoroughly washed, is usually 25 to 30 cc. If the filter paper is satisfactory, this solution should be perfectly clear. Schleicher and Schüll 5.5-cm., No. 589 Blue Ribbon, or Whatman No. 40 filter paper has proved very satisfactory for this filtration. Two cubic centimeters of gum ghatti are added to the solution and mixed, and 5 cc. of 15 per cent potassium iodide are added directly to the solution with shaking. Since it has been found that small amounts of palladium chloride are adsorbed by the filter paper, these last traces of palladium chloride are removed by washing the filter twice with 2-cc. portions of the potassium iodide solution and once with a 1-cc. portion. Each washing with potassium iodide solution is followed by small volumes of distilled water. These washings are filtered directly into the colored solution already in the volumetric flask and the contents of the flask are finally made up to volume. A trace of caprylic alcohol added to the flask will minimize the foaming due to the gum ghatti.

The standard for the colorimetric comparison is prepared by the addition of 2 cc. of the palladium chloride solution, 25 cc. of water, 2 cc. of gum ghatti solution, and 10 cc. of 15 per cent potassium iodide to a 50-cc. volumetric flask. The last solution is added with shaking and the resultant solution made up to

volume. The color produced by the addition of potassium iodide reaches maximum intensity in a few minutes and remains constant for at least 24 hours. The standard color is set at 20 mm.

SAMPLE CALCULATION. The volume of the sampling flask and the flask with which it was equilibrated was 530 cc. The sample of air was taken at 23° C. and 744 mm. pressure. From the colorimetric determination, it was calculated that 1.582 mg. of palladium chloride had been reduced by carbon monoxide. This reduction was due to the carbon monoxide in 265 cc. of air, since the flasks to which palladium chloride was added were at a pressure of 0.5 atmosphere. One milligram of palladium chloride is reduced by 0.1261 cc. of carbon monoxide at 0° C. and 760 mm. pressure. Therefore:

$$1.582 \times 0.1261 \times \frac{760}{744} \times \frac{296}{273} \times \frac{10,000}{265} = 8.34 \text{ parts of carbon monoxide per } 10,000 \text{ parts of air}$$

In the above equation, $\frac{0.1261 \times 760 \times 10,000}{273 \times 265}$, which is equal to 13.25, will appear in all calculations. Therefore, the simplified equation

$$13.25 \times \frac{\text{absolute temperature at which sample was taken}}{\text{barometric pressure in mm. at which sample was taken}} \times \text{milligrams of palladium chloride reduced} = \text{parts of carbon monoxide per } 10,000 \text{ parts of air}$$

may be used. The value for the first term of this equation will vary with the volume of the flask used in the analysis.

BLANK DETERMINATIONS. Various amounts of metallic palladium were mixed with known volumes of palladium chloride in flasks as shown in Figure 1. The separation of the palladium chloride from the metallic palladium and the subsequent colorimetric determination of the palladium chloride were made as previously described. There was always a small loss of palladium chloride, which was greater in the presence of larger amounts of metallic palladium. Since such a loss of palladium chloride would yield slightly too high results for carbon monoxide, correction factors must be subtracted. If 0.5, 1.0, 1.5, and 2.0 mg. of palladium chloride are reduced, subtract from the final values, as calculated above, 0.19, 0.28, 0.33, and 0.38 part of carbon monoxide, respectively. Occasionally, as pointed out below, when the content of carbon monoxide is high, it is desirable to divide the sample a second time, so that only one-quarter of the original sample is represented in the actual analysis. In such a case, the blanks given above would be doubled.

Results

To check the accuracy of the method, definite volumes of an analyzed sample of carbon monoxide were transferred from an accurately calibrated gas pipet to an evacuated sample flask. Air, free of carbon monoxide, was then allowed to enter the flask until equilibrium was established. The flask was then equilibrated with an evacuated flask of equal volume and the analysis completed as previously described. A typical series of results, given in Table I, represents analyses made during a period of 2 weeks from a carefully analyzed sample of carbon monoxide after the analytical procedures had been well standardized, and has been corrected for blanks as previously described. The average recovery of carbon monoxide is 95 per cent.

To check the accuracy of the method further, comparative analyses were made by this method and the iodine pentoxide method.

Five-liter samples of gas were used for the latter method; the gas was dried by passage over anhydrous phosphorus pentoxide before it reached the iodine pentoxide. The iodine pent-

oxide was prepared by the method of Lamb, Bray, and Geldard (10) and supported on granulated pumice. The oil bath containing the iodine pentoxide tube was maintained at a temperature of 160° to 165° C. All glass connections were used from the point of entry of the gas into the iodine pentoxide tube to the 10-bulb iodine absorption pipet. The iodine was titrated with 0.01 *N* sodium arsenite with all necessary precautions. Blank determinations were made before and after each analysis.

The results of the comparative analyses, given in Table II, indicate a good agreement between the two methods. In general, analyses 1 to 6, in which the gas mixture consisted of carbon monoxide and nitrogen, were somewhat higher by the present method than by the iodine pentoxide method. However, for gas mixtures prepared by mixing carbon monoxide with air, analyses 7 to 10, inclusive, and the garage air samples, analyses 11 and 12, the values obtained by the present method are 94 to 99 per cent of that of the iodine pentoxide method. These latter values are in agreement with the recoveries of carbon monoxide when known volumes of the gas were measured and analyzed (Table I).

TABLE I. ANALYSIS OF MEASURED VOLUMES^a OF CARBON MONOXIDE BY THE PALLADIUM CHLORIDE METHOD

Experiment	Present Cc.	Found Cc.	Recovery %
1	0.056	0.054	96
2	0.073	0.069	95
3	0.107	0.102	95
4	0.130	0.129	99
5	0.151	0.141	93
6	0.153	0.145	95
7	0.186	0.175	94
8	0.204	0.196	96
9	0.212	0.200	94
10	0.244	0.227	93
11	0.267	0.250	94
12	0.298	0.289	97
13	0.334	0.327	98
14	0.386	0.357	93
15	0.421	0.405	96

Av. 95

^a The volumes of gas indicated in column 2 were transferred quantitatively from the gas buret to the evacuated 500-cc. gas-analysis flasks. Air was then allowed to enter until equilibrium was established. By this means samples of air containing from 1 part of carbon monoxide per 10,000 parts of air (expt. 1) to 8 parts per 10,000 (expt. 15) were available for analysis.

The lower values by the present method as compared to the iodine pentoxide method for samples 7 to 12, inclusive, are due to the interference of oxygen in the reduction of palladium chloride by carbon monoxide. This was demonstrated in numerous experiments in the following manner:

After the gas sample had been divided between two flasks, and the palladium chloride, aluminum sulfate, and water had been added, air, free of carbon monoxide, was allowed to enter one flask until equilibrium was established. The reaction of carbon monoxide with the palladium chloride was allowed to proceed in the second flask at a pressure of 0.5 atmosphere. In every case, the values for carbon monoxide in the latter flask were from 5 to 10 per cent higher than in the flasks in which the reaction of palladium chloride and carbon monoxide occurred at atmospheric pressure. To determine why the lower values for carbon monoxide were obtained in the flasks to which air had been admitted, pure oxygen and nitrogen were substituted for air in experiments similar to that just described. The values for carbon monoxide obtained after the admission of oxygen were 20 to 25 per cent lower than control determinations made in the usual manner. The values obtained after the admission of nitrogen were only 2 to 3 per cent lower than those of control experiments. These results indicated that the major interference in the reaction of palladium chloride with carbon monoxide, when air is admitted into the reaction flask to bring it to atmospheric pressure, is due to oxygen rather than to nitrogen. To minimize this interference of oxygen, all reactions have been carried out at pressures of 0.5 atmosphere or less.

A rough correlation which is valuable for qualitative work may be made between the concentration of carbon monoxide in air and the time required for the first appearance of the metallic palladium. For 10, 8, 6, 4, and 2 parts of carbon monoxide per 10,000 parts of air, under the experimental

conditions previously described, the first appearance of the metallic palladium is approximately 5, 12, 17, 35, and 60 minutes, respectively. These are average values obtained from numerous observations. Individual variations in check determinations are sometimes as great as 5 minutes. Such a qualitative test is of great value, however, because concentrations of carbon monoxide greater than 10 parts per 10,000, which would be dangerous to breathe for a period of 1 hour, form a black scum of metallic palladium on the surface of the yellow palladium chloride in a short time. The above values are based on reactions at normal laboratory temperatures (20° to 25° C.). Berger and Yant (2) have shown that the rate of reaction of palladium chloride and carbon monoxide is retarded at temperatures below 10° C.

If one has no knowledge of the approximate concentration of carbon monoxide in the gas under examination, the sample is divided in the usual manner and palladium chloride, aluminum sulfate, and water added to only one of the flasks. If the appearance of the metallic palladium is so immediate as to suggest a concentration higher than 10 parts per 10,000, the flask at half atmospheric pressure, to which no reagents have been added, may be equilibrated with an evacuated flask, thus obtaining samples containing one-quarter of the original sample. The reagents may again be added to only one of these flasks to determine whether an additional division of the sample is desirable before the quantitative procedure is carried out.

Gases, other than carbon monoxide, react with palladium chloride. The unsaturated hydrocarbons such as acetylene and ethylene, as well as hydrogen, will reduce palladium chloride to metallic palladium and hydrogen sulfide will precipitate palladium chloride as the sulfide. The sensitivity of palladium chloride solutions to reduction by hydrogen depends upon their method of preparation. Daller (7) has noted that distinctly acid palladium chloride solutions are less sensitive to hydrogen reductions than buffered solutions. L. Winkler (13) observed no reduction of his palladium chloride solution with a 1 per cent hydrogen mixture, but did observe some reduction with a 5 per cent concentration of hydrogen. Since his preparation of palladium chloride was buffered with sodium acetate, its sensitivity to reduction by hydrogen cannot be compared with the acid solution of palladium chloride used in the present work. Five hundred cubic centimeters of air containing 0.25, 0.50, 1.0, and 2.0 cc. of pure hydrogen were shaken with 3 cc. of palladium chloride solution, prepared as previously described, without evidence of reduction in 24 hours. Palladium chloride, on the other hand, exposed to ethylene in concentrations of 6 to 8 parts per 10,000, gave evidence of reduction after 3 to 4 hours.

If the air under examination contains unsaturated hydrocarbons or hydrogen sulfide in amounts which would yield high results for carbon monoxide, these interfering substances may be effectively removed by successive passage of the gas through a scrubber solution of bromine water and a 33 per cent potassium hydroxide solution. The bromine solution is prepared by adding one volume of water to two volumes of saturated bromine water. To every 100 cc. of this mixture are added 5 grams of potassium bromide. In the present work, to ensure the formation of small bubbles of gas and permit efficient washing, aeration tubes of sintered glass were used.

Prior to taking a sample for analysis, the gas under examination must be forced through the scrubber solutions until the gas above these solutions has been replaced. The gas is then drawn through the scrubber solutions into the analysis flask at a slow rate to ensure complete absorption of the interfering substances. The rate of passage must also be slow to ensure the complete removal of bromine vapor by the alkali. After the air has stopped bubbling through the absorbent

solutions, an atomizer bulb is attached and air is forced through the solutions, and into the analysis flask until a slight positive pressure within the flask is obtained. The flask is then disconnected from the scrubber system and the stopcock opened momentarily to allow the flask to come to atmospheric pressure. In the analyses reported in experiments 11 and 12, Table II, the air was washed in the manner just described. Several samples of the air (experiment 11), without washing, indicated a content of 6.48 parts of carbon monoxide per 10,000 parts of air, as compared to 6.43 for the washed sample. This would indicate that for the analysis of garage air, the removal of interfering substances is not necessary for practical control work.

TABLE II. COMPARATIVE ANALYSES FOR CARBON MONOXIDE IN GAS MIXTURES^a

(All results are expressed as parts of carbon monoxide per 10,000 parts of air.)

Experiment	Present Method	Iodine Pentoxide Method
1	1.38	1.30
2	2.46	2.69
3	5.61	5.25
4	7.02	7.00
5	7.93	7.90
6	10.36	9.90
7	2.10	2.09
8	6.25	6.60
9	7.64	8.10
10	11.90	12.10
11	6.43	6.75
12	4.16	4.20

^a Experiments 1 to 6, inclusive, represent analyses of carbon monoxide in carbon monoxide and nitrogen mixtures; 7 to 10, inclusive, analyses of carbon monoxide in carbon monoxide and air mixtures, and 11 and 12, analyses of carbon monoxide in a gas mixture taken from a closed garage in which a motor was in operation.

Many laboratories may not be equipped with a vacuum pump which will evacuate a flask to 1 mm. of pressure as recommended. If the sampling flasks can be partially evacuated by a foot pump or water pump to a known reduced pressure, the volume of gas obtained for analysis by opening the stopcock at the site of examination may be readily calculated. Moreover, if it is not necessary to pass the gas through scrubber solutions, a sample of air may be taken by the displacement method—i. e., an analysis flask filled with water may be emptied at the site of examination and the flask re-stoppered. If the flasks with which these sample flasks are equilibrated in the analytical procedure are evacuated [to 20 to 25 mm. instead of 1 mm., the pressure within the flasks,

after the sample has been divided, is slightly greater than 0.5 atmosphere. Since, as pointed out previously, reactions carried out at full atmospheric pressure were only 5 to 10 per cent lower than those at half atmospheric pressure, the results should be but slightly lower than those obtained by the procedure recommended above.

Summary

A comparatively simple procedure requiring very little special apparatus is described for the determination of carbon monoxide in air. The method is based primarily on the fact that palladium chloride is reduced by carbon monoxide and the excess of palladium chloride which is present is determined colorimetrically after addition of potassium iodide.

Acknowledgment

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The Preparation of Thin Films

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VARIOUS means which have been suggested for the preparation of thin films of rubber and similar materials include their deposition on glass, porcelain, sheet metal, and mercury. The use of rigid surfaces is open to the objection that in the case of some materials the adhesion of the film may be troublesome. The removal from such surfaces, of films of materials which are subject to permanent deformation on stretching, tends to lessen the uniformity of their thickness. In connection with the study of the permeability to gases of thin films unsupported by fabric, a satisfactory and simple method was found for their preparation.

Regenerated cellulose sheeting, extensively employed for wrapping purposes, is used as the base upon which the films are deposited. For this purpose it is essential to employ sheeting which has not been coated with a moisture-proofing composition. The material is held taut between closely fitting steel hoops. The film-forming materials are applied

in the form of their solutions in volatile solvents. Uniformity of film thickness is obtained by using dilute solutions and a plurality of coats. After the solvents have evaporated and, when necessary, the deposited film has been cured at elevated temperatures, the uncoated surface of the regenerated cellulose is covered with water. Within a short time the film may be readily loosened and removed without any appreciable stretching or other damage.

This method of preparation is obviously suitable only for films of materials not appreciably affected by moisture. Thin films of rubber, Thiokol, Neoprene, cellulose derivatives, and oleoresinous varnishes were successfully prepared in this manner. The length of time that the film is in contact with the moist regenerated cellulose is not sufficient, with these materials, to produce any change in their appearance.

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Absorption of Hydrogen in Liquid Reagents

A New Solution for the Analytical Determination of Hydrogen in Gas Mixtures

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TECHNICAL methods of gas analysis for the determination of hydrogen in general use in the United States depend almost universally upon procedures employing explosion or combustion. Of these, the fractional combustion over copper oxide (6, 7, 16, 17, 20, 21, 25-29, 31) or the "slow combustion" (9, 10, 18, 30) over a glowing platinum spiral is generally preferred. The chief disadvantage of the copper oxide method is the time required for the determination, during which the operation must be constantly attended.

The "slow combustion" method, while accurate under proper control, is not satisfactory when more than one hydrocarbon is also present in the mixture, and is generally restricted to the determination of methane and ethane. The manipulations required are exacting and the danger of an explosion must constantly be guarded against.

While a number of absorption methods involving liquid reagents have been proposed, the use of these has been limited. Dilute palladium chloride solutions (8, 24), sodium oleate solutions containing finely divided activated nickel (1, 3), sodium chlorate solutions in contact with a palladium activator (13, 14, 15), and silver permanganate solution (11) have been suggested. The reactions involved have, however, generally been deemed slow or unsatisfactory or the preparation of the reagent and apparatus troublesome and expensive.

Among the methods previously advanced, the most satisfactory appears to be that of Paal and Hartman (23), who employed a sodium picrate solution containing a very active and stable palladium colloid (22). In accuracy, it has been shown by a number of investigators (2, 4, 5, 12) to be equal or superior to combustion methods. It is, however, time-consuming, a single determination requiring as high as 30 minutes. Furthermore, the absorbent is expensive, because of the high palladium colloid content, and with high concentrations of hydrogen it is soon spent. Brunck (4) suggested the use of a higher sodium picrate content, and also advanced a method for recovering the palladium catalyst from the spent solution.

For simplicity and ease of operation, an automatic pumping pipet has been developed in the laboratories of this department. This frees the operator from the necessity for constant vigilance and so minimizes the objections raised against the time required, and by setting up more favorable contact conditions between the solution and the gaseous mixture increases the rate of absorption. These desirable features suggested the use of reagents hitherto considered too sluggish to be practicable and so directed attention to the determination of hydrogen by liquid reagents.

While the method of Paal and Hartman (23) appeared to be the most satisfactory of those hitherto advanced, it was soon recognized that it would be desirable to replace the sodium picrate with a substance having a higher rate of absorption and having also the property of being readily reoxidized to its original form without affecting the palladium catalyst, thereby giving a much longer life.

Preliminary Experiments

A rapid preliminary study, largely qualitative in nature, was made on a variety of materials. Among the inorganic substances, sodium metavanadate catalyzed by colloidal

palladium showed some activity. To this mixture other metals were added, including silver, cerium, thorium, molybdenum, tungsten, uranium, and manganese. Molybdenum solutions when used alone gave some promise. A ferric citrate-colloidal palladium solution showed an absorption slightly greater than did the palladium colloid alone.

The colloid used was a sodium protalbinat-palladium colloid prepared in a manner essentially similar to that of Paal and Amberger (22).

Preparations

SODIUM PROTALBINATE. Fifty grams of powdered egg albumin were added slowly with stirring to 250 cc. of a 3.0 per cent sodium hydroxide solution. The mixture was heated at 95° to 100° C. on a water bath with occasional stirring, until practically all the albumin had dissolved. During this digestion considerable ammonia was evolved. The solution was filtered to remove impurities, chiefly inorganic salts. The filtrate was then made slightly acid with 6 N acetic acid, the protalbinic acid being precipitated. After settling for 12 hours the precipitated protalbinic acid was made into a thin paste with water and dialyzed for 3 days with distilled water in a Cellophane sack.

The purified protalbinic acid was dissolved by the addition of excess sodium hydroxide solution and again dialyzed until

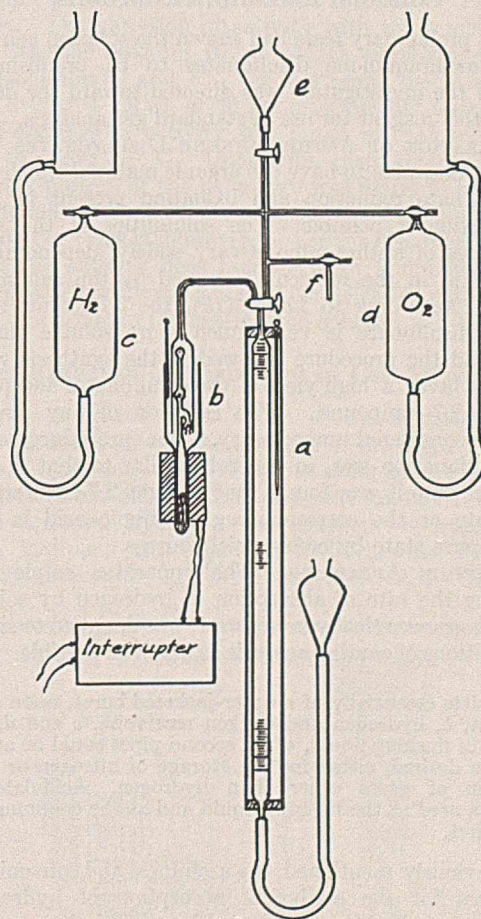


FIGURE 1. APPARATUS FOR ACTIVITY TESTS

neutral to litmus. The resulting sodium protalbinat solution was evaporated to a small bulk at 60° to 70° C. and then precipitated and freed from water by several successive additions of 95 per cent alcohol. The sodium protalbinat was further dried in a desiccator. Yield, 14.6 grams or 29.2 per cent.

SODIUM PROTALBINATE-PALLADIUM COLLOID. Three grams of sodium protalbinat were dissolved in 50 cc. of water and sufficient sodium hydroxide was added to combine with the chlorine of the palladium chloride. The palladium chloride solution, containing 4 grams of palladium chloride (2.0 grams Pd) in 70 to 80 cc. of water, was added slowly while stirring. A yellow-red precipitate first formed but redissolved. An excess of hydrazine was added drop by drop while stirring and the solution was then allowed to stand for several hours. The resulting solution was dialyzed with distilled water in a Cellophane sack until neutral to litmus and free from chlorides. During dialysis the solution increased in volume considerably because of osmosis. The colloid, thus freed from salts, was evaporated to dryness at 60° to 70° C. and further dried in a desiccator.

The palladium colloid preparation was obtained in the form of glistening black plates, soluble in water and alkaline solutions.

Early in the investigation, it was recognized that organic compounds having a quinoid structure might prove satisfactory, because of their ability to shift readily back and forth between the quinone and the hydroquinone forms on alternate oxidation and reduction. A serious difficulty in the use of the simple quinones is their extremely low solubility in water. However, 1,2-naphthoquinone and a number of the anthraquinone sulfonates are soluble to some extent. Accordingly, the use of these was investigated. The 1,2-naphthoquinone solutions tested decreased gradually in activity, but good results were obtained with the anthraquinone sulfonates.

Absorption of Hydrogen by Anthraquinone-Colloidal Palladium Solutions

As the preliminary tests had shown the solution containing sodium anthraquinone disulfonates to be promising, the course of the investigation was directed toward the development of this reagent for use in standard gas analysis.

PREPARATION OF ANTHRAQUINONE DISULFONATES. It is, of course, desirable to have the organic material which undergoes alternate reduction and oxidation present in a high concentration if possible. The solubilities of the various disulfonates of anthraquinone vary widely, depending upon the position in the molecule assumed by the sulfonic acid radicals. According to Lauer (19), the 2,7-sodium anthraquinone disulfonate is very much more soluble than the others, and the procedure followed in the synthesis was designed to favor a high yield of the disulfonates and particularly the 2,7-compound. The isolation of any particular salt was considered unnecessary. The procedure followed in the sulfonation was, in general, similar to that of Lauer. At a later date it was found that sodium 2,7-anthraquinone disulfonate or the corresponding disulfonic acid is offered in an impure state by commercial sources.

ABSORPTION APPARATUS. The apparatus employed for measuring the rate of absorption of hydrogen by solutions, shown diagrammatically in Figure 1, was designed to simulate the conditions of routine analysis as much as possible.

It consists essentially of a water-jacketed buret, *a*, an absorption pipet, *b*, hydrogen and oxygen reservoirs, *c* and *d*, and a reservoir of flushing liquid, *e*. A second pipet could be attached at *f* when desired, either for the storage of nitrogen or for the absorption of gases other than hydrogen. Acidulated salt water was used as the flushing liquid and as the confining liquid in the buret.

As previously mentioned, the usefulness and convenience of procedures for the analytical absorption of hydrogen in liquid reagents had been enhanced by the development of an automatic pumping pipet. Accordingly, the determinations

were usually made in a pipet of this kind, shown diagrammatically in Figure 2.

The pumping mechanism consists of the solenoid, *a*, glass-enclosed iron plunger *b*, valves *c* and *c'*, spray bulb *d*, and timing device *e* to make and break the circuit of the solenoid. When the circuit to the solenoid is closed the plunger rises, forcing the reagent up through tube *f*. Valve *c* is forced shut, *c'* opens, and the reagent is sprayed against the walls of the pipet. When the current to the solenoid is broken the plunger falls, valve *c'* closes, and *c* opens, allowing fresh reagent to be drawn in above the plunger. The removal of solutions and cleansing of the pipet were facilitated by constructing the pipet in three sections. Upon removal of the top section, the pumping mechanism can be lifted out and all parts readily drained and washed. During the study of the effect of temperature on the activity of the reagent, the pipet was cooled or heated by means of the water bath, *h*. Heat was supplied by an immersion heater consisting of a coil of resistance wire enclosed in Pyrex tubing.

When it was desired to operate out of contact with air, the upper and lower sections of the pipet were sealed by a rubber ring containing the thermometer and a rubber gas bag, such as is generally employed to prevent access of air to the back chamber of the usual absorption pipet.

DETERMINATION OF ACTIVITY OF REAGENT. The production of the crude disulfonates of anthraquinone by laboratory syntheses gives a mixture of compounds. Accordingly, a number of preparations were made and examined to obtain as active a solution as conveniently possible and to determine the duplicability of the results.

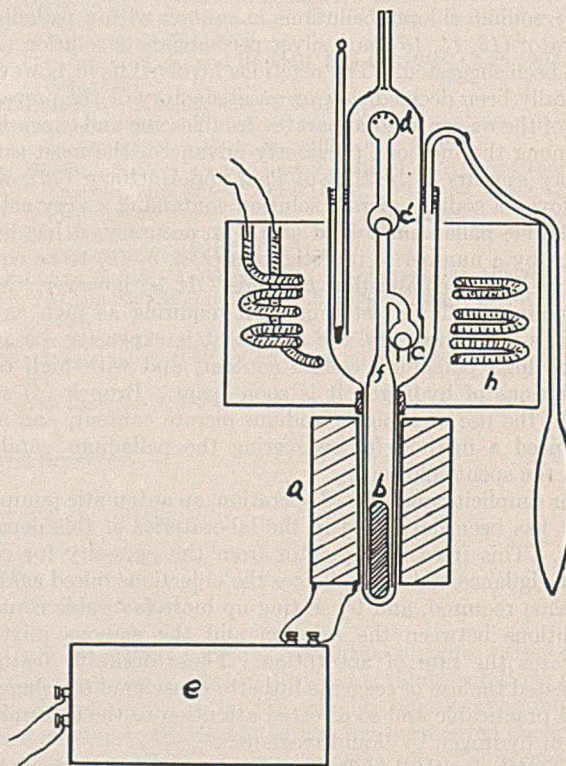


FIGURE 2. PIPET FOR ACTIVITY TESTS

The values for the sodium anthraquinone disulfonate content include soluble impurities which may result from the preparation, including, of course, important amounts of sodium chloride. The tests were carried out as follows:

The sample of hydrogen, usually about 100 cc., was measured in the buret and 50 cc. were then transferred to the absorption pipet. The pipet was closed, a stop watch started, and the circuit for the pumping device closed. After 4 minutes, the pumping action was stopped and the unabsorbed hydrogen

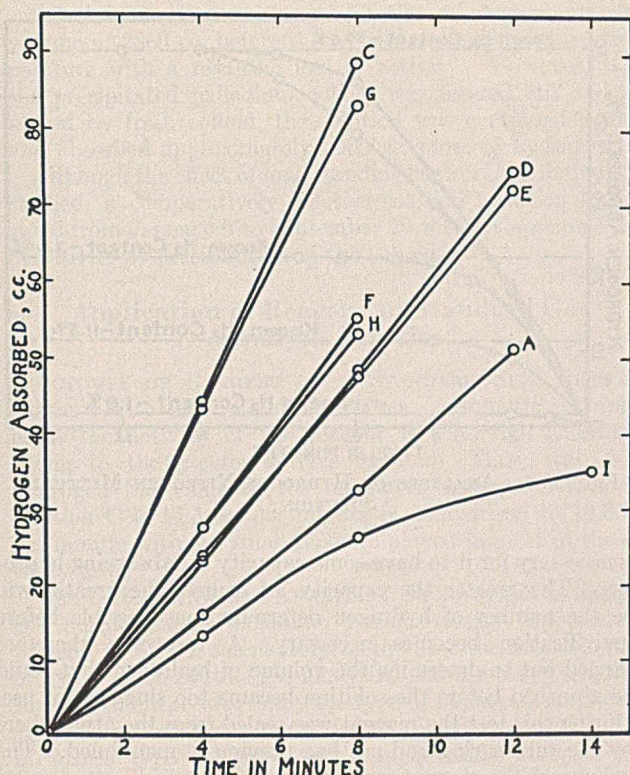


FIGURE 3. HYDROGEN ABSORPTION ACTIVITY OF ANTHRAQUINONE-PALLADIUM COLLOID SOLUTIONS (Letters on curves correspond to those shown in Table I.)

drawn back into the buret and measured. The period of 4 minutes was chosen because in most cases it gave convenient absorption values. The maximum amount that could be absorbed in any one run was 50 cc. In all tests the current of the solenoid circuit was held constant and the speed of the pumping action adjusted to 33 to 34 strokes per minute. The temperature of the solution was read during each run. The solutions were revived by oxygen between tests unless otherwise indicated.

SUMMARY OF ACTIVITY TESTS. A summary of the absorption rates of tests of a number of solutions prepared is shown in Table I. In order to present the data as briefly as possible, only one value of the absorption rate for each solution is given. The value selected is that for the maximum rate which was obtained at a temperature approaching as closely as possible 25° C. The low absorption values for solutions D, F, E, and A are probably due to high sodium chloride content in the anthraquinone, resulting in false values for the weight of sodium anthraquinone disulfonate. Moreover, the composition of the colloidal palladium employed in some of the earlier solutions was doubtful, as trouble was sometimes experienced in securing a completely soluble product.

The activity of the solutions given in Table I is shown graphically by Figure 3, in which the volume of hydrogen absorbed is plotted against the absorption time.

COMPARISON OF ABSORPTION RATES WITH PUMPING AND BUBBLING PIPET. As indicated, this reagent was intended primarily for use with the pumping pipet employed in the tests of Table I. However, because of the limited extent to which this type of pipet has been applied, a comparison of the absorption rates of the anthraquinone reagent in a pipet more generally employed should be of interest. As the bubbling pipet is commonly employed in technical gas analysis, this type was selected for the comparison (similar to Fisher Scientific Company No. 10-645). In recent years a number of modifications of the bubbling pipet have been made, many of which appreciably increase the rate of absorp-

tion. In this study, however, it was considered advisable to restrict the comparison to a single type, so the simple bubbling pipet was selected, as it is probably the most generally used.

Although the reagent used (solution F) was of rather low activity, satisfactory comparative values were obtained, as slight errors in time did not appreciably affect the absorption values. In the absorption tests with the bubbling pipet the time was noted both for the actual bubbling period and for the total elapsed time, as an appreciable amount of time is required to withdraw the hydrogen after each pass.

The results of the comparison of the absorption rate with the two types of pipet were as follows:

	Cc./min.
Automatic pumping pipet	4.76
Bubbling pipet, actual bubbling time	3.85
Bubbling pipet, total time	2.30

COMPARISON OF ABSORPTION RATE OF ANTHRAQUINONE REAGENT WITH SODIUM PICRATE REAGENT. Although the sodium anthraquinone disulfonate reagent was developed principally to give a life longer than that of the Paal and Hartman reagent by virtue of the fact that it may be readily reoxidized, it also offers the advantage of a greater activity. This is demonstrated by the comparison of the absorption rates of the two solutions:

	Cc./min.
Anthraquinone reagent (solution C)	9.30
Paal and Hartman's sodium picrate reagent	2.85

VARIATION OF ACTIVITY WITH TEMPERATURE. An increase in the activity of the reagent with increasing temperature was to be expected from the behavior of palladium black and the sodium picrate-palladium colloid solution of Paal and Hartman. The variation of activity with temperature was studied over the range of 10° to 35° C. employing two reagents (solutions C and F). In this range the increase of activity averaged 2.8 cc. or 26 per cent per 10° temperature rise. A decrease in activity was noted in each case after heating to above 35° C. Upon subsequent removal of the solutions, a portion of the palladium was found to have precipitated, indicating that the reagent becomes unstable at 35° to 40° C. This is, however, no serious disadvantage for, although the activity does increase with temperature, the rate of increase hardly warrants the complication and expense required when means for heating the solution is introduced.

Determination of Hydrogen in Gas Mixtures

In order to establish the value of the anthraquinone-palladium colloid reagent, the behavior of the reagent toward mixtures of hydrogen with the various other gases commonly encountered in technical analysis was next examined. These mixtures included hydrogen and oxygen, hydrogen and nitrogen, hydrogen and saturated hydrocarbons, hydrogen and carbon monoxide, and hydrogen and carbon disulfide.

TABLE I. SUMMARY OF ACTIVITY TESTS

Solution	Composition		Maximum H ₂ Absorption Rate Cc./min.	Temp. ° C.
	Sodium anthraquinone disulfonate Grams	Palladium Grams		
C	15.0	1.0	11.07	23.5
G	16.0	1.0	10.44	29.5
D	18.7 (NaCl?)	0.7	6.23	26.0
F	38.0 (NaCl?)	1.8	6.68	27.5
E	10.0 (NaCl?)	0.7	6.01	24.3
A	8.0 (NaCl?)	0.7	4.21	25.0
H	9.0 grams sodium nitro anthraquinone sulfonate			
		1.9	6.50	23.0
I	(Pd alone)	1.0	3.30	29.0

HYDROGEN AND OXYGEN. Hydrogen and oxygen are simultaneously absorbed by the anthraquinone reagent at a rate higher than their individual absorption rates. In the case of detonating gas ($2\text{H}_2 + \text{O}_2$) the rate is extremely rapid and no change takes place in the anthraquinone reagent. Unless the concentration of one of them is known, however, determinations of a mixture of hydrogen and oxygen can give only the total content of both gases. The simultaneous absorption of hydrogen and oxygen may be advantageous in certain procedures.

HYDROGEN AND NITROGEN. The determination of hydrogen in hydrogen-nitrogen mixtures of varying composition is shown in Figure 4. The determinations were made employing the most active solutions, C and H, which had been prepared according to the method adopted as being the most satisfactory. The time necessary for the determination of hydrogen in gaseous mixtures varies from about 2 minutes for low concentrations up to 10 minutes for a concentration of 50 per cent. For the usual gaseous mixtures encountered in routine analysis, the hydrogen concentration is seldom much above 50 per cent.

TABLE II. ANALYSES OF NATURAL GAS

	Hydrogen Found by		Copper oxide tube (Bureau of Mines apparatus)
	Anthraquinone-palladium colloid reagent	%	
C_nH_{2n}	0.8	1.0	0.8
O_2	0.8	1.0	1.0
H_2	3.0	3.0	2.9
$\text{C}_n\text{H}_{2n+2}$ and N_2	95.4	95.0	95.3

HYDROGEN AND SATURATED HYDROCARBONS. In technical gas analysis, in accordance with the usual sequence, the hydrogen would be determined in the presence of saturated hydrocarbons and nitrogen. The behavior of the reagent with hydrogen-saturated hydrocarbon mixtures was therefore examined. From analogy with the behavior of the Paal and Hartman solution it was expected that the anthraquinone reagent would be satisfactory for the determination of hydrogen in the presence of saturated hydrocarbons.

This was verified by the results shown in Table II, using in one case the anthraquinone reagent for the hydrogen determination in natural gas and in the other the fractional combustion of the same gas mixture over copper oxide.

Effect of Carbon Monoxide and Carbon Disulfide on the Activity of Reagent

Carbon monoxide and organic sulfur compounds are important catalyst poisons frequently present in industrial gases. Accordingly, the effect of the presence of carbon monoxide and carbon disulfide upon the activity of the reagent was investigated. The results of this study may be briefly summarized as follows:

CARBON MONOXIDE. (1) Hydrogen and carbon monoxide may be removed simultaneously by the anthraquinone-palladium colloid reagent. (2) The absorption rate is extremely slow because of the poisoning effect of carbon monoxide. (3) Upon complete revivification with oxygen the reagent regains its original activity.

CARBON DISULFIDE. Carbon disulfide acts as a powerful poisoning agent for both the absorption of hydrogen and the subsequent revivification with oxygen. However, after standing in contact with air for a period of from 2 to 3 weeks the reagent regains its original activity. A concentration (2.3 per cent) of carbon disulfide very much higher than that found in gases for public utility work was employed in this test to exaggerate the effect of the low concentrations in industrial gases.

Capacity, Life, and Revivification of Reagent

CAPACITY. Although the reagent has the advantage of being readily reoxidized by contact with oxygen or air, it

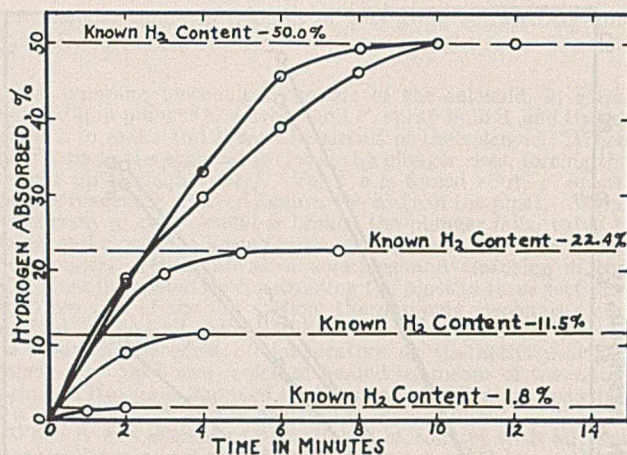


FIGURE 4. ANALYSES OF HYDROGEN-NITROGEN MIXTURES, SOLUTION C

is necessary for it to have some capacity for absorbing hydrogen. The greater the capacity, of course, the greater will be the number of hydrogen determinations possible before revivification becomes necessary. A test was therefore carried out to determine the volume of hydrogen that could be absorbed before the solution became too sluggish for use. During this test the reagent was sealed from the atmosphere by the rubber ring and gas bag previously mentioned. The volume of the reagent was 120 cc.

The results of this test are shown in Figure 5. It is seen that the hydrogen absorption rate is still satisfactory after 800 cc. have been absorbed.

REVIVIFICATION AND LIFE OF THE REAGENT. The revivification of the anthraquinone reagent by oxygen or air has been mentioned frequently. Some data showing the rate and completeness of the revivification are of interest, as it affects so greatly the life, and thereby the economy, of the reagent. The rate of revivification, as would be expected, varies with the amount of the reduced material present and the oxygen concentration. During the determination of the hydrogen absorption rates under the various conditions set up in the study of the reagent, the solutions were kept in a highly oxidized state in order to eliminate the effect of the degree of reduction. Under this condition, not necessary in practice, the revivification proceeds rather slowly. It may be said, conservatively, that with a corresponding state of reduction, the rate of oxygen absorption during revivification is as great as that of hydrogen absorption, and probably exceeds it. Apparently, the influence of the hydrogen-ion concentration upon the rate of revivification is also important.

That complete revivification may be effected has been shown repeatedly throughout the investigation by the absorption of oxygen volumes during revivification equivalent to the hydrogen previously absorbed.

The ability of the reagent to be completely revived suggests the possibility of a long life. Of the solutions so far prepared, all but two have been removed from operation in order to recover the palladium for use with other preparations and for no other reason. The two exceptions suffered loss of activity due to precipitation of the palladium by excessive temperatures purposely used during the study of the variation of activity with temperature. It so happened that these solutions (C and D) were subjected to the greatest number of hydrogen absorption tests. Solution C, whose volume was 120 cc., absorbed a total volume of 2708 cc. Prior to the drop in activity at elevated temperature, 2250 cc. of hydrogen had been absorbed with no loss in activity. The loss of activity after the absorption of 2708 cc. amounted to 10 per cent.

Solution D, whose volume was 120 cc., had absorbed a volume of 2860 cc. before it was subjected to excessive temperature with a resulting loss of activity. However, after the precipitated palladium colloid was filtered out and replaced by fresh colloid, the solution was continued in use, and absorbed approximately 2000 cc. more of hydrogen.

Although the effect of long standing has not been thoroughly studied, a comparatively inactive solution (solution A) had stood from January 9 to September 20 without apparent loss of activity or precipitation of the colloid.

Application of Reagent to Standard Gas Analysis Practice

ACTIVITY OF REAGENT IN A STANDARD SIZE PUMPING PIPET. With the standard 200-cc. automatic pumping pipet the activity of the reagent is somewhat increased, owing to the greater surface exposed. Thus, with pure hydrogen the value of the maximum absorption rate for solution C is 14.5 cc. per minute in comparison to 10.8 cc. per minute with the small pipet employed in most of the activity tests.

USE IN ROUTINE GAS ANALYSIS. From this investigation the anthraquinone-palladium colloid reagent appears, at present, to offer a satisfactory method for the determination of hydrogen in routine gas analysis. Its use may be limited to some extent, however, by the type of apparatus employed: It would probably not be applied to apparatus of the Bureau of Mines type equipped with copper oxide tube, as this apparatus would require the addition of at least two extra pipets, one for the hydrogen reagent and one, or perhaps two, for the carbon monoxide reagent. From the standpoint of both time and accuracy it would be undesirable to restrict the use of the copper oxide tube in this apparatus to the determination of carbon monoxide.

The application of this reagent seems feasible with apparatus of the types of the United States Steel Corporation,

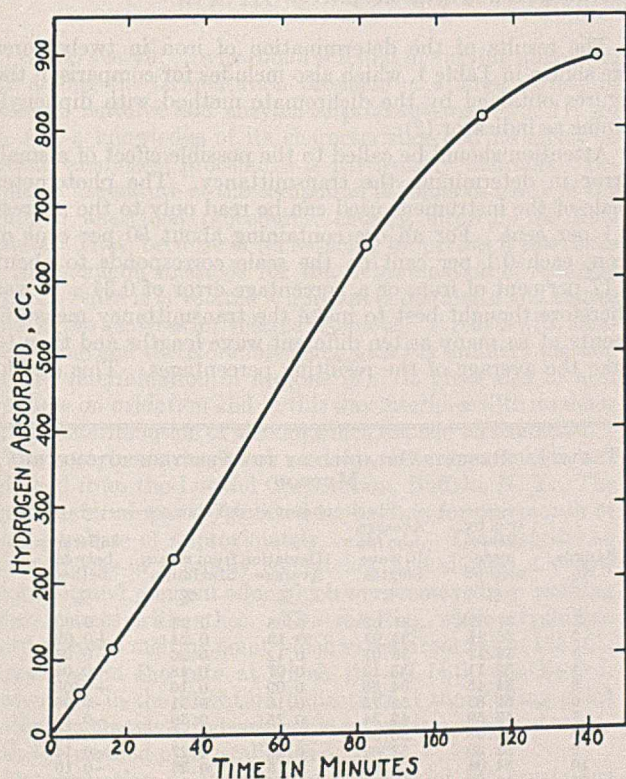


FIGURE 5. HYDROGEN ABSORPTION CAPACITY OF REAGENT, SOLUTION C

Bone and Wheeler, the Elliott, the Illinois modification of the Morehead (equipped with slow combustion pipet), Hempel, Sheppard, and the Bureau of Mines type equipped with the extra absorption pipets and without the copper oxide tube. In the analysis of gases of low hydrogen and carbon monoxide content, the use of this reagent appears to be preferred to the fractionation over copper oxide.

Further Development

In order to be economic the methods of preparation should be reduced to a production routine and, if possible, simplified. An investigation of the effect of the variation in alkalinity must be carried out. It appears that the hydrogen-ion concentration controls to a marked degree the rate of absorption of both hydrogen and oxygen and the tendency of the reagent to foam. An increase in the foaming tendency with use was attributed to the absorption of carbon dioxide from the air with accompanying increase in hydrogen-ion concentration. Upon addition of a small amount of sodium hydroxide, no foaming occurred. In the case of the two most active reagents, solutions C and H, the foam broke immediately upon stopping the pumping action.

Summary

The literature concerning the various liquid reagents which have been proposed for the determination of hydrogen has been reviewed and a brief criticism of such methods has been made.

A new reagent has been developed, consisting of an aqueous solution of sodium anthraquinone 2,7-disulfonate and colloidal palladium peptized by an alkaline albumin compound, sodium protalbinat. This reagent has the advantage of being readily revived by contact with oxygen or air, assuring active hydrogen absorption over long periods of operation.

The characteristics of the reagent, with particular reference to its application to routine gas analysis, have been studied and may be summarized as follows:

1. The reagent is more active than any liquid reagent tested by the authors for the determination of hydrogen. With pure hydrogen the absorption rate, in a suitable gas-analysis pipet, is about 15 cc. per minute.
2. The reagent operates satisfactorily at room temperature.
3. Hydrogen may be determined accurately in the presence of nitrogen and saturated hydrocarbons. The absorption is complete.
4. In routine analysis carbon dioxide, unsaturates, oxygen, and carbon monoxide should be removed prior to the hydrogen determination.
5. Although temporarily poisoned by carbon monoxide and carbon disulfide, the reagent regains its activity upon standing in contact with oxygen or air.
6. Hydrogen and oxygen may be removed simultaneously.
7. The reagent appears to remain active after standing several months and appears to be unaffected by light.
8. The capacity is sufficient to care for a number of determinations before revivification becomes necessary. The spent reagent is completely and simply revived by contact with air or oxygen.

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A Spectrophotometric Method for the Determination of Iron in Ores

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The spectrophotometric method employing the molecular extinction coefficient has been satisfactorily applied to the determination of iron, by measuring the transmittancy of light at given wave lengths through the system consisting of the amethyst-colored complex formed by the addition of salicylic acid to ferric ions in acetic acid solution.

VARIOUS constituents, either naturally colored or forming colored systems with appropriate reagents, may be determined colorimetrically by means of visual or photoelectric comparison with colorimetric standards consisting of known amounts of the constituent being measured or of some other system equivalent in color. Another colorimetric method involves the use of a spectrophotometer, with which known solutions may be used to construct a curve coordinating transmittancy of light of a given wave length and concentration of the constituent. Determination of the transmittancy of an unknown solution enables one to read off concentration from the curve, as in the determination of manganese in steel (3). A variation of the method, eliminating the curve and employing the molecular extinction coefficient, has been used in the determination of copper in ores (4).

In order to test further the reliability of the latter type of method, particularly with samples containing higher percentages of the desired constituent, determinations of iron were made on a series of ores, as shown in Table I. The system measured consisted of the amethyst-colored complex formed by the addition of salicylic acid to a solution containing ferric ions in the presence of acetic acid. All transmittancy measurements were made with the photoelectric spectrophotometer built for Purdue University by the General Electric Co. The molecular extinction coefficients as determined for solutions of known iron content varied from 1144 at 460 $m\mu$ through 1622 at 520 $m\mu$ to 1528 at 550 $m\mu$.

Procedure

A 0.2-gram ore sample was dissolved in concentrated hydrochloric acid and oxidized with concentrated nitric acid, and the solution was accurately diluted to 1000 ml. at 30°. The amethyst color was produced in 10 ml. of this solution according to the directions of Snell (5), and the volume was then accurately made up to 100 ml. at 30°. Particular care was taken to have the pH value of the final solution within rather close limits. Bech (1), in discussing the photoelectric determination of salicylic acid with ferric chloride, says that a decrease in pH value reduces the color intensity and that the pH value should not be below 2.2.

By means of the spectrophotometer the transmittancy of the amethyst solution in a 1-cm. cell was determined at intervals of 10 $m\mu$ from 460 to 550 $m\mu$, inclusive. These wave lengths were chosen because they include the flat portion of the spectral transmission curve where readings are more nearly accurate. The photometer scale was frequently checked with Bureau of Standards glasses. Using the value of the extinction coefficient determined for the wave length in question, the percentage of iron was calculated (4) and the average of the ten figures was taken as the percentage of iron in the sample.

The results of the determination of iron in twelve ores are shown in Table I, which also includes for comparison the figures obtained by the dichromate method with diphenylamine as indicator (2).

Attention should be called to the possible effect of a small error in determining the transmittancy. The photometer scale of the instrument used can be read only to the nearest 0.1 per cent. For an ore containing about 50 per cent of iron, each 0.1 per cent on the scale corresponds to about 0.17 per cent of iron, or a percentage error of 0.34. It was therefore thought best to make the transmittancy measurements at as many as ten different wave lengths and then to take the average of the resulting percentages. This should

TABLE I. RESULTS OBTAINED BY THE SPECTROPHOTOMETRIC METHOD

Sample No.	Iron by dichromate method %	Spectrophotometric Values			Difference between methods %
		Average iron for 10 wave lengths %	Deviation from mean Average %	Maximum %	
1	37.62	37.62	0.08	0.23	0.00
2	36.84	36.93	0.12	0.24	+0.09
3	36.12	36.07	0.12	0.26	-0.05
4	35.11	35.13	0.07	0.18	+0.02
5	34.45	34.53	0.09	0.16	+0.08
6	52.83	52.75	0.16	0.31	-0.08
7	49.59	49.34	0.25	0.39	-0.25
8	50.68	50.35	0.33	0.50	-0.33
9	52.20	52.09	0.13	0.27	-0.11
10	54.04	53.94	0.16	0.36	-0.10
11	56.00	55.97	0.17	0.25	-0.03
12	57.62	57.60	0.06	0.13	-0.02

give a more reliable figure than to take the average of ten readings at any one wave length.

The spectrophotometric method, provided a spectrophotometer possessing the precision of the Purdue instrument is used, is capable of giving results for iron in ores which will be within ± 0.30 per cent of the values given by the dichromate titration method and many will be within ± 0.10 per cent. Results may be duplicated on the same sample with a precision of about ± 0.10 to ± 0.20 per cent.

TABLE II. COMPARISON OF PERCENTAGE ERRORS IN IRON AND COPPER DETERMINATIONS

	Percentage Error		
	Maximum	Minimum	Average
Iron, 12 samples	0.65	0.00	0.20
Copper, 11 samples	1.98	0.00	0.69

In Table II is shown a comparison of the reliability of the results for iron, on a percentage basis, with those previously obtained by the writer (4) for copper ores, where the actual percentages were much lower. The figures indicate that the spectrophotometric method involving the use of the molecular extinction coefficient can be satisfactorily extended to the determination of iron where the percentage of the constituent determined is relatively high.

Summary

The spectrophotometric method employing the molecular extinction coefficient has been applied to the determination

of iron in ores. Although the iron content is relatively high, the percentage error is smaller than when similar transmittancy measurements were made on the copper-ammonia system where the copper content was relatively very low.

The spectrophotometric method gives results for iron in ores which check well with those given by the dichromate method.

Acknowledgments

The writer wishes to express his sincere appreciation to M. G. Mellon, Department of Chemistry, Purdue University, in whose laboratory this investigation was conducted, and to thank him for his kind interest, helpful criticism, and profitable suggestions and for the use of the Purdue spectrophotometer. Thanks are also given to H. W. Swank, G. Dragt, and E. R. Wright of Purdue for their aid in adjusting the spectrophotometer.

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Determination of Acetylmethylcarbinol

Effect on Certain Analytical Procedures

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SINCE acetylmethylcarbinol is found in varying quantities among the fermentation products of a large variety of bacterial cultures and enzymatic preparations (3, 8, 11, 13, 14, 15), a knowledge of its characteristics and its effect on various analytical procedures is particularly desirable. Because of the nature of the compound it reacts in many of the common analytical procedures, causing error in the final results. Thus, because of its reducing properties it interferes in the common methods for the determination of reducing sugars. Since it is volatile it appears in distillates and causes error in the analyses for volatile products. It reacts with alkaline iodine and therefore interferes with the ordinary method for the determination of acetone (6). It gives rise to acid products on oxidation and in this way interferes with methods for the determination of alcohol which depend on oxidation.

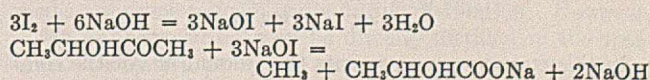
The acetylmethylcarbinol used for these experiments was obtained from the Lucidol Corporation, Buffalo, N. Y. The liquid material was crystallized by holding for one month at a temperature of approximately -10° C. The material so obtained was of a mushy consistency and showed a yellow coloration and pungent odor which were removed by washing several times with ether. The resulting white crystalline powder gave a melting point which varied from 84° to 125° C., depending on the rate at which the oil bath was heated. Statements in the literature indicate that the melting point of dimeric acetylmethylcarbinol is rather irregular and varies with the method of crystallization (1, 2).

Determination of the molecular weight of the crystalline material by elevation of the boiling point indicated an initial value of about 160 which dropped to 101 after boiling for 25

minutes because of conversion to the monomer. Other investigators (1, 2) have found molecular weights for acetylmethylcarbinol dimers which ranged from 170 to 195 as compared to the theoretical value of 176.

Reaction with Alkaline Iodine

Since acetylmethylcarbinol contains the acetyl group ($\text{CH}_3\text{CO}-$) directly linked to carbon, it will react with alkaline iodine to form iodoform (5). To verify the nature of the reaction between acetylmethylcarbinol and iodine, aliquots of standard aqueous solutions of the compound (containing 3 to 10 mg.) were made alkaline with 1 N sodium hydroxide and standard iodine solution was added. Iodoform was precipitated and, after standing for 10 to 15 minutes, the excess iodine was liberated by the addition of 1 N sulfuric acid and titrated. The averages of a large number of determinations are presented in Table I. The iodine used approaches six atoms per molecule of iodoform, which supports the following formulation for the reaction:



The iodoform isolated from one reaction sublimed at 118° to 119° C. as compared to the reported value of 119° (9). Lactic acid was recovered from the products of the reaction by extraction of the acidified solution with ether. From the ether extract the zinc salt was prepared and analyzed. The water of crystallization was determined by drying to a constant weight at 110° C., the zinc content by ignition, and lactic

TABLE I. REACTION OF ACETYL METHYL CARBINOL WITH ALKALINE IODINE

Sample	0.1 N I ₂ per	Atoms I per	Per Cent of
	Mg.	Molecule	
	CH ₃ CHOH- COCH ₃	CH ₃ CHOH- COCH ₃	Theory
	Cc.		
Crystals washed with ether	0.671	5.91	98.5
Ether-washed product recrystallized from acetone	0.672	5.92	98.7
Theoretical for reaction	0.681	6.00	100.0

TABLE II. VOLATILITY OF ACETYL METHYL CARBINOL IN AQUEOUS SOLUTION

Fractions, Percentage of Total Distilled	Acetylmethylcarbinol in Distillate Concentration of Solution:				Av.
	0.005% %	0.02% %	0.072% %	0.10% %	
25	31.8	32.1	31.5	..	31.8
50	59.7	60.3	59.6	59.2	59.7
75	83.7	83.9	83.1	..	83.6

acid by the method of Friedemann and Graeser (4) with the following results:

Calcd. for Zn(C₂H₃O₂)·3H₂O:H₂O 18.2. Found: 18.0

Calcd. for Zn(C₂H₃O₂):Zn 26.9, CH₃CHOHCOOH 74.0. Found: Zn 29.0, CH₃CHOHCOOH 73.9.

The data show that the product isolated was nearly pure inactive zinc lactate containing three molecules of water of crystallization. The high zinc content is probably due to the presence of small amounts of excess zinc—e. g., zinc hydroxide—which raise the zinc value but have no appreciable effect on the other analyses.

Volatility

The rate of distillation of acetylmethylcarbinol from aqueous solution was determined by a modification of the method of Virtanen and Pulkki (18). In order to prevent condensation and reflux, an insulating hood made from a large metal can was used to cover the distillation flask and in order to ensure uniform heating, a metal shield was used to protect the Bunsen burner. In the experiments 200 cc. of solution were distilled and three 50-cc. fractions were collected. These fractions as well as the residue were analyzed by application of the iodoform reaction. The percentage of acetylmethylcarbinol in the distillates was found to be independent of the rate of distillation when the precautions to prevent reflux were observed. The data for the distillation of solutions varying in concentration from 0.005 to 0.1 per cent are presented in Table II.

As shown by the data, the distribution of acetylmethylcarbinol during distillation is constant and independent of the concentration of the solution. A quantitative expression for the volatility may be calculated by application of the formula used by Virtanen and Pulkki (18):

$$k = \frac{\log y_1 - \log y_2}{\log x_1 - \log x_2}$$

In this equation y_1 represents the amount of volatile compound in the solution at the beginning of distillation and y_2 the amount at the end, while x_1 represents the amount of water at the beginning and x_2 the amount at the end. The values for the distillation constant, k , as calculated from the average figures for the first, second, and third fractions (Table II) were 1.330, 1.297, and 1.298. On comparison with the figures of Virtanen and Pulkki (18) it is seen that acetylmethylcarbinol is a little more volatile than propionic acid

($k = 1.239$ to 1.245) and less volatile than butyric acid ($k = 1.940$ to 2.035).

In the determination of acetone in a fermented medium containing acetylmethylcarbinol, a correction must be made which depends on the concentration of acetylmethylcarbinol and the volume of distillate collected. If 25 per cent of the liquid is distilled off, approximately 32 per cent of the acetylmethylcarbinol will be contained in the distillate. For other volumes distilled, the correction may be applied most conveniently by plotting a curve using the values of Table II, or the correction may be made by calculation using the equation

$$\log \frac{y_1}{y_2} = k \log \frac{x_1}{x_2}$$

When 35 per cent of the liquid is distilled, $\frac{x_1}{x_2} = \frac{100}{65}$, and setting k equal to 1.31 the value for y_2 , the amount of acetyl-

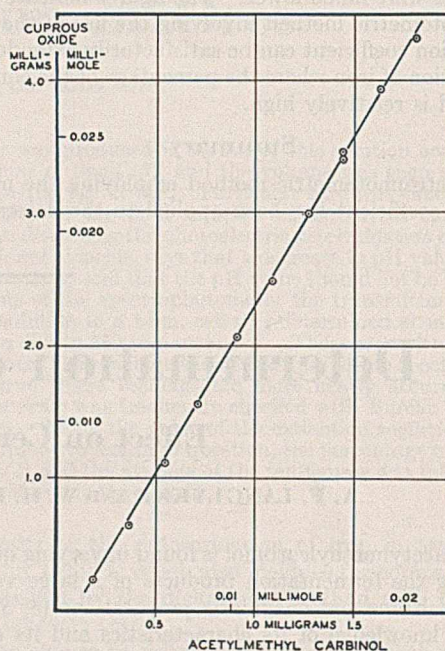


FIGURE 1. CUPROUS OXIDE PRODUCED IN REDUCTION OF SHAFFER-HARTMANN SUGAR REAGENT BY ACETYL METHYL CARBINOL

methylcarbinol remaining undistilled, is found to be 56.8 per cent. Therefore, 43.2 per cent of the acetylmethylcarbinol will be found in the distillate.

Reaction with Oxidizing Reagents

In order to determine the corrections to be applied in the analyses for reducing sugar, two methods for the determination of glucose were investigated. These were the Shaffer-Hartmann method as modified by Stiles, Peterson, and Fred (17), which depends on the reduction of copper and iodometric determination of the cuprous oxide produced, and the Hagedorn-Jensen method (7), which depends on the reduction of potassium ferriocyanide to ferrocyanide and titration of the excess ferriocyanide with dilute standard thiosulfate solution. In each case varying amounts of an aqueous solution of acetylmethylcarbinol were submitted to the procedure used in the determination of the reducing sugars and the extent of reduction of the reagent was determined. The results are shown graphically in Figures 1 and 2.

REDUCTION OF CUPRIC SULFATE. According to Kling (12), acetylmethylcarbinol is oxidized by alkaline cupric oxide

to acetic acid, but such a result was not obtained in these experiments. Stahly and Werkman (16) report that 3.01 grams of cuprous oxide are produced from each gram of acetylmethylcarbinol under the conditions of the Munson-Walker method. In the copper-reduction method used, the tubes are only loosely stoppered to prevent oxidation by the air and loss of volatile products is not prevented. It is also possible that the 15-minute reaction period is not long enough for complete reaction. For these reasons the amount of copper reduced does not bear a stoichiometric relation to the amount of acetylmethylcarbinol in the sample, although there is a regular relation between these two variables.

If acetylmethylcarbinol is oxidized to diacetyl, two hydrogen equivalents per mole are required, while for the oxidation to acetic acid four hydrogen equivalents are necessary. As calculated from the graph of Figure 1, 2.95 hydrogen equivalents are actually used in the oxidation, which shows that only about one-half of the diacetyl formed is further oxidized to acetic acid. The points described a straight line, which does not, however, pass through the origin. This apparent anomaly can be explained only on the assumption that a constant small amount of acetylmethylcarbinol escapes oxidation, or that a constant small amount of diacetyl is lost through evaporation.

REDUCTION OF FERRICYANIDE. As in the reduction of copper, the reduction of ferrieyanide proceeds without complete conversion of the acetylmethylcarbinol to acetic acid. In this case 2.67 hydrogen equivalents are required, although more variation was observed in this reaction. This is shown by the fact that the individual points on the graph of Figure 2 do not correspond so well to a straight line as in the case of the reduction of copper.

Oxidation with Acid Potassium Dichromate

In the determination of butyl and ethyl alcohols by the method of Johnson (10), a distillate containing the neutral volatile products from a bacterial fermentation is oxidized by means of acid potassium dichromate solution and the acid resulting from the oxidation is removed by distillation. Two fractions are collected and the content of butyl and ethyl alcohols in the original sample is calculated from the titrations of these fractions. Since acetylmethylcarbinol yields

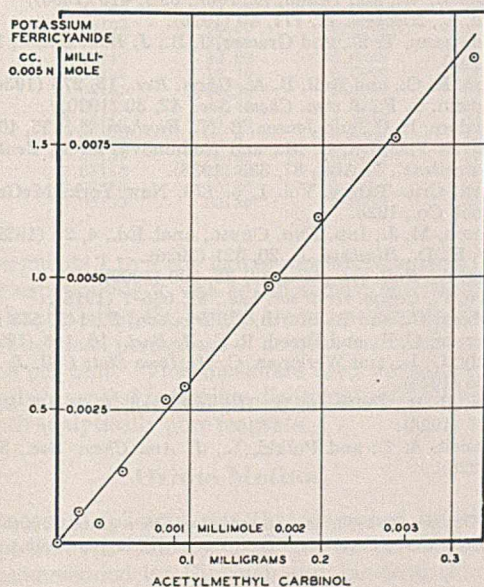


FIGURE 2. REDUCTION OF POTASSIUM FERRICYANIDE (HAGEDORN-JENSEN REAGENT) BY ACETYL METHYL CARBINOL

acid products on oxidation, it is of interest to know what effect this compound will exert in the alcohol method.

TABLE III. EFFECT ON JOHNSON METHOD FOR BUTYL AND ETHYL ALCOHOLS

Acetylmethylcarbinol Sample Mg.	Alcohol Indicated			
	Butyl alcohol Mg.	Ethyl alcohol Mg.	Theoretical ^a Butyl alcohol Mg.	Ethyl alcohol Mg.
5	-0.01	5.26	0	5.23
10	0.14	10.48	0	10.46
15	0.14	15.87	0	15.69
Av. (per mg. acetoin)	0.007	1.053	0	1.046

^a Based on assumption that one mole of acetylmethylcarbinol is equivalent to two moles of ethyl alcohol.

Samples of 5, 10, and 15 mg. of acetylmethylcarbinol in aqueous solution were analyzed according to the procedure for the determination of alcohols by the Johnson method (10). In Table III the results obtained are expressed as milligrams of butyl and ethyl alcohols. The oxidation of acetylmethylcarbinol by the acid dichromate yields acetic acid, and therefore for purposes of correcting any alcohol determinations one mole of acetylmethylcarbinol corresponds to two moles of ethyl alcohol.

Determination of Acetylmethylcarbinol

Since acetylmethylcarbinol reacts quantitatively with alkaline iodine reagent and since the carbinol is distilled from aqueous solution at a definite rate which is independent of the concentration, it was possible to develop a method for its determination in which these properties were applied. Attempts to separate the carbinol from the fermented medium were unsuccessful, as neither ether extraction nor constant volume distillation gave a quantitative recovery of the compound.

In order to apply the iodoform reaction directly to the determination of acetylmethylcarbinol it is necessary to eliminate from the sample any other compounds which will react with the iodine reagent. Acetone is commonly present in large excess over the acetylmethylcarbinol content in some fermentations, but this compound is practically completely eliminated by distillation of half the volume of an aqueous solution. Ethyl alcohol in appreciable concentration will also react with alkaline iodine, although this reaction is very incomplete at room temperature and in the short reaction time used. However, it is also completely eliminated by half distillation. Butylene glycol is also likely to occur in association with acetylmethylcarbinol in fermentations and will react with alkaline iodine in 15 minutes at room temperature to produce an apparent acetylmethylcarbinol content equivalent to 10 per cent of its own weight. However, because of the nonvolatility of this compound, the error resulting by analysis of the third quarter of distillate is negligible.

By far the most convenient method for the determination of acetylmethylcarbinol involves direct distillation from the fermentation mixture, and by this method quantitative results could be obtained. The disadvantage of direct distillation from the culture medium lies in the fact that many of the media are prone to foam badly during distillation. However, many ordinary media may be directly distilled in the fractional distillation procedure and certain procedures may be applied to minimize foaming when this characteristic is displayed.

It was found that a mineral salts-peptone-glucose medium which had been fermented by *A. aerogenes* in the presence of an excess of calcium carbonate could not be distilled, because of excessive foaming. To correct this condition the culture was acidified with sulfuric acid, heated just to boiling and, after cooling, filtered by suction through an asbestos mat.

TABLE IV. DIRECT DETERMINATION OF ACETYLMETHYLCARBINOL BY FRACTIONAL DISTILLATION OF CULTURE

Sample	Acetylmethylcarbinol			Recovery of Added Acetylmethylcarbinol	
	Found Mg./100 cc.	Added Mg./100 cc.	Found (after addi- tion) Mg./100 cc.	Mg./100 cc.	%
Sterile salts- peptone medium	{ ..	49.2	50.3	50.3	102.1
	{ ..	21.0	21.4	21.4	101.9
<i>Cl. polymyxa</i> in 6% corn mash	40.3	49.6	89.5	49.2	99.2
<i>A. aerogenes</i> in salts-peptone medium	29.1	37.8	67.9	38.8	102.7
<i>A. aerogenes</i> in salts-peptone medium (excess CaCO ₂)	39.4	44.0	85.1	45.7	103.9
<i>A. aerogenes</i> in salts-peptone medium	18.2	10.0	28.1	9.9	99.0
<i>Cl. acetobutyli- cum</i> in 6% corn mash	37.4	49.8	87.1	49.7	99.8

The resulting product showed considerable less tendency to foam, but as an added precaution the sample was diluted to four times the volume before applying the distillation procedure. By this procedure quantitative results could be obtained.

For the results reported in Table IV the following general procedure was used:

Enough of the culture to give 100 cc. of clear filtrate is filtered through a fluted filter and 100 cc. of the clear filtrate are then pipetted into the 300-cc. distillation flask which contains 6 or 8 glass beads to prevent bumping. The flask is directly connected to a short condenser by means of a ground-glass joint and is supported by a ring bearing a wire gauze with an asbestos mat center. The insulating hood is placed over the flask, and heating is started with a burner which is protected by a shield so as to guarantee uniform heating. The rate of heating is so adjusted that the distillate which collects is cold and the medium under distillation boils evenly. A fraction of exactly 50 cc. is collected in a volumetric flask and may either be discarded or used in the determination of the more volatile products of the fermentation. A second fraction of exactly 25 cc. is then collected and analyzed by the iodoform reaction.

The contents of the 25-cc. volumetric flask are added to 15 cc. of 1 *N* sodium hydroxide in a 150-cc. Erlenmeyer flask. The volumetric flask is rinsed with 3 portions of a few cubic centimeters of water and the rinsings are added to the sample in the Erlenmeyer. Then while the flask is constantly shaken in one hand, exactly 5 cc. of 0.2 *N* iodine are added by rapid dropping from a pipet held in the other. The precipitation of iodoform begins almost immediately and after 10 minutes the reaction is complete. After standing for 10 to 15 minutes out of direct sunlight, 20 cc. of 1 *N* sulfuric acid are run into the flask and the liberated iodine is titrated immediately to the starch end point with standard 0.1 *N* sodium thiosulfate solution. A semimicroburet which may be read accurately to 0.01 cc. is used. A blank for the purpose of standardizing the iodine solution is run on 5 cc. of the iodine solution, with distilled water replacing the sample in the ordinary procedure.

Since one mole of acetylmethylcarbinol is equivalent to 6 atoms of iodine, one millimole (or 88 mg.) is equivalent to 60 cc. of 0.1 *N* iodine. Then, for each cc. of 0.1 *N* iodine used in the iodoform reaction there are 1.467 mg. of acetylmethylcarbinol in the sample. According to Table II, 23.9 per cent of the acetylmethylcarbinol in the sample appears in the third quarter of distillate. Therefore, to obtain the total acetylmethylcarbinol content of the 100-cc. sample distilled, the content of the third quarter of distillate is divided by the factor 0.239.

The results reported in Table IV were obtained on a variety of cultures as shown. The salts-peptone medium used consisted of 0.07 per cent dibasic ammonium phosphate, 0.5 per cent peptone, 0.1 per cent asparagine, and tap water. In the case of the fermentations 3 per cent of glucose was added. The corn mash was made up with 6 per cent of corn meal in tap water. In the second column of Table IV are given the concentrations of acetylmethylcarbinol as determined directly on the culture by the procedure outlined. Acetylmethylcarbinol was then added in the amounts given in the third column and the content of the samples so prepared was again determined with the results expressed in the fourth column. In the fifth and sixth columns are entered the recoveries of the added acetylmethylcarbinol as obtained from the difference between the determinations before and after the addition of a known quantity of acetylmethylcarbinol. The data reported are the averages of triplicate analyses. The deviation of individual results from the average ranged from 0 to 4.1 per cent and averaged 1.13 per cent. The average error in the recovery of added acetylmethylcarbinol was 2.2 per cent.

The recoveries are in general a little high, and the average recovery is about 101.2 per cent. Therefore, a somewhat higher degree of accuracy may be obtained if the recovery is determined separately for each different medium used, as this value will vary somewhat with the nature of the solution under analysis. Thus, if instead of using the value of 23.9 per cent recovery as determined for aqueous solutions a corrected value of 23.6 per cent is used, the errors in the determinations reported would vary from -2.2 to +2.7 per cent.

Summary

Because of the unique nature of the compound, acetylmethylcarbinol affects a variety of common analytical procedures. Methods for the correction of acetone, alcohol, and reducing sugar determinations in the presence of acetylmethylcarbinol are described. Based on its volatility and iodoform reaction, a method for its quantitative determination has been developed.

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Estimation of Acetone

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AMONG the best-known methods for the quantitative estimation of acetone are the iodoform and oxime methods. In estimating samples of pure acetone by these methods, however, the author was surprised to find that results of over 102 per cent were obtained. The details of procedure in the estimations are set out below.

Iodoform Method

About 2 cc. of the acetone were pipetted into a weighed 250-cc. standard flask containing about 50 cc. of water, making sure that the sample fell into the water without touching the glass. The flask was shaken gently to mix and weighed again, and water was then added to the 250-cc. mark. Now 20 cc. of *N* sodium hydroxide were run into a glass-stoppered bottle of 150-cc. capacity, and after thoroughly mixing, 5 cc. of the dilute acetone solution were added to the bottle and mixed. Fifty cubic centimeters of 0.1 *N* iodine solution were then added drop by drop from a pipet, swirling the contents of the bottle during the addition which took about 3 minutes. Originally the 50 cc. were run from the pipet at full rate, the addition taking about 30 seconds, till it was found that low results were liable to be obtained, as observed by Goodwin (4) and others (1). After adding the iodine, the stopper was inserted and the bottle left 10 minutes. Then 21 cc. of *N* sulfuric acid were added, mixed, and the liberated iodine was estimated by titration with 0.1 *N* sodium thiosulfate, using starch as indicator. A blank determination was also carried through, the difference between the two titrations giving the cubic centimeters of thiosulfate equivalent to the iodine absorbed.

The results are given in Table I. In experiments 1 to 3 commercially pure acetone was used, containing less than 0.2 per cent of water as estimated by the gasoline method.¹ In experiments 4 to 17 the acetone was dried by standing over barium oxide several days and then redistilled. The acetone used in experiment 18 was obtained by fractionation, taking the portion boiling at 55.7° C. at 760 mm. pressure; the specific gravity at 20° C. was 0.792.

TABLE I. RESULTS FOR PURE ACETONE BY IODOFORM METHOD

Expt.	Sample Titrated Gram	Thiosulfate Cc.	Factor	Acetone %
1	0.01265	13.30	0.0996	101.3
2	0.03163	33.30	0.0996	101.5
3	0.03169	33.45	0.0996	101.7
4	0.03129	33.08	0.0998	102.0
5	0.03152	33.10	0.0999	101.5
6	0.03152	33.10	0.0999	101.5
7	0.03152	33.40	0.0999	102.4
8	0.03152	33.40	0.0999	102.4
14	0.03149	66.8	0.0500	102.5
15	0.03159	33.60	0.0999	102.8
16	0.03128	33.36	0.0993	102.4
17	0.02573	25.86	0.1054	102.5
18	0.03139	33.35	0.0999	102.8

In experiments 1 to 6 the iodine was added rapidly, but in the other experiments it was added slowly, as already mentioned. In the latter the results are more consistent though higher. The mean percentage of acetone in experiments 7 to 18 is 102.5 per cent. The thiosulfate used was standardized every few days against potassium dichromate and once against iodine, both analytically pure reagents.

Oxime Method

The procedure followed was that described by Marasco (6), except that the indicator used was the modified methyl orange recommended by Hickman and Linstead (5). This

¹ This method consists in adding gasoline to a sample of the acetone till a cloud is formed at 20° C., the gasoline being checked against acetone of known water content.

was found to give the same end point in the titration, but it was much more sharply defined (7).

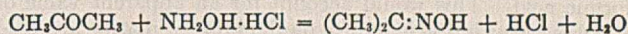
The acetone solutions were made up as described under the iodoform method. Two beakers, each containing 400 cc. of the hydroxylamine hydrochloride solution (0.2 per cent) neutralized to a steel-gray color with the modified indicator, were placed on a sheet of white paper, 25 cc. of the acetone solution were added to one of the beakers, and the acid liberated was titrated with 0.1 *N* sodium hydroxide till the colors in the two beakers matched again. The end point can be determined to one drop of 0.1 *N* sodium hydroxide and is permanent for 5 minutes.

Taking Marasco's factor as correct—i. e., 1 cc. of 0.1 *N* sodium hydroxide is equivalent to 0.00614 gram of acetone—the results shown in Table II were obtained.

TABLE II. RESULTS FOR PURE ACETONE BY OXIME METHOD

Expt.	Sample Titrated Gram	Sodium Hydroxide Cc.	Sodium Hydroxide Factor	Acetone %
10	0.1574	26.30	0.1000	102.6
11	0.1579	26.50	0.1000	103.0
12	0.1579	26.40	0.1000	102.6
13	0.1579	26.45	0.1000	102.8
19	0.1578	26.40	0.1000	102.7
20	0.1571	26.05	0.1011	102.9
21	0.1588	26.30	0.1011	102.8
22	0.1586	26.20	0.1011	102.5

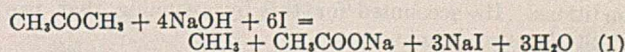
The mean percentage of acetone given by this method is 102.7 per cent, which agrees closely with the value obtained by the iodoform method. This is to be expected, since Marasco's factor 0.00614 was obtained by checking the strength of his acetone solution by means of Messinger's iodoform method, assuming Messinger's method to be correct. Marasco's factor should therefore be changed to 0.00598—i. e., 1 cc. of 0.1 *N* sodium hydroxide is equivalent to 0.00598 gram of acetone. In other words, the oxime reaction



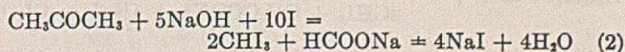
when carried out as described by Marasco, goes to 97.1 per cent of completion and not 94.4 per cent as he states.

Test for Formate in Iodoform Reaction Products

From the above experiments it appears that acetone, when estimated by Messinger's method (following the precautions advised by Goodwin, 4) reacts with about 2.5 per cent more iodine than is required by the equation



It is possible that a small portion of the acetone reacts with iodine according to the equation



By this reaction 10 atoms of iodine instead of 6 are used.

To test if any formate is present in the reaction products the following procedure was adopted:

About 1 gram of acetone was added to 600 cc. of *N* sodium hydroxide in a 2-liter flask, and 1.17 liters of 0.1 *N* iodine were run in very slowly from a tap funnel, shaking continuously. When all the iodine had been added (45 minutes) the flask was left standing for 15 minutes and then the iodoform was filtered off. After acidifying the filtrate with 20 cc. of pure sulfuric acid diluted to 60 cc., about 5 cc. of mercury were added and the flask was shaken for an hour to remove the excess iodine. (Sodium thiosulfate was first used for neutralizing the iodine, but

it was found to decompose into sulfur dioxide and sulfur in the subsequent steam-distillation. Then iron filings were tried, but the ferrous iodide formed also appeared to decompose in the steam distillation, giving free iodine. Hence, mercury was used instead.)

The solution, having been completely decolorized by the mercury, was filtered and the filtrate was steam-distilled after the addition of 2 cc. of sulfuric acid. When all the volatile acid had distilled over, about 5 liters of distillate having been collected, the distillate was neutralized with *N* sodium hydroxide, using phenolphthalein as indicator. Then 3 cc. of *N* sodium hydroxide were added in excess and the solution was evaporated down to 200 cc. Now 50 cc. of 5 per cent mercuric chloride solution were added to the clear solution (filtered, if necessary) and boiled for an hour under a reflux condenser (2). The white precipitate was filtered through a Gooch filter, washed with cold water, dried, and weighed.

A blank experiment was made taking 1 gram of glacial acetic acid in 600 cc. of *N* sodium hydroxide and adding 225 cc. of 0.1 *N* iodine, 27 grams of potassium iodide, 1 liter of water, then 20 cc. of concentrated sulfuric acid diluted to 60 cc. The iodine was decolorized by adding mercury and the rest of the experiment carried out exactly as before.

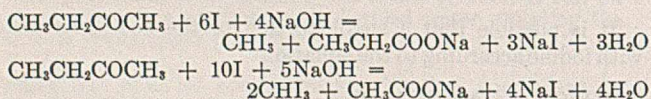
Finally a check experiment was made like the blank, except that the acetic acid contained a known weight of formic acid. The results are given in Table III.

TABLE III. FORMIC ACID FOUND IN IODOFORM REACTION PRODUCTS

Expt.	Sample Taken		Mercuric Chloride Ppt.	Formic Acid Found
	Gram		Gram	Gram
1	0.96	Me ₂ CO	0.045	0.0044
2	1.0	AcOH (blank)	None	None
3	1.0	AcOH containing 0.04 gram HCOOH (check)	0.331	0.0323
4	0.96	Me ₂ CO	0.0664	0.0064
5	1.0	AcOH (blank)	0.0004	Negligible

The blank experiments, 2 and 5, show a negligible weight of formic acid. Experiment 3 shows that the method is satisfactory for estimating small amounts of formic in acetic acid. Experiments 1 and 4, though apparently carried out under the same conditions, do not agree very well in the weight of formic acid found, which is low in both cases. In experiment 4, 0.96 gram of acetone gave 0.0064 gram of formic acid. This would account for an apparent value of 100.6 per cent in the iodoform method for estimating acetone, which is considerably lower than the figure 102.5 actually found. However, the acetic acid found in the steam-distillation was only 80 per cent of the theoretical amount; it may be that both formate and acetate were occluded in the iodoform. The experiments, therefore, support the view that Reaction 2 takes place to some extent.

In applying Messinger's method to the estimation of methylethyl ketone, Cassar (3) found that constant results of 110.5 per cent were obtained for the ketone under specified conditions. He accounted for this by assuming that two simultaneous reactions occur.



The first reaction is the normal one, but the second one also occurs in which more iodine is taken up, thus giving results 10.5 per cent too high; this explanation is analogous to the one given in this paper to account for the high result of 102.5 per cent obtained in the estimation of pure acetone.

Summary

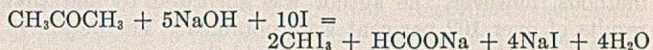
Messinger's method (4) was found to give results of 102.5 per cent acetone in the estimation of pure samples.

Marasco's oxime method (6) gives results in good agreement with Messinger's method, but as his factor is obtained

from Messinger's method of analysis it is incorrect. The value 0.00614 should be changed to 0.00598 for the weight of acetone equivalent to 1 cc. of 0.1 *N* sodium hydroxide.

The indicator methyl orange-xylene cyanol (5) was found to give a very sharp end point in the oxime titration.

A small amount of formic acid was detected among the products of Messinger's iodoform reaction, showing that some of the acetone probably reacts according to the equation



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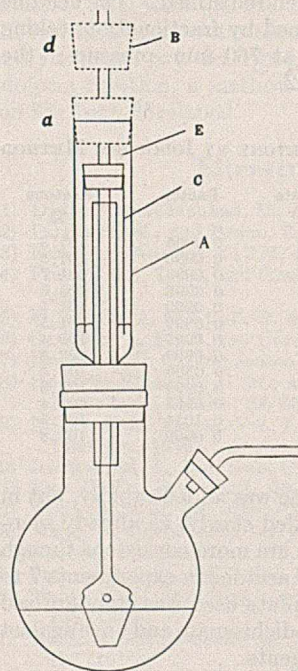
RECEIVED November 16, 1936.

A Modified Mercury Seal for Stirrers

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THE mercury seal for stirrers here described has been found useful in catalytic hydrogenations and oxidations where absorption of gas is measured at atmospheric pressure. Usually in such reactions stirring must be done with a gas-tight stirrer or else some system of shaking employed, both of which methods are simplified by use of the present seal for stirrers.

In the accompanying figure a cross section of the seal and stirrer is shown. The outer tube, *A*, is elongated thus enabling a stopper, *B*, to be slid down the stirrer rod, closing the top of the seal. In order to fill the reaction vessel with the desired gas, mercury is first added in just sufficient quantity to cover the lower end of the tube, *C*, as shown, and stopper *B* is slid down to position *a*. The flask is then evacuated, the air in *E* bubbling past the mercury without forcing any over. The required gas is then admitted up to atmospheric pressure, which automatically again closes the ends of *C*, and the stopper is slid up the stirrer rod to position *d*. More mercury can then be



added to the seal to increase the safety margin and the stirrer set in motion.

Care must be taken to ensure that mercury is not forced into the reaction flask by a fall in pressure which must be kept approximately at atmospheric pressure.

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Determination of Zirconium in Steels with *n*-Propylarsonic Acid

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THE usefulness of *n*-propylarsonic acid as a reagent for the determination of zirconium in the presence of other metallic ions has been shown (1, 3). However, the determination of a constituent in an alloy steel presents a special case because of the large amount of iron present and varying amounts of other elements that may be present. Benzene-arsonic acid has been investigated for this determination (4).

Materials

With the exception of the determinations in the presence of large amounts of tungsten, 3-gram samples of Bureau of Standards steel No. 55 were used. For high-tungsten steels a reference sample containing 18.17 per cent of tungsten, 3.85 per cent of chromium, and 0.95 per cent of vanadium was used. To the solutions of these steels were added measured amounts of zirconium in the form of zirconyl chloride and measured quantities of other salts as desired.

A saturated water solution (approximately 5 per cent) of Eastman's *n*-propylarsonic acid was used as the reagent. Further purification of the reagent was found unnecessary.

Other Constituents

IRON. The presence of the constituents commonly found in alloy steels causes little difficulty in this determination. The precipitation of zirconium is complete in the presence of these large amounts of iron. A small quantity of iron is adsorbed in the zirconium precipitate, but a complete separation is obtained by reprecipitation.

TITANIUM, ALUMINUM, CHROMIUM, COBALT, NICKEL, COPPER, URANIUM, VANADIUM, THORIUM, AND MOLYBDENUM. The separation from these elements is complete in one precipitation. It is not necessary to precipitate from a solution containing hydrogen peroxide to avoid interference of titanium. In this respect *n*-propylarsonic acid differs from the other acids of this group so far investigated.

CARBON, SILICON, AND TUNGSTEN. These constituents are removed by filtration, following the usual procedure of evaporation of the solution and dehydration of the residue. The small amount of tungsten that possibly escapes removal by this procedure does not interfere in the subsequent determination.

PHOSPHORUS. As suggested by Simpson and Schumb (5), any zirconium remaining in the silica residue as phosphate can be recovered by a sodium carbonate fusion.

TIN. At the acidity used tin is partially precipitated by *n*-propylarsonic acid and the ignited zirconium dioxide contains some tin oxide. The method suggested by Caley and Burford (2) for the removal of tin oxide—treatment with ammonium iodide and ignition—was found to be very satisfactory and residues containing only zirconium dioxide were obtained.

Procedure

Dissolve 3 grams of steel in 40 cc. of concentrated hydrochloric acid and add sufficient concentrated nitric acid to oxidize the iron. Evaporate to dryness, moisten the residue with concentrated hydrochloric acid, evaporate again to dryness, and bake for about 30 minutes at 105° to 110° C. Take up the residue with 10 cc. of concentrated hydrochloric acid and warm gently until solution is complete. Dilute the solution to 100 cc., filter while hot, and wash the residue well with hot water. Reserve the filtrate and treat the residue as follows:

Ignite the residue in a platinum crucible and volatilize the

silica by treatment with hydrofluoric and sulfuric acids in the usual manner. Fuse the residue with sodium carbonate. Extract with hot water, filter, and wash well with hot water. Discard the filtrate. Ignite the residue in platinum and fuse with potassium pyrosulfate, avoiding a large excess. Extract with water and a few drops of sulfuric acid, filter, and wash with hot water; add the filtrate to the main filtrate.

Dilute the combined filtrates to a volume of 300 cc. Heat to boiling and precipitate the zirconium with 40 to 50 cc. of a 5 per cent water solution of *n*-propylarsonic acid. Digest for 30 to 60 minutes, filter while hot, and wash with hot water. (Suction may be employed if desired, the filter paper being fortified with a platinum or a paper cone.)

Return the filter paper containing the precipitate to the original beaker and disintegrate by warming gently with 10 cc. of concentrated hydrochloric acid. Add 100 cc. of water and reprecipitate the zirconium by adding 10 cc. of the *n*-propylarsonic acid solution. Digest for 30 minutes, filter, and wash well with hot water as previously described. Ignite in porcelain over a Meker burner. If tin is absent, no further treatment is necessary. If tin is present, add ammonium iodide and ignite. Repeat the treatment with ammonium iodide until constant weight is obtained. Weigh as zirconium dioxide.

Experimental Data

In the analyses made by the procedure described above, steels of varying composition were made by dissolving 3-gram samples of Bureau of Standards steel No. 55 and adding to the solution measured quantities of zirconyl chloride and solutions of salts of other metals desired. For the determination of zirconium in a high-tungsten steel 3-gram samples of a reference steel containing 18.17 per cent of tungsten were used. The results are given in Tables I and II.

TABLE I. DETERMINATION OF ZIRCONIUM IN STEELS

Constituents Added ^a	Zirconium Found					
	Gram ^b	% ^b	Gram ^c	% ^c	Gram ^d	% ^d
Ti ⁺⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Cu ⁺⁺ , UO ₃ ⁺⁺ , VO ₃ ⁻ , MoO ₄ ⁻⁻	0.0101	0.34	0.0489	1.60
....	0.0091	0.30	0.0495	1.62
....	0.0094	0.31	0.0489	1.60
....	0.0494	1.62
....	0.0504	1.66
....	0.0502	1.65
Above elements and Sn ⁺⁺⁺	0.0034	0.11	0.0500	1.64
....	0.0032	0.11	0.0508	1.67
....	0.0031	0.10	0.0508	1.67
....	0.0028	0.09	0.0500	1.64
....	0.0030	0.10	0.0500	1.64
Ti ⁺⁺⁺ , Al ⁺⁺⁺ , UO ₃ ⁺⁺ , MoO ₄ ⁻⁻ , VO ₃ ⁻ , WO ₄ ⁻⁻	0.0495	1.62
....	0.0488	1.60
....	0.0491	1.61
....	0.0492	1.61
Th ⁺⁺⁺ , Ni ⁺⁺ , Cu ⁺⁺	0.0491	1.61
....	0.0488	1.60
....	0.0491	1.61

^a 0.02 gram of each metal.

^b 0.0035 gram = 0.11%.

^c 0.0098 gram = 0.33%.

^d 0.0490 gram = 1.61%.

TABLE II. DETERMINATION OF ZIRCONIUM IN A HIGH-TUNGSTEN STEEL

Constituents Present	Zirconium Found ^a				
	Gram	Gram	Gram	Gram	%
W	0.5451	P	0.0007	0.0498	1.63
Cr	0.1155	Si	0.0054	0.0496	1.62
V	0.0285	C	0.0225	0.0492	1.61
Mn	0.0105				

^a Zr present, 0.0487 gram = 1.60%.

Summary

Zirconium can be determined in steels with *n*-propylarsonic when present in amounts as low as 0.1 per cent and in the presence of titanium, aluminum, chromium, cobalt, nickel, copper, uranium, vanadium, thorium, molybdenum, and tungsten.

Tin is partially precipitated by this reagent, but the zirconium dioxide residues obtained upon ignition may be freed from tin oxide by adding powdered ammonium iodide and igniting.

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Quantitative Spectrographic Analysis

Increased Accuracy in the Logarithmic Sector Method

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A new eyepiece for making readings on sector lines has internal comparison densities and an internal scale. Results obtained with it on logarithmic sector lines give a mean error per individual reading of ± 0.060 mm., which is one-third the error that has been reported for readings made with the ordinary measuring eyepiece. A high degree of accuracy is attainable in the determination of relative intensities of spectrum lines by means of the logarithmic sector and the new eyepiece. The result is an increase in the accuracy of this system of quantitative analysis.

TWYMAN and Simeon (5) have described the logarithmic sector method of obtaining relative intensities of spectrum lines, and have discussed the use of this method of photometry in quantitative spectrographic analysis. In this system of quantitative analysis, a metal disk having a logarithmic periphery is placed directly in front of and very close to the slit of a stigmatic spectrograph. Rotation of the disk during an exposure causes the effective time of the exposure to vary along the slit; therefore the lines that are produced on the photographic plate decrease in density along their lengths and fade out at one end.

The lengths of the lines in spectrograms that are produced by this kind of exposure vary according to the intensities of the spectrum lines in the light source. Since the intensities of the lines are dependent on the quantities of the elements giving the lines, accurate readings that are simply related to lengths of lines are necessary in analyses made with the logarithmic sector. The purpose of this paper is to present an accurate, rapid, and convenient method for making readings on such lines.

The common practice in line measurement is to use a low-power eyepiece (containing an internal millimeter scale graduated in 0.1 mm.) directly on the gelatin of the plate which is placed on an illuminated opal glass. The length of a line is determined as the distance from the intense end of the line to a point at which the line seems to fade out.

Consistent results are not always obtained in making such

measurements with the ordinary measuring eyepiece because the weaker end points of fading lines are difficult to determine. The analyses are, therefore, subject to considerable error. Errors of ± 0.1 and ± 0.2 mm. in these measurements are equivalent to errors of ± 4.5 and ± 9 per cent, respectively, in the intensities of the spectrum lines.

Martin, Burke, and Knowles (3) have determined a mean error of ± 0.18 mm. per individual reading with an ordinary measuring eyepiece. Some workers who use this method of measurement consider that an average of three independent determinations must be made in order to keep the error within ± 0.2 mm.

Many devices and processes for decreasing the errors in line length determinations have been investigated. Smith (4) has reviewed several of these investigations, and recently a method for making the measurements by means of a reversed measuring microscope has been described (3). However, each of these methods requires additional time, special apparatus, or both; and none shows promise of generally replacing the ordinary measuring eyepiece.

Basis for New Method of Reading Lines

In the "internal standard" method, which is usually employed in a spectrographic analysis by the logarithmic sector, the composite spectrum of the sample includes the spectrum of the unknown quantity of the element being determined and the spectrum of a known fixed quantity of another element, the internal standard. Two lines, one from the spectrum of each of these two elements, make a "line pair"; and the difference in the lengths of these two lines, when referred to a working curve, gives the quantitative result. The working curve is a graph showing the differences in lengths of the lines of the "line pair" for a series of known compositions of the element that is under estimation. Differences in lengths of lines are, therefore, the important values to be determined from spectrograms in this system of analysis.

It has been shown (3) from the equation of the logarithmic sector and the Schwarzschild relation that the gradation of density toward the ends of the long and the short lines should be exactly similar. This has been tested at points within 10.5 mm. from the dense ends of the sector lines and found to hold for lines on the same plate. Therefore, if measurements are made from points of a certain density on spectrum lines to the more exposed ends of the lines, the difference in the measured distances on two lines will be exactly equal to the difference in the entire lengths of the two lines. In addi-

tion, if a fixed point on the scale of a measuring eyepiece is always placed on the lines at the points having this density and the scale is read at the intense ends of the lines, the difference in the readings on two lines will be exactly equal to the difference in lengths of the two lines. Differences in such readings will serve the same purpose as differences in lengths

and, when possible, between R and the scale, as shown in the figure. The scale is then moved along A until the density of A at D_1 is equal to that of R at D_1 . With the eyepiece in this position, a reading is made on the scale at the dense end of A . The difference in this reading and one made in the same way on B gives the difference in lengths of the two lines which is necessary for the analysis.

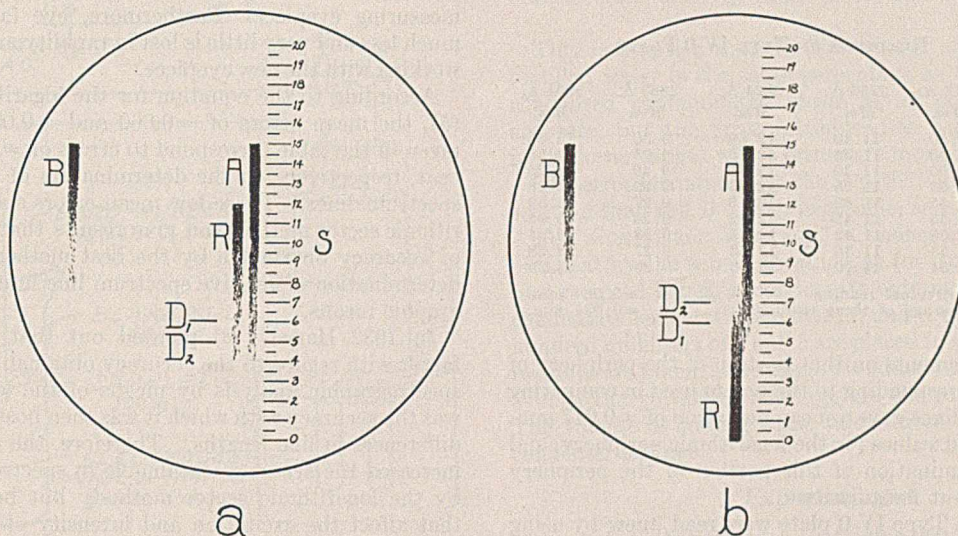


FIGURE 1. DIAGRAM REPRESENTING TWO ARRANGEMENTS OF REFERENCE LINE

of lines for the construction of working curves and for the subsequent analyses.

The internal comparison density eyepiece, described below, is used for making readings from points of equal density on the lines.

The New Eyepiece

The description and use of the comparison density eyepiece, which the present author has designed for the determination of differences in line lengths, are given with the aid of Figure 1.

a and b represent two arrangements of the reference spectrum line, R , in the field of the eyepiece. An eyepiece with either arrangement can be used in making the readings. The 20-mm. glass scale, S (drawn without its 0.1 mm. divisions), the reference spectrum line, R , and the lines, D_1 and D_2 , that point out comparison densities are within the eyepiece. The lines of the "line pair," A and B , are on the spectrogram.

The reference spectrum line, R , is a sector line that has been removed from a spectrogram and permanently mounted on the glass beside the scale. In order to make this transfer, the original spectrogram and the glass scale are placed in dust-free water and the line, with sufficient gelatin to cover the field of the eyepiece, is cut from the plate by means of a razor blade. The film of gelatin is transferred to the glass scale, and the scale with the adhering gelatin film is then removed from the water. The gelatin is dried in the proper position and then covered with a clear colorless lacquer.

A high-contrast plate of low graininess and a slit of the same width as that used in the analytical work should be used when producing the reference line for the eyepiece. An Eastman spectroscopic Type 144-0 plate (1), a slit width of 0.04 mm., and the copper arc spectrum were used in the production of the reference spectrum line for the material presented in this paper.

D_1 is a fine line that points out an easily perceptible comparison density on the reference spectrum line at a point about 2 to 3 mm. from the faint end of the spectrum line. This density corresponds to a point on or near the contrast part of the characteristic curve for the plate and is sufficiently low to allow the eye to distinguish readily between it and another density of slightly different value.

The rest of the optical system and the mounting of the parts of this eyepiece are the same as for the ordinary measuring eyepiece with an internal scale.

A reading on the spectrum line, A , is made by placing the eyepiece on the plate in such a manner that A appears parallel to

Other comparison densities, such as D_2 , are used in making readings when singularities exist on the spectrum lines at D_1 . Also, a density less than that at D_1 can be used in reading very short lines, and a density greater than that at D_1 can be used in reading exceedingly long lines. In any case, the same comparison density must be used on both lines of the "line pair" in order to get one value for the difference in their lengths.

Although all readings for Table I were made with the reference spectrum line, R , fading in the same direction as the line being observed (Figure 1, a), the arrangement with R fading in the opposite direction to the line being observed (Figure 1, b) gives very good results.

Accuracy Obtainable

In order to make an estimate of the mean error of the readings made with the comparison density eyepiece, the copper arc spectrum was recorded by means of a Hilger E.1 spectrograph and the logarithmic sector on Types II-0, III-0, IV-0, and 144-0 Eastman spectroscopic plates (all plates used in this work were developed for 8 minutes at 18° C. in an Eastman developer, Formula D-19); and five lines on each plate were chosen for the test readings. A series of twenty readings, one on each of the five lines on each plate, was taken and then the series repeated until a total of five readings had been made on each line on each of three consecutive days. This gave fifteen nonconsecutive readings, which were made on the scale at the nearest 0.05 mm., for each of the five lines on each plate.

Although the Type 144-0 plate gave best results, the small errors made on Types III-0, IV-0, and 144-0 were practically identical; so the values in Table I, which represent the seventy-five readings that were made on the Type IV-0 plate, give also the order of errors made in the readings on Types III-0 and 144-0.

Series 1, 2, and 3 of Table I show the first three readings that were made on each of the lines on the Type IV-0 plate, and average 1 shows the averages of these readings for each of the spectrum lines. In averages 2, 3, 4, and 5 are the averages by threes for the other twelve series of readings on this plate that are not given in the table, and in average 6 are the averages of the fifteen readings on each line. The mean error per individual reading was determined by com-

paring individual readings with the corresponding values in average 6, and the mean error per average of three readings was determined by comparing averages 1, 2, 3, 4, and 5 with the corresponding values in average 6. These mean errors are arithmetical mean errors that have been increased by ± 0.006 mm., the mean error of the mean of seventy-five readings.

TABLE I. READINGS ON TYPE IV-0 PLATE

Copper Arc Lines:	2618 Å.	2766 Å.	2824 Å.	2883 Å.	2961 Å.
	Mm.	Mm.	Mm.	Mm.	Mm.
Series 1	11.50	11.40	12.60	9.30	13.35
Series 2	11.60	11.35	12.65	9.25	13.25
Series 3	11.50	11.40	12.75	9.40	13.25
Average 1	11.53	11.38	12.67	9.32	13.28
Average 2	11.55	11.42	12.75	9.27	13.30
Average 3	11.55	11.45	12.62	9.20	13.25
Average 4	11.55	11.42	12.65	9.23	13.35
Average 5	11.53	11.35	12.63	9.27	13.28
Average 6	11.54	11.40	12.66	9.26	13.29
Mean error per individual reading					± 0.060 mm.
Mean error per average of three readings					± 0.034 mm.

Twenty measurements on that portion of the periphery of the sector disk corresponding to the points used in comparing densities on these lines gave a mean deviation of ± 0.017 mm. from the calculated values for the logarithmic periphery, and a microscopic examination of this portion of the periphery showed no apparent irregularities.

The lines on the Type IV-0 plate were read anew by using D_2 instead of D_1 as comparison density and the values obtained, when compared with those in Table I, showed, within the limits of error indicated by the table, a common difference that was attributable to the difference in the gradation of the reference spectrum line, R , and the gradation of the lines on the plate. Apparently, the effect of singularities on the readings for the table was negligible and the low mean errors, which indicate the precision of the readings, also represent the accuracy obtained with the comparison density eyepiece on the Type IV-0 plate.

The lower contrast and the graininess of the Type II-0 plate introduced a little more variation in the readings, but calculations based on the seventy-five readings on this plate gave a mean error per reading of only ± 0.071 mm. and a mean error per average of three readings of ± 0.048 mm.

Readings with the new eyepiece were also made on fogged plates and the errors of readings on these plates seem to be about the same as on clear plates.

The ability to make consistent readings on fogged plates and on plates with graininess and the ability to increase the accuracy of the readings on other plates show definite advantages of the comparison density eyepiece over the ordinary measuring eyepiece. Furthermore, eye fatigue effects are much less and very little is lost in rapidity and convenience in working with the new eyepiece.

According to the equation for the logarithmic sector disk (5), the mean errors of ± 0.060 and ± 0.034 mm. that are given in the table correspond to errors of ± 2.8 and ± 1.6 per cent, respectively, in the determination of the intensities of spectrum lines. These low mean errors show that the logarithmic sector method can give results that are of the order of accuracy obtainable by the best methods in use for the determination of relative spectrum line intensities by photographic means.

In 1932 Harvey (2) pointed out that the determining factor with regard to the accuracy obtainable in quantitative spectrographic analysis by means of the logarithmic sector was the accuracy with which it was then possible to determine differences in line lengths. Therefore, the new eyepiece has increased the accuracy obtainable in spectrographic analysis by the logarithmic sector method; but because of factors that affect the excitation and intensity of a spectrum line, the accuracy indicated by reading with the new eyepiece will not be fully attained in some quantitative determinations.

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Foaming and Priming of Boiler Water and Condenser Leakage

Electrometric Method of Measurement

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THE usual methods for measuring carry-over of liquid water into the steam from a boiler are by the steam calorimeter (3), electrical conductivity (2), and chemical titration (1). These methods are time-consuming, require expensive equipment, or give questionable results. This paper describes a new electrometric procedure, accurate and rapid, which requires comparatively inexpensive apparatus.

The method is dependent on the fact that condensed contaminated steam from a boiler or condenser has a different electrical conductance than condensed pure steam. Two cells containing identical electrodes are used. A sample of condensed pure steam (distilled water) is placed in one cell

and a sample of the condensed contaminated steam in the other. The contaminating solution (boiler water or cooling water as the case may be) is added from a buret to the cell containing the distilled water until the indicating device shows that the electrical conductance is the same as that of the contaminated condensate in the other cell. This indicates that the concentration of contaminant is the same in each cell and therefore the amount of contaminating solution added is a measure of the amount of contamination. This method directly measures the volume of the contaminating boiler or condensing water and is independent of the concentration of these waters.

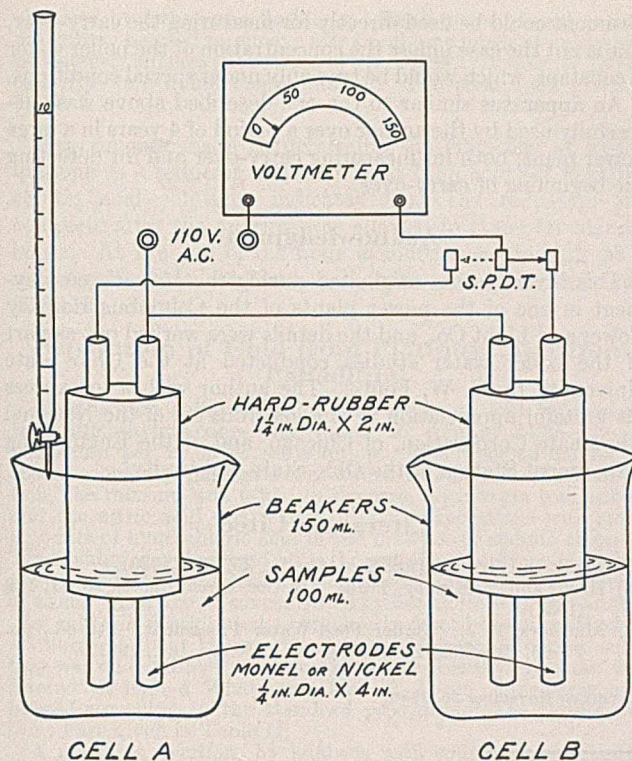


FIGURE 1. APPARATUS FOR ELECTROMETRIC DETERMINATION OF CARRY-OVER AND CONDENSER LEAKAGE

Apparatus

The apparatus employed is shown in Figure 1.

CELLS. The samples are placed in 150-ml. beakers, in each of which is an electrode assembly of Monel or nickel rods 0.65×10.8 cm. (0.25×4.25 in.) fixed with water-tight connections in 3.2×5.1 cm. (1.25×2 in.) hard-rubber holders. The distance which the electrodes extend into the solution is adjusted so that they are just covered by a 100-ml. sample, and so that the same voltmeter reading is obtained for each cell when filled with 100 ml. of dilute salt solution at room temperature.

BURET. A 10-ml. buret graduated in 0.05 ml. is preferable, although any ordinary one may be used.

SWITCH. A single-pole double-throw switch is required.

VOLTMETER. Any ordinary alternating current voltmeter with a 0- to 150-volt range may be used, but one with a resistance of about 2500 ohms is most satisfactory for use with a 110-volt alternating current circuit.

At first thought an ammeter would seem more suitable and, of course, one of appropriate range could be used. An outside resistance would, however, be necessary, and since the instrument is employed only as an indicating device, a voltmeter is more practical because it already has a high resistance.

Procedure

FOR CARRY-OVER. Three samples are required, *a*, condensed pure steam leaving the boiler when carry-over is known not to be occurring, or recently boiled distilled water; *b*, condensed steam leaving the boiler when carry-over is suspected; and *c*, a sample of the boiler water obtained at the same time as *b*.

The electrodes in each cell are connected in either a 110- or a 220-volt alternating current circuit with the voltmeter in series as shown in Figure 1. It will be observed that either cell can be thrown in by the switch. Measurements are made as follows:

One hundred milliliters of the sample taken when carry-over was not occurring or 100 ml. of distilled water are placed in cell *A*, and 100 ml. taken when carry-over is suspected, in cell *B*. Voltmeter readings are then taken for both cells. If the

readings are the same, indicating that both solutions have the same concentration of electrolytes, there is no carry-over. If the reading for cell *B*, however, is greater than for cell *A*, there is carry-over, the percentage of which is then obtained by adding boiler water (sample *c*) from the buret to cell *A*, until the reading for cell *A* has increased to that for cell *B*. This indicates that the electrical conductance, and hence the concentration of boiler water, is the same in both cells. The number of milliliters of boiler water added gives the percentage of carry-over.

This assumption that the boiler water added to 100 ml. of distilled water is the same percentage as that in 100 ml. of condensed contaminated steam is, of course, not strictly accurate, but the error introduced is negligible, especially in the lower ranges where errors are more significant.

The error introduced by the fact that cell *A* contains more solution than cell *B* is also negligible, as experiment showed.

FOR CONDENSER LEAKAGE. Condenser leakage may be obtained by the same procedure as for carry-over, the samples required being, *a*, condensate entering the condenser, *b*, condensate leaving the condenser, and *c*, cooling water. One hundred milliliters of *a* and *b* are placed in the cells, voltmeter readings are taken, and sample *c* is added to the cell containing *a* until the voltmeter readings are the same for both cells. The volume of cooling water added gives the percentage of condenser leakage.

Experimental

A synthetic boiler water containing 250 p. p. m. of sodium chloride was used in obtaining the results in Table I. Samples in cell *B* were made by diluting a known amount of this standard solution, and distilled water was used in cell *A*. The experiments of Tables I and II were conducted with a set of electrodes having the dimensions shown in Figure 1. All readings were made at 22° C.

Discussion of Results

TABLE I. The difference between any two adjacent readings in columns 2 or 3 shows the sensitivity of the method in the concentration range as given in column 1. As might be expected, the sensitivity is greater at low concentrations than at high and is also greater when using the 220-volt circuit. This greater sensitivity at low concentrations is a decided advantage, because it is in this region that accuracy of measurement is needed. The sensitivity and accuracy of the method increase with the concentration of the boiler water. If this is as much as 1000 p. p. m., a few hundredths of a per cent of carry-over can be detected and measured.

TABLE II. Since the titration of chlorides by the Mohr method is frequently employed in measuring carry-over, the

TABLE I. VARIATION OF VOLTMETER READINGS WITH CHANGE IN CONCENTRATION OF SODIUM CHLORIDE

Sodium Chloride Present P. p. m.	Readings	
	110-volt circuit and voltmeter with 150-volt scale and 5364 ohms resistance	220-volt circuit and voltmeter with 300-volt scale and 10,760 ohms resistance
	Volts	Volts
0.0	16.0	53.0
0.5	20.0	65.0
1.0	23.0	76.0
2.0	29.0	93.0
4.0	38.0	115.0
6.0	46.0	133.0
8.0	52.0	147.0
11.0	60.0	161.0
15.0	66.5	174.0
18.0	71.5	180.0
21.0	76.0	185.0
26.0	80.0	191.0
36.0	86.0	199.0
46.0	91.0	205.0
56.0	94.0	209.0
66.0	96.0	211.0

TABLE II. COMPARISON OF MOHR AND ELECTROMETRIC METHODS FOR DETERMINATION OF CARRY-OVER

Sample	Percentage of Carry-Over		Mohr method
	Calculated	Electrometric method	
1	0.10	00.09	Too low to determine
2	0.20	0.23	
3	1.00	1.02	
4	1.50	1.50	
5	4.00	4.21	
6	6.00	6.3	
7	7.50	7.8	
8	12.00	12.1	
9	20.00	20.4	
10	30.00	30.3	

results in Table II are of special interest. They show that the Mohr method is of no value if carry-over is much below 1 per cent. The proposed electrometric procedure, however, gives excellent results at such low concentrations.

Detection of Carry-Over

It is evident from the above data that a suitable alternating current voltmeter connected in a 110- or a 220-volt circuit to electrodes in a cell through which condensed steam bled from the line is flowing makes an inexpensive and highly sensitive means for detecting the beginning of carry-over. Although it might be thought that by suitable calibration such an in-

strument could be used directly for measuring the carry-over, this is not the case unless the concentration of the boiler water is constant, which would be true only under special conditions.

An apparatus similar to the one described above was successfully used by the author over a period of 4 years in a large power plant, both for measuring carry-over and for detecting the beginning of carry-over.

Acknowledgment

This investigation originated during the author's employment in one of the power plants of the Columbus Railway Power and Light Co., and the details were worked out as part of the boiler water studies conducted at the Ohio State University by C. W. Foulk. The author wishes to express his grateful appreciation of the generous aid of the National Aluminate Corporation, of Chicago, and of the Engineering Experiment Station of the Ohio State University.

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The Determination of Gold

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A new procedure has been developed for the analysis of gold and its separation from the platinum group of metals. Precipitation is extremely rapid, the gold is easily filtered, and occlusion of the platinum metals is negligible. The precipitation can be made from cold solutions. A considerable number of organic reagents may be used for the determination of gold and the results obtained by means of these reagents are included in this report.

THE separation of gold from the platinum group of metals in an assay bead is generally accomplished by means of reduction with sulfur dioxide, ferrous sulfate, or oxalic acid. The use of ferrous salts is restricted by the difficulties incident to the subsequent separation of iron from the rest of the platinum metals. The authors have had very little success with oxalic acid because of the slow precipitation of gold previously treated with aqua regia and sodium chloride. The gold precipitated by means of oxalic acid separates in a fine state of division which makes the complete filtration difficult and uncertain, and reprecipitation is necessary because of the persistent tendency of the gold to carry palladium with it. Sulfur dioxide precipitates gold from acid solution, but in this case there is a pronounced tendency of the gold to occlude platinum.

The following is a summary of an investigation instigated to find a more efficient reagent for the separation and estimation of gold when present together with the platinum metals. Lenher (3), in the report of his attempt to find methods by

which derivatives of the aurous type of gold might be prepared, gives a list of photographic developers and other organic reagents which precipitate gold instantly from either acid or alkaline solutions. It was decided to determine whether these reagents could be used for the quantitative estimation of gold and for its separation from the platinum metals.

Precipitation of Gold by Hydroquinone

The weighed sample of gold was dissolved in aqua regia, evaporated to dryness in the presence of sodium chloride, and moistened 3 times with hydrochloric acid, and the residue was dissolved in about 15 cc. of water and 5 cc. of concentrated hydrochloric acid. The solution was filtered through a 7-cm. paper, and the volume was adjusted to 50 cc. by washing, and then brought to boiling. Precipitation was slowly induced by means of 5 per cent aqueous hydroquinone solution (this solution retains its efficiency as a reducing reagent for as long as a week), and then a volume of 3 cc. was added for every 25 mg. of gold. Boiling was continued for 20 minutes, and the mixture was allowed to cool and filtered through a porous-bottomed filtering crucible of grade A2. (These crucibles may be purchased from Staatliche Porzellan Manufaktur, Wegelystrasse 1, Berlin NW 87, Germany, or from the usual apparatus supply houses in North America.) Whatman's 7-cm. No. 42, and Munktell's No. 00 filter paper were used in some cases and found entirely satisfactory. The precipitate was washed with about 100 cc. of hot water. Precautions must be taken at this point to see that all the gold is washed out. Fine particles remain in the bottom of the beaker and can best be

TABLE I. PRECIPITATION OF GOLD BY MEANS OF HYDROQUINONE

Gold Added	Gold Recovered	Gold Added	Gold Recovered
Mg.	Mg.	Mg.	Mg.
4.698	4.700	34.64	34.64
4.477	4.479	36.07	36.09
4.414	4.430	30.83	30.85
27.31	27.31	151.2	151.4
26.44	26.44	151.7	151.9
24.84	24.84	152.5	152.3

observed by means of a flashlight. Small pieces of ashless filter paper may be used to remove any small precipitate of gold which persistently adheres to the walls of the beaker. Beakers of 150-cc. capacity were found most suitable. The results are given in Table I.

Experiments made to determine the efficiency of hydroquinone as a reducing agent for gold from cold 1.2 *N* hydrochloric acid solutions indicated that the reduction was complete after the mixture was allowed to stand for about 2 hours. At the end of 0.5 hour a solution containing 33.79 mg. of gold yielded 33.33 mg. and at the end of 2 hours yielded 33.79 mg. of gold.

Separation of Gold from Platinum and from Palladium

A palladium sulfate solution was made up and by analysis with dimethylglyoxime was found to contain 24.85 mg. of palladium per 25.00 cc. of solution. The weighed sample of spectroscopically pure gold was added to 25.00 cc. of this solution, the mixture was taken to dryness, aqua regia was added, and the nitric acid was removed by 3 evaporations with small amounts of hydrochloric acid in the presence of sodium chloride. The residue was dissolved with the aid of a few drops of hydrochloric acid and the solution was filtered and washed to a volume of 45 cc. Then 5 cc. of concentrated hydrochloric acid were added. The gold was precipitated as previously described and washed to a volume of about 150 cc. of solution. Dimethylglyoxime solution was added directly. The palladium dimethylglyoxime was filtered through a Whatman's No. 42, 11-cm. filter paper and burned according to the standard procedure. The results obtained are given in Table II.

A platinum solution, by analysis with sodium formate, was found to contain 25.75 mg. of platinum per 25.00 cc. of solution. A gold solution was made up to contain 25.07 mg. of gold per 25.00 cc. of solution and by analysis was found to contain 25.04 mg. of gold.

TABLE II. SEPARATION OF GOLD FROM PALLADIUM AND GOLD FROM PLATINUM

Added			Recovered		
Gold Mg.	Palladium Mg.	Platinum Mg.	Gold Mg.	Palladium Mg.	Platinum Mg.
16.85	24.85	...	16.83	24.85	...
13.70	24.85	...	13.69	24.85	...
17.14	24.85	...	17.10	24.90	...
18.33	24.85	...	18.36	24.85	...
25.07	...	25.75	25.05	...	25.75
25.07	...	25.75	25.03	...	25.70
25.07	...	25.75	25.06	...	25.85

Twenty-five cubic centimeters of each of these solutions were mixed and 5 cc. of concentrated hydrochloric acid added. The gold was precipitated as previously described, except that 3 cc. of 1 per cent hydroquinone solution were used. The filtrate was taken to dryness on a steam bath and the residue baked over a Meker burner for about 5 minutes. The walls of the beaker were exposed to the full flame until the small amount of organic matter was burned off. Aqua regia was added and the platinum dissolved over the steam bath. The cover and the walls were washed down with water and the nitric acid was removed by 3 evaporations with small amounts of hydrochloric acid in the presence of sodium chloride. The walls of the beaker were again washed and the solution was evaporated to dryness. Water was added and the solution filtered through a 7-cm. Whatman's No. 40 paper.

In order to avoid possible loss of traces of platinum, the paper was burned in a large porcelain crucible and the residue dissolved in aqua regia and evaporated to remove nitric acid. About 10 cc. of water were added and the liquid was filtered into the original platinum solution. The volume was made up to about 225 cc., boiled, and adjusted to pH 6 by means of sodium bicarbonate solution and bromocresol purple, as described by Beamish and Russell (1). The solution was boiled and the platinum precipitated by careful addition of about 100 to 125 mg. of sodium formate crystals. Boiling was continued for about 45 minutes and the mixture set aside for about 10 hours and filtered. Adhering platinum was removed with 1 or 2 small pieces of ashless filter paper and the residue was washed with 200 cc. of water. It was found that if the precipitate was allowed to stand, filtration was considerably accelerated and addition of an electrolyte to the wash water was not necessary, as in no case did platinum pass through the filtering crucible. The small blank obtained by this procedure was determined and subtracted. The results obtained are given in Table II.

An attempt was made to precipitate platinum directly from the gold filtrate by means of hydrogen sulfide, but it was found that the precipitation was not complete.

Comparison of Hydroquinone and Sulfur Dioxide

When a precious-metal assay bead is parted by means of sulfuric acid, platinum, palladium, and gold appear in the aqua regia extract, accompanied sometimes by small proportions of rhodium, iridium, osmium, and ruthenium; consequently it is necessary to know the effect of the hydroquinone reagent on acid solutions of each of these metals. The authors include results in Table III comparing the action of these two reagents with respect to the properties of occlusion of platinum and palladium. This is done because it has been generally accepted that gold precipitated by means of sulfur dioxide carries with it appreciable amounts of platinum metals. The procedure followed in the case of reduction with sulfur dioxide is that outlined by Hillebrand and Lundell (2).

TABLE III. OCCLUSION OF PLATINUM AND PALLADIUM IN THE PRECIPITATION OF GOLD

Reagent	Added		Gold Recovered Mg.	Error %
	Gold Mg.	Platinum Mg.		
Sulfur dioxide	33.79	...	33.78	-0.03
	33.79	25.75	34.15	+1.07
	33.79	...	33.81	+0.06
	33.79	...	33.86	+0.21
Hydroquinone	33.79	...	33.81	+0.06
	33.79	50.00	33.80	+0.03
	32.19	23.41	32.30	+0.34
	36.07	23.27	36.09	+0.06
	33.57	22.93	33.55	-0.06
	33.79	...	33.78	-0.03
	168.97	25.75	168.73	-0.15

The results indicate that gold precipitated by means of sulfur dioxide carries with it appreciable amounts of platinum and that gold precipitated with hydroquinone does not seem to occlude platinum or palladium when these metals are present up to double the weight of the gold present.

Sodium sulfite reagent was also tried and here again the occlusion of salts produced very appreciable errors.

Experiments were made to determine the effect of hydroquinone on 1.2 *N* hydrochloric acid solutions of rhodium, iridium, osmium, and ruthenium and proved that precipitation did not occur even after standing some days. In the case of platinum when the solution was adjusted to pH 6 and hydroquinone added, no precipitate appeared. When a solution of palladium was adjusted to pH 6 and just sufficient hydrochloric acid added to dissolve the brown oxide, hydroquinone immediately produced a gray precipitate from the boiling solution. The filtrate obtained from this precipitate after the mixture had been left standing for about 1 hour failed to show palladium with either dimethylglyoxime or *p*-dimethylamino benzilidene rhodanine.

Hydroquinone in the Determination of Gold in Alloys

A solution containing 33.83 mg. of gold and 25.0 mg. of copper was evaporated to dryness and taken up with aqua regia, and the nitric acid removed by the usual method. The gold was precipitated from a 1.2 *N* hydrochloric acid solution as previously described and weighed 33.80 mg.

A second solution was prepared containing 25.07 mg. of gold, 7 mg. of nickel, and 5 mg. of zinc. The gold was precipitated from this acid solution and weighed 25.07 mg. A second sample weighed 25.08 mg. Gold was precipitated from two solutions containing the above proportions of gold, zinc, and nickel and the precipitate was left standing in contact with the solution for a period of about 10 hours. The results were 25.16 and 25.16 mg. of gold. This indicates that occlusion occurred, because hydroquinone left in contact with 1.2 *N* hydrochloric acid solutions of nickel, zinc, and copper produced no precipitate. In the case of dental alloys which contain silver, the silver can be removed as the chloride; the remaining solution can be treated directly

for gold after removal of nitric acid. Tungsten interferes, because it precipitates as tungstic acid in acid solutions and must first be removed.

TABLE IV. PRECIPITATION OF GOLD BY VARIOUS ORGANIC REDUCING REAGENTS

Reagent	Gold Added Mg.	Gold Recovered Mg.
Amidol (hydrochloride salt of 1,3-diamino-4-hydroxybenzene)	33.83	33.86 33.83
Rhodinal (<i>p</i> -aminophenol hydrochloride)	33.83	33.82 33.81
Resorcinol	33.83	33.79 33.83
Pyrogallol	33.83	33.83 33.84
Hydroxyhydroquinone	33.83	33.85 33.82
Phenylenediamine	33.83	33.86 33.82
Pyrocatechol	33.83	33.86 33.83
Photol (sulfate salt of <i>p</i> - <i>N</i> -methyl amino-phenol)	33.83	33.83 33.86
Phloroglucinol	25.07	25.06 25.08
<i>o</i> -Aminophenol	25.07	25.07 25.08
Phenol	33.83	6.82

In view of the fact that hydroquinone precipitates gold so efficiently, it seemed worth while to investigate the possible application of related organic compounds to the estimation of gold. The procedure used for these determinations was identical to that described for hydroquinone. A few of the reagents tried are given in Table IV.

The Rapid Analysis of Zinc-Sodium Amalgams

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A RECENT study of the reactivities of zinc amalgams (2) has shown that the absolute rates at which they are oxidized by various oxidizing agents—e. g., the oxygen of the air—increases only slightly with the concentrations of the amalgams. As a result, concentrated amalgams seem inert; dilute amalgams appear to be extremely reactive. This peculiar behavior of zinc amalgams makes possible a satisfactory, rapid analytical method, which can probably be modified to suit other cases, for the determination of zinc and sodium in zinc-sodium amalgams, provided the zinc concentration exceeds 0.01 per cent.

To a weighed sample of the amalgam in a dry Erlenmeyer flask, approximately twice the volume of standard acid equivalent to the sodium is slowly added from a pipet. The acid and amalgam are gently whirled about in the flask for 20 seconds, at which time violent hydrogen evolution should have ceased. The excess of acid remaining is determined by titrating with standard base, phenolphthalein being used as indicator. The amalgam, which will now contain no sodium and will have lost no appreciable amount of zinc if the procedure has been properly carried out, is next transferred to a cell—e. g., of the H type—where its electromotive force is measured against a concentrated known zinc amalgam as reference electrode with a 1 *M* zinc sulfate-0.05 *M* sulfuric acid solution serving as electrolyte. The unknown concentration of zinc is then calculated from the measured electromotive force by means of the Nernst equation, $E = RT/NF \ln (Zn)_1/(Zn)_2$. (It has long been known that zinc amalgams deviate systematically from the Nernst equation, 1. The accuracy of the analytical method described above is usually not great enough to warrant considering these deviations; their effect can be minimized by choosing as reference electrode an amalgam of nearly the same concentration as the unknown.)

The results in Table I were obtained by the above method and

Summary
A 1 per cent aqueous solution of hydroquinone precipitates gold rapidly and completely from 1.2 *N* acid solutions. Occlusion of platinum and palladium is negligible when they are present even in the proportion of 2 to 1 of gold. Hydroquinone will precipitate gold from cold acid solutions but about 2 hours' contact is necessary for complete precipitation.

Hydroquinone precipitates gold directly from acid solutions containing copper, nickel, and zinc and consequently offers a rapid method for the determination of gold in alloys containing these base metals.

Palladium dimethylglyoxime can be precipitated directly from the filtrate of the gold precipitation.

Platinum can be determined in the filtrate from the precipitation of gold after heating the evaporated residue to destroy the organic matter and then digesting it with a little aqua regia.

Acknowledgment

The authors are indebted to E. C. Forbes of the Department of Chemistry for assistance in obtaining some of the results.

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serve to test its reliability. For analysis 50- to 75-gram samples of known zinc-sodium amalgams were taken; 5 cc. of *N* sulfuric acid, 0.5 *N* sodium hydroxide, zinc amalgams of known concentration for reference electrodes, and the electrolyte solution were the reagents used. The zinc-sodium amalgams were prepared by dilution from more concentrated known zinc and sodium amalgams. The most concentrated (1 per cent) known zinc amalgam was prepared by dissolving a weighed amount of zinc in a weighed amount of mercury in a hydrogen atmosphere; the known sodium amalgam was obtained by dissolving sodium in mercury and determining the sodium content acidimetrically.

TABLE I. ANALYTICAL RESULTS FOR ZINC-SODIUM AMALGAMS

	1	2	3	4	5	6
Na added, %	0.082	0.063	0.077	0.082	0.040	0.063
Na found, %	0.084	0.062	0.076	0.080	0.038	0.062
Zn added, %	0.87	0.098	0.059	0.0088	0.0030	1.7(10 ⁻⁴)
Zn found, %	0.88	0.107	0.059	0.0080	0.0024	Nil

The data in Table I and general experience in this laboratory indicate that the analytical method will usually give results accurate to about 2 to 5 per cent, provided the zinc concentration exceeds 0.01 per cent. As the zinc amalgams become more and more dilute, the inertness of which this analytical method makes use tends increasingly to disappear; and the results obtained are consequently low. Table I clearly illustrates this point; for amalgams more dilute than 0.001 per cent, the method is obviously of little value (No. 6).

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Fractionation and Composition of Sulfonated Oils

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A rapid and reliable procedure is given for the quantitative fractionation or separation of the various fatty components contained in sulfonated saponifiable oils. Data obtained as a result of the application of this method to samples of commercial sulfonated olive and castor oils indicate that the reaction between concentrated sulfuric acid and a fatty glyceride is comparatively simple and that no polymers, or very little, are formed. These findings are contrary to the generally accepted view of the sulfonation reaction. The probable composition of each of the fractions separated is given and the probable course of the sulfonation reaction is represented by an equation.

IN THE manufacture of the ordinary commercial grade of sulfonated oil, made from such oils as castor, olive, neat's-foot, etc., the raw oil is usually treated with about 25 per cent of strong sulfuric acid. In the case of glycerides whose fatty acids have either one double bond or one hydroxyl group, this quantity of acid corresponds approximately to 3 moles of sulfuric acid to 4 of the fatty acids. Actual sulfonation, however, occurs only to the extent of 25 to 30 per cent instead of the theoretical yield of about 75 per cent; hence, the ordinary sulfonated oil is a mixture of sulfonated fat, unchanged glycerides, free fatty acids, and polymerized oils. Because of the complexity of the mixture and of troublesome emulsions formed during extractions with solvents, very little headway has heretofore been made in developing a method to fractionate or separate the different components existing in a sulfonated oil.

There seems to be a feeling among users of sulfonated oils, particularly among leather chemists, that a knowledge of the structural composition of a sulfonated oil might help to explain certain variations and nonuniformity sometimes noted in materials treated with such products. This information would also be of great value in determining the nature of the raw oil or oils used in the process and whether or not the sulfonated product contains any admixture of raw oil. Attempts have therefore been made recently to develop methods for fractionating sulfonated oils. The American Leather Chemists' Association (3, 6) had appointed a committee, which left the matter pending, to investigate the determination of neutral fat in sulfonated oils. Winokuti, Igarasi, and Yagi (10) outlined a procedure for determining neutral fat, fatty acids, and sulfo oil, which is not supported by sufficient quantitative data, and which yields imperfect separations of the components as well as troublesome emulsions during extractions.

Schindler Method

The best known of the fractionation methods is that of Schindler (1, 7, 8). The writer finds the method involved, tedious, uncertain, and inexact. Burton and Robertshaw (2) state that the Schindler method, although valuable, is very complicated and gives incomplete separation of the

fractions, and that when the sulfated oil contains a high proportion of water or added neutral saponifiable and/or unsaponifiable oil, the fractionation does not yield quantitative results. Some changes in the Schindler method proposed by Theis and Graham (9) seem to have improved it very little.

New Method

A procedure is here outlined which separates quantitatively (A) sulfo oil, (B) fatty acids, and (C) neutral fat. The method is not affected by admixtures of saponifiable oils, mineral oils, or water, and is applicable to oils of the type of ricinoleic acid as well as oleic acid. The method is accurate and simple, and check results are easily obtained. A complete fractionation in duplicate may be carried out in about 4 hours. The analysis of the various fractions has also led to a theory of the composition of the sulfo oil and of the chemical reactions that may take place between the acid and the glycerides during sulfonation.

During this investigation it was found that no emulsions are formed and that sharp separations occur when a somewhat concentrated solution of sulfonated oil in water, on either the acid or neutral side, is extracted with ethyl ether or petroleum ether. The extractions may be successively repeated any number of times with the same result, but any attempt to wash the solvent layer with water results in unsatisfactory separations. The ether layer, however, is contaminated with a variable but small amount of sulfo oil—the quantity depending upon the efficiency of the extractions and the ratio of solvent to solution. Every effort made to remove the sulfonated oil from the ether layer proved unsuccessful. Although the emulsions formed upon washing with water were easily broken by small quantities of electrolytes, such as sodium sulfate, the sulfonated oil was found to be redissolved in the ether layer.

By the proper proportioning of the solvent and solution, all the neutral fat and the fatty acids may be quantitatively separated from the sulfo oil by extraction with ether. The ether extract, containing the neutral fat and the fatty acids (and some sulfo oil), is then neutralized and the neutral oil is extracted in a similar manner. The water layer from the ether extraction contains the sulfo oil, substantially free from all unsulfonated fractions. By applying a correction factor for the sulfo-oil contaminant in the ether layer, the neutral fat, fatty acids, and sulfo oil may be quantitatively estimated.

Procedure

FRACTION A, SULFO OIL. Dissolve 10 grams of the sample in 25 cc. of water in a 250-cc. separatory funnel and add 50 cc. of ethyl ether, 5 drops of methyl orange indicator (0.1 per cent solution), and 0.5 *N* sulfuric acid until the lower layer after vigorous shaking and settling is faintly pink. Shake the mixture vigorously for about 1 minute and allow the layers to separate well. Excess water used in dissolving the sample often results in emulsions or the formation of gels, which, however, may be overcome by the addition of 5 to 15 cc. of alcohol. A moderate turbidity in the water layer after this extraction may be disregarded. Separate the two layers and again extract the water layer—which contains the sulfo oil—with two 25-cc. portions of ether.

Add to the water layer in the separatory funnel 10 grams of solid sodium chloride, 5 drops of phenolphthalein solution (1.0 per cent), and 50 cc. of ether, and titrate with 0.5 *N* sodium hydroxide solution until the lower layer after vigorous shaking and settling is faintly pink. Now add 5 drops of methyl orange and sufficient 0.5 *N* sulfuric acid with vigorous shaking until the lower layer is again faintly pink. Add enough dry salt

until a slight excess is present. After settling, discard the lower or salt layer, evaporate the ether from the upper layer, and determine the organically combined sulfuric anhydride and the fatty matter in the residue in the usual way—the former preferably by the acid-titration method (4). The ratio of fatty matter to combined sulfuric anhydride gives the correction factor to be used in determining the sulfo oil found in the other fractions. The amount thus determined is ultimately added to fraction A.

FRACTION B, FREE FATTY ACIDS. To the combined ether layers from fraction A, containing the free fatty acids and the neutral fat, add 25 cc. of a concentrated solution of sodium chloride, 5 drops of phenolphthalein indicator, and 10 cc. of alcohol, and carefully neutralize the free fatty acids with 0.5 *N* sodium

TABLE I. FRACTIONAL ANALYSIS OF SAMPLES OF SULFONATED OLIVE AND CASTOR OILS

	Sulfonated Olive Oil			Sulfonated Castor Oil		
	I %	II %	Av. %	I %	II %	Av. %
Fraction A, sulfo oil						
Fatty matter, uncorrected	16.8	16.5	16.7	19.4	18.9	19.2
Combined SO ₂	3.33	3.39	3.36	3.98	4.01	4.00
Correction factor (fatty matter/combined SO ₂)	4.97	4.80
Correction for sulfo oil in fraction B	3.6	2.0
Correction for sulfo oil in fraction C	0.9
Total correction for sulfo oil	4.5	2.0
Fatty matter, corrected	21.2	21.2
Fraction B, free fatty acids						
Fatty matter, uncorrected	24.5	25.3	24.9	28.8	27.6	28.2
Combined SO ₂	0.70	0.74	0.72	0.45	0.37	0.41
Correction for sulfo oil	3.6	2.0
Fatty matter, corrected	21.3	26.2
Fraction C, neutral fat						
Fatty matter, uncorrected	22.3	21.8	22.1	11.7	12.7	12.2
Combined SO ₂	0.20	0.16	0.18	...	Trace	...
Correction for sulfo oil	0.9
Fatty matter, corrected	21.2	12.2
Totals						
Fatty matter found	63.7	59.6
Fatty matter theoretical	63.2	60.2
Combined SO ₂ found	4.26	4.40
Combined SO ₂ theoretical	4.40	4.52

hydroxide solution with vigorous shaking until the lower layer is faintly pink. Add sufficient dry salt until there is a slight excess present, and after shaking well and settling, discard the lower layer. Shake the ether layer vigorously with 50 cc. of water, settle and separate the layers, and extract the water layer with two 25-cc. portions of ether.

Add to the water layer containing the neutralized fatty acid, 50 cc., of ethyl ether, 10 grams of solid sodium chloride, and 5 drops of methyl orange solution, and titrate with 0.5 *N* sulfuric acid with vigorous shaking until the lower layer is faintly pink. Add a slight excess of dry salt, allow the layers to separate completely after shaking, discard the water layer, evaporate the ether in the upper layer, and determine the combined sulfuric anhydride and fatty matter in the residue in the usual manner. In determining the combined sulfuric anhydride in this fraction as well as in the following, boil with the acid for several hours and agitate frequently, to make sure of complete decomposition. Correct for the presence of sulfo oil by deducting the product of the combined sulfuric anhydride contained in this fraction and the correction factor determined in fraction A.

FRACTION C, NEUTRAL FAT. Add 25 cc. of saturated salt solution and 5 drops of phenolphthalein solution to the ether layer from fraction B, containing the neutral fat, and neutralize the free fatty acids, if any, with 0.5 *N* sodium hydroxide solution with vigorous shaking until the lower layer is faintly pink. Now add 5 drops of methyl orange indicator and titrate with 0.5 *N* sulfuric acid, shaking vigorously until the lower layer is again faintly pink. Add a slight excess of salt, discard the lower layer after settling, evaporate the ether from the upper layer, and determine the combined sulfuric anhydride and fatty matter in the residue as outlined above. Correct for the presence of sulfo oil as for fraction B. For greater accuracy, the free and combined fatty acids as soap contained in this fraction, which is usually very small, may be calculated from the acid titration, and the result deducted from this fraction and added to fraction B.

Experimental

Samples of sulfonated olive and sulfonated castor oils of approximately the same concentration in fatty matter were

fractionated by this method and the results, based on the weight of the original samples, are given in Table I. Under "totals" at the end of the table, the fatty matter and combined sulfuric anhydride are compared with the results obtained by a direct analysis of the original samples, which results are considered to be the correct or theoretical values. In the sample of sulfonated olive oil the fatty matter is practically equally divided among the three fractions; in the case of the sulfonated castor oil, however, the neutral fat is only about half as much (with a corresponding larger amount of free fatty acids in fraction B), and the amount of sulfo oil is about the same as in the other sample.

PURITY OF SULFO OIL IN FRACTION A. To determine whether or not the sulfo oil fraction was substantially free from unsulfonated fat and fatty acids, the water layer containing the sulfo oil after the regular extraction with ether was further extracted with three 100-cc. portions of the solvent, with the results shown in Table II. Because of the small quantities involved, the results for the combined sulfuric anhydride are necessarily approximate. It will be noticed that the total amount extracted is comparatively small and that successive extractions continued to extract some fatty matter, though in decreasing quantities. The ratio of fatty matter to combined sulfuric anhydride indicates that the total residue had approximately the same composition as the sulfo-oil fraction in Table I. It is therefore reasonable to assume that the latter fraction is substantially free from unsulfonated ingredients.

PURITY OF FREE FATTY ACIDS IN FRACTION B. To determine whether or not the free fatty acids in fraction B in the case of the sulfonated olive oil contained any neutral fat, the following tests and calculations were made: The saponification value of the desulfated fatty matter of this fraction was determined and found to be 190.8. The alkali equivalent of the free fatty acids in this fraction, determined as given in the method, was found to be 34.5 mg. of potassium hydroxide per gram based on the original sample, corresponding to 18.1 per cent of free fatty acids (34.5/190.8), compared with 21.1 per cent actually found. A similar result was obtained for the sample of sulfonated castor oil. While the discrepancy between the calculated fatty acids and the fatty matter found may indicate the presence of some neutral oil, the difference is small and of slight practical importance, and it is believed that a more careful analysis would bring the results into closer

TABLE II. SUCCESSIVE EXTRACTIONS OF FRACTION A WITH ETHYL ETHER

Sample	Extraction No.	Volume of Ether C.	Fatty Matter %	Combined SO ₂ %
Sulfonated olive oil	1	100	2.2	0.50
	2	100	1.1	0.18
	3	100	0.7	0.18
	Total	300	4.0	0.86
			(Fatty matter/combined SO ₂) ^a	4.65
Sulfonated castor oil	1	100	1.5	0.32
	2	100	1.2	0.23
	3	100	1.2	0.16
	Total	300	3.9	0.71
			(Fatty matter/combined SO ₂) ^a	5.49

^a Approximate.

agreement. Furthermore, some experiments carried out with the neutral fat fraction, discussed below, indicate that all the neutral fat and unsaponifiable matter had probably been quantitatively extracted; hence, the discrepancy probably indicates some polymerization.

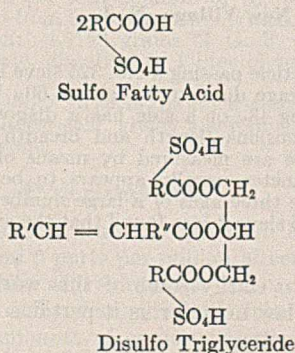
PURITY OF NEUTRAL FAT IN FRACTION C. The free fatty acids and combined sulfuric anhydride in this fraction were found to be from a trace to 1.5 mg. of potassium hydroxide for the former and from a trace to 0.25 per cent for the latter,

based on the original samples. These results indicate that the neutral fat fraction is comparatively free from either of these ingredients. To determine whether or not all of the neutral fat in the original sample is contained in this fraction, 100 parts of the sulfonated olive oil were mixed with 50 parts of neutral raw olive oil and the mixture was analyzed for neutral fat. The quantity found was 48.4 per cent, compared with the theoretical value of 47.5. In calculating the theoretical value it was assumed that the neutral fat in the original sample was equal to a 21.2 per cent in accordance with Table I. As a further check, the same oil was mixed with half its weight of mineral oil and the combined neutral fat and unsaponifiable were determined. The latter was then saponified and the mineral oil determined in the usual way. The amount recovered was 32.8 per cent, compared with the theoretical value of 33.3 per cent. The latter does not include the small amount of unsaponifiable matter naturally occurring in the oil.

Composition of Sulfonated Oils

A study of the data obtained in the fractional analysis of sulfonated olive and castor oils, discussed above, has led to some very interesting speculations as to the probable composition of each of the fractions separated and also as to the reactions that may take place during the sulfonation process. It has heretofore been assumed by many investigators that the reactions are very complicated, resulting in the formation of many involved polymers, but this investigation does not bear out these assumptions. The data obtained in this study and the conclusions arrived at follow.

SULFONATED OLIVE OIL. *Fraction A, Sulfo Oil.* The complete data obtained for the uncorrected sulfo oil in fraction A, Table I, are given in Table III. According to Jamieson (5), olive oil consists of 80 to 85 per cent of oleic acid, 4 to 7 per cent of linoleic acid, and the rest saturated fatty acids. For the purpose of this discussion it is assumed that the fatty acids in sulfonated olive oil consist entirely of the oleic acid type and also that the saponification value found for the desulfated fat, which has undoubtedly suffered some hydrolysis and condensation during the heating with mineral acid, is the same as for the fatty matter in the sulfo oil before decomposition. According to Table III, the composition of the sulfo oil corresponds approximately to 40 per cent free fatty acids; sulfonated oil, 80 per cent of maximum sulfonation; and 20 per cent unsaturated oil. In other words, out of every 5 fatty acid residues, 2 consist of free fatty acids, 4 are completely sulfonated, and 1 contains a double bond. There seems to be only one feasible composition that meets with all these conditions—namely,



That is, the sulfo oil apparently consists of only two sulfonated compounds—namely, sulfo fatty acids and disulfo triglycerides and precisely in the proportion of 2 molecules of the former to 1 of the latter. The triglyceride may be either symmetrically or unsymmetrically sulfonated.

Fraction B, Free Fatty Acids. It has already been shown that this fraction consists almost entirely of simple free fatty acids. The desulfated fat had a cloud test of 30° C. and a solidification point 1° lower. It had an iodine value of 40.8, indicating that more than half of the unsaturated bonds in the original had been converted to hydroxyl groups, which would also serve to explain the comparatively low saponification value obtained for this fraction—namely, 190.8 instead of about 200 for olive oil fatty acids. Evidently considerable sulfonation had at first taken place but the product decomposed before it was finished.

TABLE III. ANALYSIS OF SULFO OIL IN FRACTION A OF SAMPLE OF SULFONATED OLIVE OIL

	Based on Original Sample	Based on Desulfated Fatty Matter
Fatty matter, %	16.7	100
Saponification value ^{a,b}	13.7	190.8
Acidity, mg. of KOH per gram	13.7	82.0 ≈ 40% free fatty acids
Combined SO ₃ , %	3.26	20.1 ≈ 80% of maximum sulfonation
Iodine No.	...	19.2 ≈ 20% unsaturated
Cloud test, ° C.	...	38
Solidification point, ° C.	...	33

^a Sulfonation equivalent as SO₃ = 26.3%.

^b Iodine equivalent = 86.0

Fraction C, Neutral Fat. The fatty matter of this fraction had the lowest solidification point—namely, 21° C.—a saponification value of 180.8, and an iodine number of 52.5. The low iodine number indicates that sulfonation followed by decomposition has taken place almost to the same extent as in the case of the free fatty acids in fraction B. However, the saponification value is 10 points lower than for fraction B—namely, 180.8 compared with 190.8; hence, the average molecular weight of the fatty matter in this fraction must be greater than for the fatty acids fraction. This indicates that at least part of the neutral fat must be in the form of glycerides, since the polymers would have a lower average molecular weight. Moreover, the extent of the difference in the saponification values indicates, assuming that the nature of the fatty acids is alike in both fractions, that the neutral fat is practically all in the form of glycerides and that practically no polymers can be present. The neutral fat, as shown below, consists probably of di- and triglycerides.

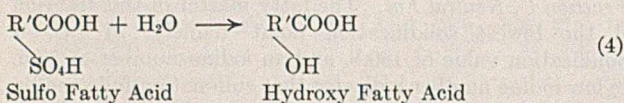
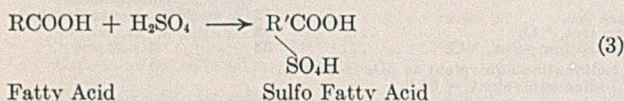
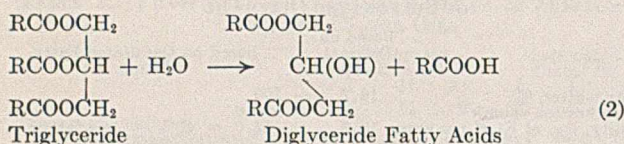
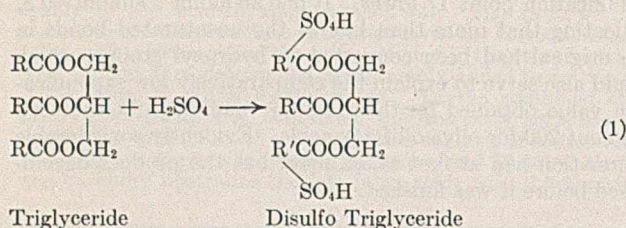
SULFONATED CASTOR OIL. The sulfo oil in fraction A of the castor oil sample had an iodine number of 77.8, indicating very little sulfonation on the double bond. The degree of sulfonation was about equal to that of the olive oil—namely, about 80 per cent—and the acidity corresponded to about 50 per cent of free fatty acids instead of 40 per cent. It is therefore assumed that the composition of this fraction is similar to that of the corresponding fraction of the olive oil sample, with the exception that the number of double bonds in the former is practically the same as for the raw castor oil.

The free fatty acids in fraction B had an iodine number of 78.9 and an acidity of 176 mg. of potassium hydroxide per gram of desulfated fat. These data indicate that the free fatty acid is nearly all pure ricinoleic acid, with the possibility of a small percentage of polymerized fatty acids. The neutral fat fraction has an iodine number of 81.8 and its composition, as in the case of the olive oil sample, is probably a mixture of di- and triglycerides of ricinoleic acid.

Reactions during Sulfonation

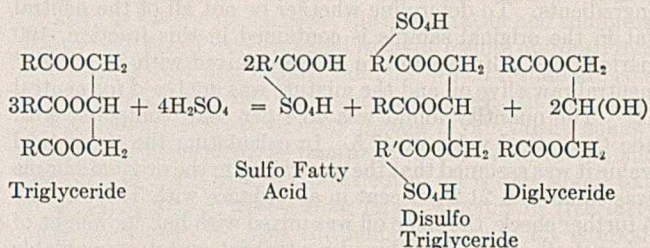
After a careful consideration of the data obtained in this investigation, it is suggested that the following reactions occur when neutral olive oil is treated with concentrated sulfuric acid in the usual commercial practice. Similar reactions probably hold true also for castor oil, except that a

larger amount of free fatty acids is formed because of the greater ease with which the triglyceride of ricinoleic acid is hydrolyzed.



Four reactions seem to take place—namely, the triglyceride is sulfonated, yielding a disulfo triglyceride, probably symmetrically arranged; one-third of another molecule of triglyceride is hydrolyzed, yielding a diglyceride and free fatty acids; the free fatty acid is sulfonated, giving sulfo fatty acid; and finally part of the sulfonated glyceride and fatty acid is decomposed to yield the corresponding hydroxy compounds. These reactions, with the exception of the partial and total hydrolysis of the glyceride and the decom-

position of the sulfo oils, may be represented by the following equation:



The unsulfated di- and triglycerides would be found in the neutral fat fraction and the sulfo fatty acid and the disulfo triglyceride would be found in the sulfo-oil fraction. The composition of the sulfo oil according to this equation corresponds to the analytical data obtained for this fraction. Hydrolysis of the disulfo triglyceride and the sulfo fatty acid would account for the low iodine numbers obtained for the neutral fat and the free fatty acids, respectively.

Acknowledgment

The writer is indebted to Morris Mytelka of this laboratory for assistance with the analytical work.

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Average Diameter of Particles Just Passing the 325-Mesh Sieve

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IN THE determination of the specific surface in terms of square centimeters per gram as given by the Wagner turbidimeter (2), it is generally assumed that the 325-mesh sieve separates the fraction at 60 microns, although actually it has an aperture of 44 microns. This difference assumes major proportions when calculating the surface area of any finely divided substance such as Portland cement. The errors involved amount to as much as 200 sq. cm. per gram in the finer high-early-strength cements, while for the ordinary grades (1400 to 1900 surface area) the errors may be from 50 to 150 sq. cm. per gram.

About a year ago Traxler and Baum (1) made a very comprehensive study of the Wagner turbidimeter and set forth several conclusions and limitations as to its use for the determination of the size distribution of particles in finely divided powders. One of their conclusions was that the 325-mesh sieve separated at nearly 45 microns (1).

The largest particle passing a No. 325 sieve is usually assumed to have an average diameter of about 60 μ because a square opening measuring 43 μ on a side has a diagonal of about 60 μ . If only two dimensions (length and breadth) of particles just passing this sieve are measured by means of the microscope, the average diameter usually appears to be 60 μ . However, by measuring the three axes of a large number of particles just passing a No. 325 sieve it was found that the average diameter is nearer 45 μ .

In an effort to clarify some of this work the writer has applied Stokes' law in so far as it pertains to the use of the Wagner turbidimeter.

The material under consideration was that issued by the U. S. Bureau of Standards, No. 46r, for the calibration of the No. 200-mesh sieve. It was carefully washed through the 325-mesh sieve having a correction factor of -0.5 to the residue. The retained material was dried in the oven, and 0.3 gram of the residue was prepared for suspension in accordance with the standard method of procedure as applied to the Wagner turbidimeter. The micro-

TABLE I. PARTICLE SIZE DETERMINATION

Micron	$(F_0 = 23.00)$		
	Test No. 1	Test No. 2	Test No. 3
60	21.90	22.05	22.40
55	22.40	22.50	22.70
50	22.70	22.90	22.90
45	22.90	23.00	23.00
40	22.90	23.00	23.00
35	22.90	23.00	23.00
30	22.90	23.00	23.00
25	22.90	23.00	23.00
20	22.90	23.00	23.00
15	22.90	23.00	23.00
10	22.90	23.00	23.00
7.5	22.90	23.00	23.00

ammeter was adjusted to give a reading of 23.00 through the tank plus the clear kerosene, with the light filter remaining in place throughout the period of the test. The suspension was then agitated, and placed in the path of the light, and readings were taken as the kerosene in the timing buret passed the marks corresponding to the particle sizes 60, 55, 50, 45, 40 7.5 microns, and recorded in Table I.

Test 1 consisted of the standard procedure for preparing the suspension, where the sample is placed in a test tube with about 15 cc. of kerosene, stirred for 1 minute, transferred to the tank, and diluted to 335 cc., oleic acid being added to the original mixture to act as a dispersing agent.

Test No. 2 consisted of modifying the procedure by adding the sample to about 100 cc. of kerosene in the tank together with the oleic acid (8 drops) and stirring the mixture for 1 minute as before. The difference was in the elimination of the close contact between the brush and the walls of the test tube, thereby removing all possibilities of a grinding action of the brush on the material under consideration.

Test 3 consisted of merely agitating the mixture of the sample, plus oleic acid, plus 335 cc. of kerosene by rotating the tank through 180° for approximately 1 minute.

It may be seen that for all tests the particles have either dropped out of suspension or approached a constant value at 45 microns, indicating that the 325-mesh sieve separates at 45 microns and not 60 microns as originally supposed. As for test 1, it may be concluded that the brush has some effect in grinding, although the data may indicate more complete dispersion where the material is in more intimate contact with the agitating medium, which in this case is the brush. This appears to be beyond the purpose of the present paper.

Another point is the introduction of correction factors to the various sieves and in particular the 325-mesh sieve. The standard specifications (A. S. T. M. Designation E11-26) permit a tolerance of 90 per cent in the maximum opening of the No. 325 sieve or a maximum aperture of 84 microns on the side. Consequently, since manufacturing conditions will not permit the fabrication of a perfect sieve having apertures of 43 (or 44) microns, it is necessary to introduce correction factors, either plus or minus, in order to establish some standard or reference value. This is a regular procedure as practiced by the process industries using sieves as a basis of fineness control. The designation of the aperture alone should establish the nominal size of the particles.

The data, as presented from a new viewpoint, give additional experimental proof that the 325-mesh sieve separates at an average particle diameter of 45 microns.

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A New Reagent for the Detection of Cerium

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INVESTIGATION of various substituted phenylarsonic acids as possible reagents for the determination of cerium revealed a specific colorimetric reaction between ceric cerium and arsanilic acid. A deeply colored solution formed immediately upon the addition of the reagent to a sulfuric acid solution of ceric ammonium sulfate.

Solutions

Arsanilic acid: a 5 per cent solution of the sodium salt of arsanilic acid prepared from Eastman arsanilic acid.

Stock ceric solution: 4.5148 grams of G. F. Smith & Co. ceric ammonium sulfate, dissolved in 1 liter of solution, 0.5 M in sulfuric acid.

Standard ceric solution: 10 cc. of the stock solution, diluted to 1 liter with 0.5 M sulfuric acid, giving a solution containing 10 parts per million of cerium.

Experimental

Solutions were made up from the standard ceric solution containing 2, 3, 4, and 5 parts per million of cerium. Upon the addition of arsanilic acid solution to 50 cc. of these solutions, a pink color, easily distinguishable from blanks containing equivalent amounts of cerium but no reagent, was obtained. The intensity of the color produced varied directly with the concentration of cerium present, but was not affected by the concentration of the reagent nor the acidity up to 2 N sulfuric acid. Acidities above this were not investigated. In more concentrated solutions of cerium the color produced is red-brown.

Ceric cerium can be detected by this reagent in the presence

of cerous cerium and the other rare earths. In this investigation it was easily detected in the presence of the following ions: thorium, praseodymium, neodymium, lanthanum, samarium, erbium, terbium, scandium, yttrium, sodium, potassium, ammonium, cupric, beryllium, magnesium, calcium, zinc, strontium, aluminum, titanous, germanium, stannous, vanadate, arsenate, bismuth, molybdate, tungstate, uranyl, manganous, ferric, nickel, nitrate, phosphate, chloride, and acetate.

Fluorides, even in small concentrations, interfere. Zirconium precipitates with the reagent; on filtering, the filtrate is clear, and the precipitate from solutions containing 30 parts per million of cerium has a red color. Zirconium alone gives a white precipitate. Cobalt and chromium, because of the color of the ions, interfere. Cerium can be detected in solutions in which the concentration is about 10 parts per million and that of the other ions is about 100 times as much, except in the cases of cupric, ferric, tungstate, and uranyl, where the cerium concentration must be 20 parts per million and that of the other ions only 50 times as much. For vanadate the concentration of cerium must be 50 parts per million and that of vanadate only 20 times as much. The color obtained is usually pink or red-brown. Care must be taken to avoid excess reagent when thorium is present, as this precipitates slightly.

The tests were made by placing 0.5 cc. of stock ceric solution in a 50-cc. Nessler tube, adding enough of the other ion to give a concentration of 1000 parts per million, and then diluting with 0.5 M sulfuric acid to within 5 cc. of the mark. Arsanilic acid solution was then added to the mark and the

solution shaken or stirred. The formation of a pink or red-brown color when compared with a blank indicated a positive test for ceric cerium.

In applying this test to the determination of the presence of cerium in a mineral, the usual methods of decomposition of the mineral are satisfactory, except that the resulting solution must be free of fluorides. Columbium and tantalum are only slightly soluble in most acid solutions not containing fluorides, and it is assumed that they will be removed with silica. After decomposition and solution, the cerium must be oxidized to the ceric state by use of sodium persulfate, sodium bismuthate, or any of the other oxidizing agents used for cerium. The solution may then be tested by addition of 5 cc. of arsanilic acid solution to 50 cc. of the solution. The production of a pink or red-brown color indicates cerium.

An investigation was made of the quantitative possibilities of arsanilic acid as a reagent for cerium, but it was found unsatisfactory for exact work. This is due to a slow fading of the color produced by the reagent in dilute solutions of cerium, or to the formation of a red-brown precipitate in the case of more concentrated solutions. These interferences

are noticeable even in the short time of 2 minutes. Precipitation in the case of concentrated solutions is not complete.

Arsanilic acid was investigated as a possible indicator for ceric sulfate titrations, but was found to be unsatisfactory as an inside indicator. When used as an outside indicator, the results obtained in the titration of ferrous iron checked with those obtained using *o*-phenanthroline ferrous complex as indicator.

Summary

The red-brown color produced by arsanilic acid with ceric solutions is very sensitive and can be used in the qualitative detection of cerium in the presence of the elements with which it is commonly found. Fluoride, zirconium, cobalt, and chromium interfere.

The reaction is unsatisfactory for exact quantitative work.

Arsanilic acid can be used as an outside indicator for ceric sulfate titrations, but not as an inside indicator.

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Examination of Rubber Latex and Rubber Latex Compounds

I. Physical Testing Methods

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Physical testing methods for the control of processing of rubber latex are reviewed critically, and methods for measuring accurately the pH, viscosity, and surface tension of preserved and compounded latices are recommended. An improvement in the high-speed stirring test for the "mechanical stability" of latex is described.

PRECISE control is essential to the successful operation of any commercial process, particularly of those processes involving the use of rubber latex. Latex is, of course, a complex natural product; it contains a variety of nonrubber constituents, such as proteins, soaps, and others which control or influence its colloidal properties. In order to ensure uniform behavior of latex in process, it is obviously desirable to test its uniformity as a raw product. It is furthermore important that such tests should be, wherever possible, fundamentally sound and free from the personal equation. Unless the results can be expressed in basic fundamental units, which are independent of the apparatus used and of the operator, confusion will result.

It is the purpose of this paper to review critically the more important general physical tests and methods of analysis which can be applied to latex, particularly from the standpoint of accuracy and sources of error, and to recommend certain procedures on the basis of commercial experience in the authors' control laboratories. Some of the recommended

methods have been developed in these laboratories, while others have been improved over procedures given in earlier works on latex (3, 6, 9). Part I is concerned with physical tests such as pH, surface tension, viscosity, and mechanical stability, while Part II is concerned with analytical methods.

Sampling

It may appear superfluous to discuss methods of sampling latex, which are based on the same principles as sampling for any type of analysis. However, in view of the tendency of any type of latex to cream to a greater or less extent, it cannot be stressed too strongly that care should be taken to obtain a sample which is representative of the entire lot of material.

In the case of latex in drums, particularly concentrated latex, it is advisable to stir with a high-speed stirrer of the propeller type for a period of 10 to 15 minutes before taking the sample. In the case of tank-car lots, the latex should be agitated with an air line which should be moved from one end of the car to the other, and agitation should be continued for at least one-half hour.

Measurement of pH

The pH of latex is probably one of its most important properties, inasmuch as it is related in a fundamental way to the stability of the latex as a colloid. However, only one of the methods which are generally employed for the measurement of pH is adapted to the accurate measurement of the pH of latex.

Indicators are unsatisfactory even for approximate measurements on account of protein errors and difficulties in matching colors. In view of the fact that the glass-electrode apparatus is commercially available, the use of indicators is to be avoided entirely.

The hydrogen electrode is also unsuited for use in latex, on account of the ease with which it is poisoned by certain sulfur-containing proteins and traces of hydrogen sulfide. Other difficulties are also encountered, such as frothing of the latex and a tendency for rubber to deposit on the electrode.

The quinhydrone electrode can, of course, be used only in solutions having pH values lower than 8, or below the pH region of most common practical interest in latex processing. For this reason its use in latex has not been extensively investigated in these laboratories. This electrode has, however, been used extensively by van Harpen (5) for measurements of the pH of natural latex.

TABLE I. COMPARATIVE PH VALUES

Samples	Total Solids, %	pH Determined by		Difference (B-A)
		Glass Electrode A	Antimony Electrode B	
Normal latex				
A ^a	30	8.64	8.71	+0.08
B ^a	30	9.46	9.88	+0.42
C ^a	30	9.86	10.27	+0.41
D ^a	30	10.60	11.02	+0.42
E ^a	30	11.96	12.14	+0.18
F	30	9.57	10.11	+0.54
F	35	9.56	9.87	+0.31
G	37.9	9.89	10.26	+0.37
H	36.9	10.31	10.70	+0.39
I	39.3	9.62	10.03	+0.41
Concentrated latex				
A	30	9.46	9.58	+0.12
B	30	9.14	9.32	+0.18
C	30	9.32	9.56	+0.24
3-X creamed latex				
A	30	11.16	11.26	+0.10
B	30	10.60	10.51	-0.09

^a Modified.

Before the glass electrode was manufactured commercially by Leeds & Northrup and other companies, considerable careful work was done on the calibration and use of the antimony electrode. While the potentials were sufficiently reproducible in buffer solutions to indicate that an accuracy of 0.1 to 0.3 pH could be obtained (depending upon the pH of the solution), the accuracy was found to be less in the case of latex. This is indicated in Table I by a comparison of pH values obtained for latices of various types by means of the antimony electrode and glass electrode, respectively, both of which were carefully calibrated with standardized buffer solutions. All the samples listed were diluted to 30 per cent total solids before measurement, except where indicated.

Inspection of Table I indicates that the difference in pH values between the two electrodes becomes less as the latex is purified to a greater degree—for example, the greatest difference is in normal latex, and the least difference is in the case of three-times-creamed latex. It is well known that hydroxy acids such as citric and tartaric acids, as well as certain sugarlike substances, affect the potential of the antimony electrode. It appears probable that some serum constituent of one of these types is responsible for the difference in results.

These data show that the pH values obtained with the antimony electrode are from 0.1 to 0.5 unit higher than those obtained with the glass electrode. While these differences are reasonably constant for the normal latices tested, this does not necessarily indicate that measurements with the antimony electrode can be accurately corrected to obtain the true pH. It seems entirely possible that samples of latex obtained from different plantations might require corrections of different magnitudes because of differences in the kinds and concentrations of serum constituents. Of course, the antimony elec-

trode cannot be used in latex compounded with sulfur, sulfur-containing accelerators, and certain other chemicals. The use of the antimony electrode is not recommended for latex work.

The glass electrode when properly used is believed to be the most reliable and accurate means for measuring the pH of latex. Very constant and reproducible potentials are obtained, and there is no evidence that the glass electrode is poisoned or affected by any of the latex constituents or common compounding ingredients, with the exception of sodium hydroxide and sodium salts. However, the glass electrode is an empirical electrode and the values obtained by it in latex cannot be checked by a basic standard electrode such as the hydrogen electrode.

Full descriptions of the construction of the electrode and the potentiometric setups are given in manufacturers' pamphlets and in the literature (7).

Briefly, the complete cell is as follows:

Standard half-cell (calomel or quinhydrone)	0.120 N HCl (pH = 1.0)	glass	solution or latex pH = X	standard half-cell
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That portion of the entire potential which measures the pH is, of course, the one arising at the glass-solution interface.

There are certain experimental precautions which have been found advisable on the basis of considerable experience in control work. While the commercially available glass shells are made with remarkable reproducibility, the calibration charts furnished with the glass electrode or printed on the dials of potentiometers of various types are not sufficiently accurate for all electrodes, particularly after the electrodes have been used in alkaline solutions for a considerable length of time. It is advisable to calibrate the electrodes daily in buffer solutions which have been standardized with the hydrogen electrode. The following buffer solutions have been found to be particularly practical for this purpose and if properly stored in stoppered Pyrex containers, they will remain at a constant pH for a period of 2 or 3 months.

Solution I:	
1.0 N KOH	50 cc.
2.0 N acetic acid	50 cc.
Distilled water to make (pH about 4.5)	500 cc.
Solution II:	
Anhydrous KHCO ₃	10 grams
1.0 N KOH	50 cc.
Distilled water to make (pH about 10.0)	500 cc.

From the calibration data is obtained a calibration chart (pH versus e. m. f.) by drawing a straight line through the two experimental points. More careful calibrations have indicated that this procedure is justified.

On account of the high resistance of the glass electrode, it is necessary to use a very sensitive galvanometer. The Leeds & Northrup type 2500B is generally satisfactory for use with their glass-electrode shells, although difficulties are encountered if the galvanometer cannot be insulated from vibration. A vacuum-tube galvanometer which is marketed by the Hellige Company has been used successfully in control work. The Beckmann acidimeter, which is a portable vacuum-tube potentiometer, has been used successfully in one of the divisions of the company.

On account of the high resistance of the glass electrode, leakage of current around the electrode is occasionally encountered during humid weather unless proper precautions are taken. Such leakages are characterized by difficulty in balancing the circuit and by erratic behavior of the galvanometer. These difficulties can be eliminated by shielding

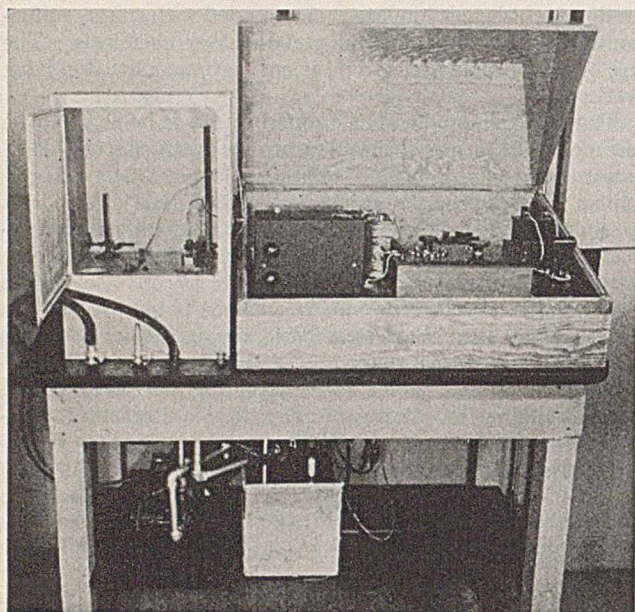


FIGURE 1. pH APPARATUS AND THERMOSTAT

the glass-electrode apparatus, and by making the leads to the galvanometer as short as possible. A suitable setup of this kind is illustrated in Figure 1. The glass electrode and calomel half-cell are enclosed in a metal box with a screen door, and water from a thermostat is pumped through the bottom of the container.

It cannot be too strongly emphasized that the potential of the glass electrode is affected by certain metallic ions above pH 9 to 10, one of the most important of which is sodium ion. This is illustrated by the graph taken from Dole (1) which shows the variation in salt error of the glass electrode with pH in solutions containing different metallic ions. In alkaline solutions above pH 10, the potential of the glass electrode is depressed by sodium ion and to a lesser extent by potassium ion. This means that pH measurements of alkaline latices containing sodium hydroxide or sodium soaps would be considerably in error.

Surface Tension

The surface tension of latex is often assumed to be an indication of the foaming and related properties of latex. This relationship has not been too clearly established, but inasmuch as considerable importance is often attached to surface tension values, a standard and accurate procedure should be used for measuring them. Of the methods available, the capillary-rise and bubble-pressure methods are unsuitable. Accurate results can be obtained by the drop-weight method, but the technic is somewhat more cumbersome than is desirable for control.

The ring method is simple in manipulation and gives accurate values if the results are calculated properly. However, very inaccurate results are often obtained because no attention is paid to the important corrections required for the experimental data. Inasmuch as the theory and experimental technic have been treated by Freud and Freud (2), and by Harkins and Jordan (4), only the more common sources of experimental error will be discussed in this paper.

In outline, the ring method consists in determining the maximum pull of the liquid on a circular wire ring when the ring is withdrawn, and from this pull the surface tension can be calculated. A number of types of apparatus have been

developed, all of which consist in principle of a torsion, spring, or chainomatic balance. Directions for operation are given in manufacturers' pamphlets, but the following experimental points should be stressed:

Great care should be taken to maintain scrupulous cleanliness. Glassware should be cleaned with chromic acid solution, and the ring, after cleaning in chromic acid, should be heated to red heat in the oxidizing portion of a Bunsen flame. In this connection care should be exercised to make sure that any salts or latex have been removed from the ring before flaming, or serious damage will result. The wire of the ring should all lie in one plane and the ring should hang in such a way that its plane is parallel to the surface of the liquid.

One of the most common sources of experimental error is that the liquid is often contained in too small a dish, or in a watch glass, with its surface open to evaporation in the air. Accurate measurements can be obtained under such conditions only by accident. It is preferable that the liquid be contained in a fairly large dish which is enclosed in a deep vessel, as illustrated in Figure 3. The outer vessel is covered with a plate with a hole in its center of sufficient size to permit connection of the ring to the balance arm with a fine platinum wire. This is particularly important in the case of latex because of the tendency of this material to "skin over" on its surface. Such skinning over, although invisible to the eye, may increase the values obtained by several dynes. In order to ensure a fresh surface, it is advisable to overflow the inner dish before making measurements.

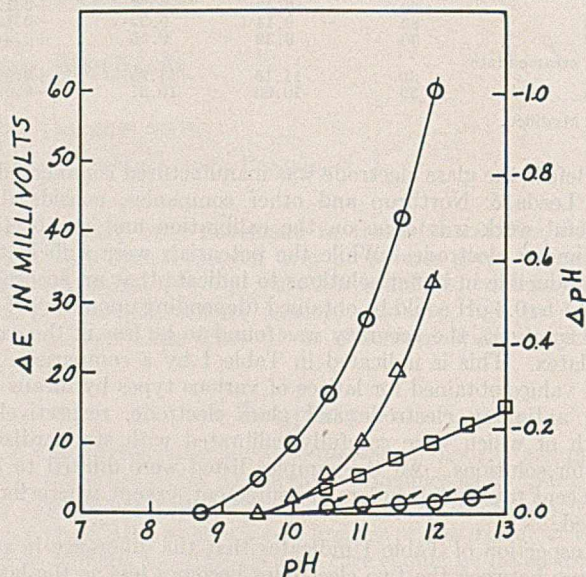


FIGURE 2. ERRORS OF GLASS ELECTRODE IN 1N SOLUTIONS (AFTER DOLE)

Δ Li+, ○ Na+, □ K+, ◇ Ba⁺⁺

Another common source of error lies in the assumption that either the scale gives values directly in dynes per cm. or, in the case of certain apparatus, that the reading in grams is correct. It is important that the balance be directly calibrated in grams, and that the surface tension be calculated from the total pull on the ring by the method given below.

Many surface tension results obtained by the ring method which have appeared in the literature are of no value because it has been incorrectly assumed that the surface tension is related to the pull on the ring by the equation

$$\gamma = \frac{Pg}{4\pi R}$$

where P is the total pull in grams on the ring, g is the acceleration of gravity, and R is the radius of the ring. In order to obtain correct surface tension values, the right-hand member of the above equation must be multiplied by a correction factor to give the equation

$$\gamma = \frac{Pg}{4\pi R} F$$

where the correction factor, F , is a function of $\frac{R^3}{V}$ and $\frac{R}{r}$. V is the volume of liquid raised by the ring above the free surface and is equal to the total pull in grams divided by the density. $\frac{R^3}{V}$ is therefore equal to $\frac{R^3 d}{P}$. $\frac{R}{r}$ is the ratio of the radius of the ring to the radius of the wire from which it is made, and its value is generally given by the manufacturer.

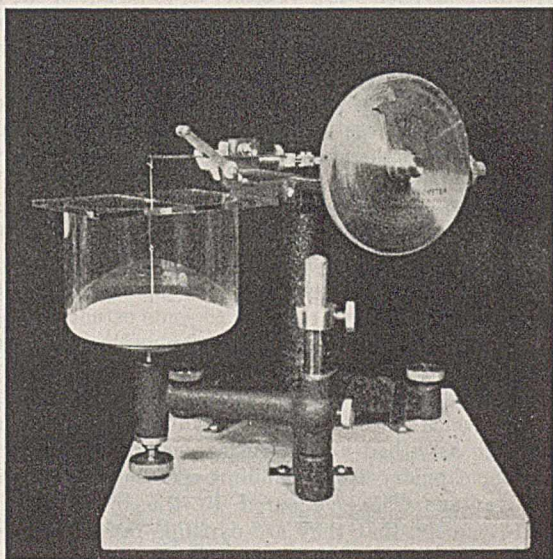


FIGURE 3. SURFACE TENSION APPARATUS

Tables of correction factors for various values of $\frac{R^3}{V}$ and $\frac{R}{r}$ are given by Harkins and Jordan (4). From these tables a correction curve for any particular ring (whose $\frac{R}{r}$ value is of course constant) can be constructed. Unless such corrections are made, the results may be considerably in error, depending upon the dimensions of the ring and the material measured.

This is illustrated by the following comparison of corrected and uncorrected ring method results with results obtained by the drop-weight method (Table II). The latices were diluted as indicated in the second column.

In the case of the ring used in these experiments, the uncorrected results obtained by the ring method are approximately 3 dynes per cm. higher than the correct values.

Considerable difficulty has been found in obtaining reproducible results on latex if the total solids content is substantially above 40 per cent, because the viscosity is sufficiently great to prevent the liquid from attaining its equilibrium shape in a reasonable length of time. For this reason, it is desirable to make surface tension measurements on concentrated latex at a standard condition—as, for example, 40 per cent total solids and 0.5 per cent ammonia.

Viscosity

The flow properties of latex and latex compounds are frequently of importance in the handling and processing of

TABLE II. COMPARATIVE RESULTS

	Total Solids %	Scale Reading	Total Pull (P) Gram	Surface Tension		Drop-weight method
				Ring method ^a Uncorrected	Ring method ^a Corrected	
				Dynes per cm.		
Normal latex, A	30	38.7	0.316	38.7	35.6	35.9
Concentrated latex, A	40	34.9	0.285	34.9	31.9	32.2
Concentrated latex, B	40	39.0	0.318	38.9	35.9	35.7
Benzene	—	30.7	0.251	30.8	28.0	28.2 ^b

^a $R = 0.637$ cm., $R/r = 38.8$.

^b Value taken from International Critical Tables.

these materials. As illustrations may be cited dipping and spreading processes. For practical reasons it is convenient to treat the flow properties of latex in a special way, introducing some new terminology. It will be found that viscosity data can be expressed in this terminology in a form which is convenient in the making of practical calculations.

THEORETICAL. A Newtonian or perfectly viscous liquid is characterized by the existence of a linear relationship between an impressed shearing stress and the rate of shear produced. The coefficient of viscosity of such a liquid is defined as

$$\eta = \text{coefficient of viscosity} = \frac{\text{shearing stress per unit area}}{\text{rate of shear produced}} \quad (1)$$

and is a constant over the range of shearing stresses in which the liquid does not exhibit turbulence. The situation is pictured by the solid straight line OX in Figure 4, and the coefficient of viscosity is equal to the reciprocal slope of the line OX .

Liquids in which the relationship between shearing stress and rate of shear is not linear are termed non-Newtonian. Latex is such a non-Newtonian liquid, and a typical stress-rate of strain diagram is shown by the solid line in Figure 4. Now the definition of the coefficient of viscosity remains unchanged in the transition from Newtonian to non-Newtonian liquids and is defined by Equation 1. It is thus plain that the value of η for a non-Newtonian liquid is not a constant over the range in which no turbulence occurs. For instance, η

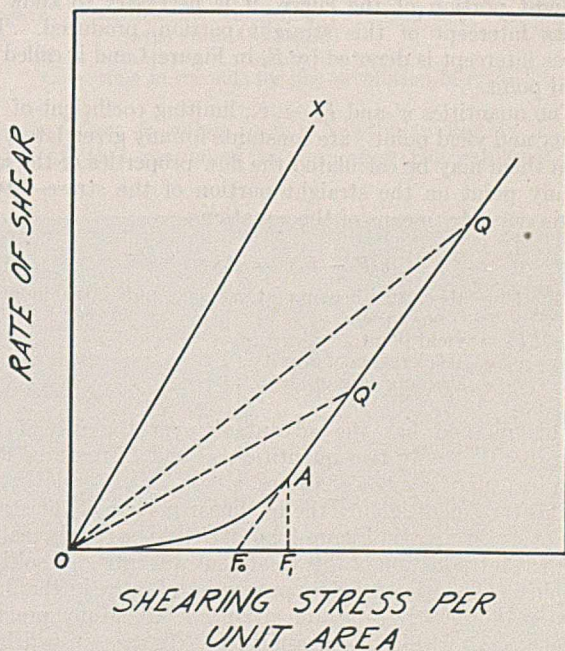


FIGURE 4. SHEARING STRESS-RATE OF SHEAR DIAGRAM For a Newtonian liquid (OX) and for a Non-Newtonian liquid like latex ($OQ'Q$)

at Q in Figure 4 is the reciprocal slope of OQ , whereas η at Q' is the reciprocal slope of OQ' . Consequently in the case of a non-Newtonian liquid it is impossible to use the coefficient of viscosity at one shearing stress to calculate the rate of shear at another shearing stress.

It is an experimental fact that the stress-rate of strain diagram of latex becomes a straight line for a range of shearing stresses above a given value. This situation is represented by the portion of the solid curve to the right of A in Figure 4. As the shearing stress increases, the coefficient of viscosity of the non-Newtonian liquid approaches the reciprocal slope of the straight portion of the curve. These considerations suggest the following definition in connection with non-Newtonian liquids:

η' = limiting coefficient of viscosity
 = reciprocal slope of straight portion of stress-rate of strain curve

In the case of a Newtonian liquid the quantity η determined at a single shearing stress completely specifies the flow properties of the liquid throughout the shearing stress interval in which no turbulence occurs, since the straight line constituting the stress-rate of strain curve passes through the origin of the stress-rate of strain diagram.

This is not true in the non-Newtonian case, and in order to complete the specification of flow properties in the straight portion of the curve, it is necessary to know the stress intercept of this straight portion, produced. This stress intercept is denoted by F_0 in Figure 4 and is called the yield point.

The quantities η' and F_0 —i. e., limiting coefficient of viscosity and yield point—are constants for any given latex, and from them may be calculated the flow properties of the latex at any point on the straight portion of the stress-rate of strain curve by means of the equation

$$g(F - F_0) = \eta' S \quad (2)$$

where F = absolute shearing stress per unit area in grams per sq. cm.

F_0 = yield point
 g = acceleration of gravity
 S = absolute rate of shear

This method has the advantage over the use of true viscosity that only two quantities, η' and F , must be dealt with instead of a series of values, η .

This treatment ignores the nonlinear portion of the stress-rate of strain curve in Figure 4, but it should be clearly realized that the introduction of this treatment was intended solely to simplify calculations of flow properties of latex in the linear portion of the stress-rate of strain curve. Many practical problems fall within this classification. In cases in which the nonlinear portion of the stress-rate of strain curve must be dealt with, it is probably best to resort to the use of true viscosity.

METHODS. In the experience of the authors, two methods of measuring viscosity have been used and found satisfactory for control work: the capillary-flow method and the rotating-cylinder method. Both provide rapid and precise means of measuring the flow properties of latex. The former possesses the advantage that the apparatus may be made from materials stocked in the laboratory. For the control of raw latex the capillary-flow method employing the simple apparatus shown in Figure 5 fulfills all requirements, but with many compounds either a modified capillary-flow apparatus (Figure 6) or a rotating-cylinder viscometer (Figure 7) must be resorted to.

The rotating-cylinder apparatus possesses a wider field of applicability than the capillary-flow setup, but the details of its construction make it rather expensive. The rotating-cylinder method can be made to replace the capillary method in all departments of latex work with the exception of normal latex, which has such a low viscosity as to be out of the most useful range of the rotating-cylinder apparatus with dimensions specified by Mooney and Ewart (8). Data on viscosity and limiting viscosity as obtained by these two methods are found to be in good agreement if the points obtained on the stress-rate of strain diagram are on the straight portion of the curve. Yield results show variations, particularly in compounds of high viscosity. There are reasons for feeling that the rotating-cylinder values are more reliable. These difficulties are probably traceable to the fact that latex does not possess an actual yield point. It is easily shown that the yield value as calculated on the basis of preceding definitions is actually to some extent dependent on the nature of the nonlinear portion of the real stress-rate of strain diagram.

Recent work on the falling-sphere method has resulted in apparatus which may very likely be suitable for use in latex. The writers have had no experience with this method. In general the capillary-flow and falling-sphere methods possess a disadvantage when compared to the rotating-cylinder method—namely, that they are dynamic rather than kinematic methods, and require a knowledge of the density of the material under test.

In order to render the results of viscosity measurements comparable, it is necessary to carry out all determinations on a given type of latex at the same total solids content. A precaution which should be observed in preparing the latex

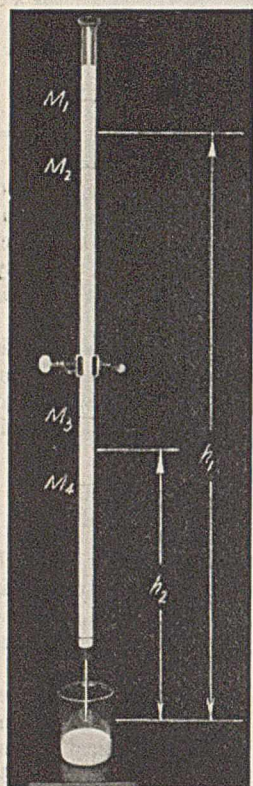


FIGURE 5. CONTROL CAPILLARY VISCOMETER

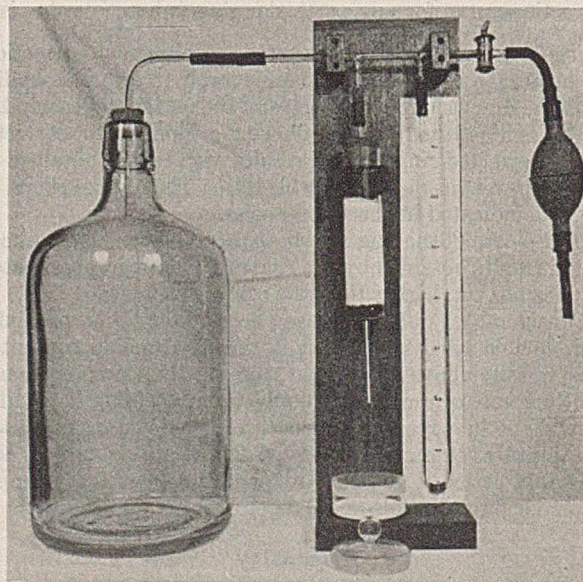


FIGURE 6. MODIFIED CAPILLARY-FLOW APPARATUS

for measurement is to eliminate all gas bubbles. This may be done by deaerating the latex under reduced pressure for several hours.

CAPILLARY-FLOW METHOD. In the capillary-flow method of measuring viscosity the shearing stress is usually produced by the hydrostatic pressure of the liquid above the capillary tube. The apparatus is pictured in Figure 5. It consists of an 80-cm. glass tube 1 cm. in inside diameter with scratches M_1, M_2, M_3, M_4 as shown and a capillary tube of known dimensions inserted in the lower end of the 80-cm. tube by means of a rubber stopper. The method consists of measuring the lengths of time necessary for two equal given volumes of latex, as estimated by the passage of the meniscus through two intervals bounded by scratches on the 80-cm. tube, to flow through the capillary under two different hydrostatic pressures. In terms of Figure 5 the following dimensions have been found suitable for the manipulation of latex:

- h_1 and h_2 = heights of midpoints of intervals M_1M_2 and M_3M_4 , respectively, above bottom of capillary ($h_1 = 65$ cm.; $h_2 = 30$ cm.)
 R = radius of capillary ($R = 0.040 \pm 0.002$ cm. for normal latex; $R = 0.070 \pm 0.004$ cm. for creamed or centrifuged latex)
 L = length of capillary (10 cm.)
 V = volume included in each of intervals M_1M_2 and M_3M_4 (10 cc.)

The numerical values of $h_1, h_2, R,$ and L are so chosen that the two stresses under which the rates of flow are measured both fall on the linear portion of the stress-rate of strain diagram.

With the aid of the following additional notation it is possible to write down formulas for viscosity and yield point in terms of the above characteristics of the apparatus:

- t_1 and t_2 = times in seconds for latex meniscus to pass through intervals M_1M_2 and M_3M_4 , respectively
 d = density of latex in grams per cc.
 g = acceleration of gravity (980.6 grams per second per second)
 T = temperature in °C.
 η = coefficient of viscosity in poises at temperature T
 η_{25} = coefficient of viscosity in poises at 25° C.
 η' = limiting coefficient of viscosity in poises at temperature T
 η'_{25} = limiting coefficient of viscosity in poises at 25° C.
 F_0 = yield point in grams per sq. cm. at T° C.
 V = volume of latex (= weight of latex/density of latex)

Then

$$\eta' = K_1 \frac{t_2 t_1}{t_2 - t_1}$$

$$F_0 = K_2 - K_3 \frac{\eta'}{t_2}$$

where

$$K_1 = \frac{\pi R^4 g d (h_1 - h_2)}{8 L V}$$

$$K_2 = \frac{3 R h_2 d}{8 L}$$

$$K_3 = \frac{3 V}{\pi R^2 g}$$

In the testing of highly viscous samples a modified capillary-flow apparatus is sometimes desirable. The modification consists of augmenting the hydrostatic pressure used in the simple apparatus by means of an external superimposed pneumatic pressure. The apparatus for this procedure is pictured in Figure 6. The pneumatic pressure is developed with the aid of a syringe bulb by pumping air into the large glass bottle reservoir shown in the figure. When the desired pressure, as read on the U-tube differential manometer, has

been attained, the stopcock in the line leading to the syringe bulb is closed and latex is allowed to flow through the capillary for a given length of time into a large weighing dish. The latex is weighed to an accuracy of 1 per cent, and the process is repeated at one or more different values of the impressed pneumatic pressure. It will be noted that the 80-cm. tube of the simple apparatus has been replaced by a short tube of much larger diameter. The following additional notation will be necessary in order to write down formulas:

- d_1 = density of latex in grams per cc.
 d_{Hg} = density of mercury in grams per cc.
 P_1 and P_2 = pneumatic pressure in cm. of mercury
 h_1 and h_2 = average heights in cm. of top of latex column above bottom of capillary at pressures P_1 and P_2 , respectively
 w_1 and w_2 = weights in grams of liquid delivered at pneumatic pressures P_1 and P_2 , respectively, in times t_1 and t_2 , respectively

$$\eta' = K_4 \frac{d_{Hg}(w_2 P_1 - w_1 P_2) + d_1(w_2 h_1 - w_1 h_2)}{w_1 w_2} \frac{t_1 t_2}{t_2 - t_1} d_1$$

$$F_0 = K_5 P_2 - K_6 \frac{\eta' w_2}{d_1 t_2}$$

where

$$K_4 = \frac{\pi R^4 g}{8 L}$$

$$K_5 = \frac{3 R}{8 L}$$

$$K_6 = \frac{3}{\pi R^2 g}$$

ROTATING-CYLINDER METHOD. In this case the shearing stress is produced by falling weights which, by means of a system of strings and pulleys, cause rotation of the cylinder. The complete theoretical expression for the instrument constant may be found in the afore-mentioned article by Mooney and Ewart, but it is too complex to be reproduced here. The form of the equation from which the viscosity of a Newtonian liquid may be calculated from rotating-cylinder viscometer data is, using the same notation as in the discussion of the capillary flow method with some additions

$$\eta = K M t \quad (3)$$

where K = instrument constant, experimentally determined (with standard liquid)

M = total mass of weights and pans

t = time in seconds for one revolution of rotor

The procedure in going to non-Newtonian liquids is very similar to that employed in discussing the capillary flow

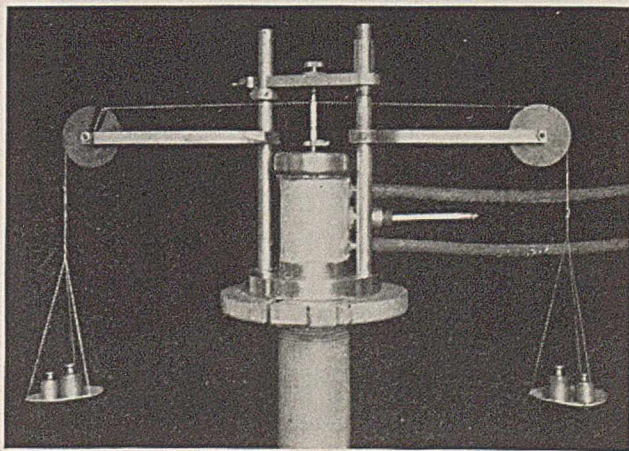


FIGURE 7. ROTATING-CYLINDER VISCOMETER

method. Instead of two pressure heads, two values of M are employed.

$$\text{Then } \eta' = K(M_1 - M_2) \frac{t_2 t_1}{t_2 - t_1} \quad (4)$$

The value of M corresponding to the yield point F_0 is

$$M_0 = M_2 - \frac{\eta'}{K t_2} = \frac{M_2 t_2 - M_1 t_1}{t_2 - t_1}$$

$$F_0 = L M_0 \quad (5)$$

where

$$L = \frac{3C}{4\pi^2 R_0^2 l_0 \left[1 + \frac{R_0}{3l_0 \sin \Theta_0} \right]} \quad (6)$$

C = circumference of pulleys

R_0 = mean radius of inner and outer cylinders as defined by

$$\frac{1}{R_0^2} = \frac{1}{2} \left[\frac{1}{R_1^2} + \frac{1}{R_2^2} \right]$$

R_1 and R_2 being the radii of the rotor and stator, respectively
 Θ_0 = mean angle between bottom of stator and bottom of rotor
 l_0 = effective length of cylindrical section of rotor

TEMPERATURE CORRECTION. The capillary methods as described above have the disadvantage that thermostatic temperature control is difficult. However, if measurements are made within a few degrees of 25° C., it has been found satisfactory to correct the viscosity values for temperature by means of the following equations:

$$\eta_{25} = \eta [1 + 0.02 (25 - T)] \quad (7)$$

$$\eta'_{25} = \eta' [1 + 0.02 (25 - T)] \quad (8)$$

These equations are of a form which is known to be valid over small temperature intervals for water. The data of the following table permit the calculation of an average temperature coefficient for viscosity measurements in latex of 2.2 per cent per degree Centigrade, but the accuracy of the data is not sufficient to warrant considering the difference between 2 and 2.2 per cent as significant. In short, Equations 7 and 8 represent the best available method of temperature correction of viscosity data. Over a 5° interval on each side of 25° C. they are sufficiently accurate for practical purposes,

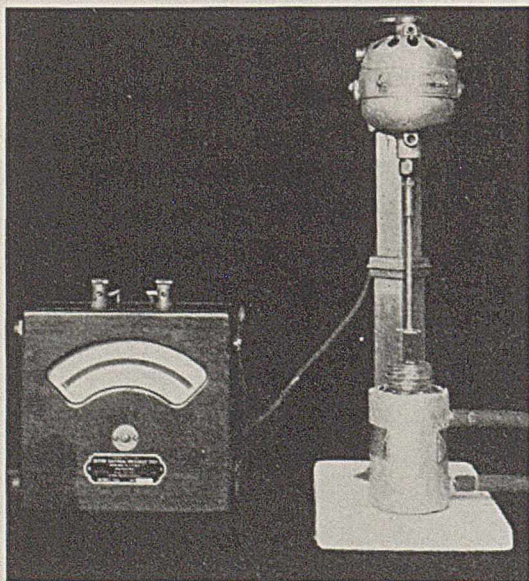


FIGURE 8. APPARATUS FOR MECHANICAL STABILITY TEST

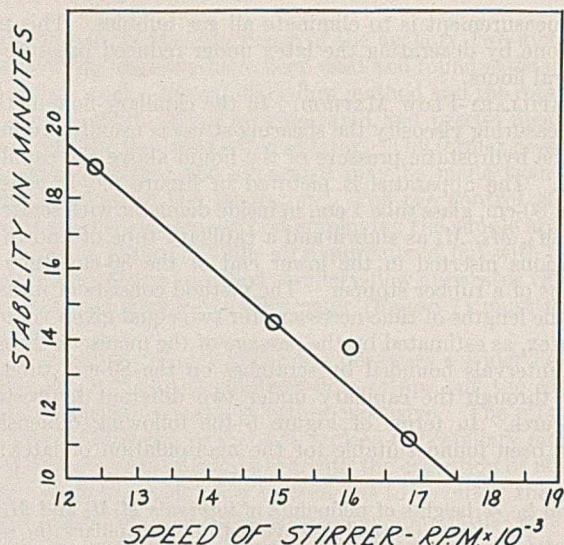


FIGURE 9. RELATION OF MECHANICAL STABILITY TO SPEED OF STIRRER

except in the case of latices of very high total solids content or those highly thickened with soaps, gums, etc.

Temperature, ° C.	At Total Solids:			
	44%	46%	48%	50%
25.0	8.50	10.0	11.4	14.2
30.6	7.78	9.62	10.4	12.3
36.1	6.24	7.91	9.24	10.0

RELATION BETWEEN η AND η' . As a matter of interest the following relation between the true and limiting coefficients of viscosity is listed:

$$\eta = \eta' \frac{F}{F - F_0} \quad (9)$$

where F is the absolute shearing stress

Mechanical Stability

In the course of handling and processing, latex is often subjected to violent shearing stresses produced by mechanical treatments such as pumping and stirring, which tend to destabilize it. When it is considered that such situations as these are rather frequently encountered, it is unfortunate that there is no adequate means of evaluating the ability of all types of latex to withstand the effects of mechanical agitation. A major hindrance to the setting up of a general mechanical stability test lies in the lack of any precise concept of stability. The notion is a rather vague one at best and varies considerably in different connections.

In the experience of the authors, the high-speed stirring test is the only one which gives results even approximately in accord with the practical stability behavior of latex. The test, apparatus for which is shown in Figure 8, consists of stirring a sample of latex until it coagulates. The stirring is done by means of a small slotted propeller blade which is driven by a high-speed Hamilton Beach motor. It fails in two cases: (1) in very thick compounds, (2) in compounds containing foaming agents. In the first case, the propeller blade tends to beat out a cavity in the latex so that actual stirring ceases after a short time. In the second case, the entire sample may be whipped to a very stable foam which will not coagulate. In uncompounded normal, creamed, and centrifuged latex and in many latex compounds, however, the high-speed stirring test for mechanical stability possesses the most practical advantages of any test known to the authors at present.

The customary procedure for measuring mechanical

stability has been modified in two important details. These are (1) the application of a correction for the speed of the motor, and (2) the method of selecting the end point. Another item of importance is temperature control.

The speed at which the latex is stirred has been found to produce an inverse linear variation of the time required for coagulation. The data to support this conclusion, presented here, were obtained on one normal latex at 26.4 per cent total solids at various motor speeds.

Speed of Motor R. p. m.	Stability Min.
12,400	18.9
14,900	14.3
16,000	13.8
16,840	11.2

From the data a table of correction factors to 15,000 r. p. m., the arbitrarily chosen standard speed, can be constructed (Table III).

TABLE III. CORRECTION FACTORS

Speed of Motor R. p. m.	Correction Factor
12,000	0.74
12,500	0.77
13,000	0.80
13,500	0.85
14,000	0.90
14,500	0.94
15,000	1.00
15,500	1.07
16,000	1.14
16,500	1.22
17,000	1.32

When a mechanical stability value is obtained at a motor speed different from 15,000 r. p. m., multiplication of the observed value by the appropriate correction factor from Table III will give the value which would have been obtained at 15,000 r. p. m. For example, if a stability of 10 minutes were obtained at a motor speed of 13,500 r. p. m., then the corrected stability would be given by $10 \times 0.85 = 8.5$ minutes. The motor speed should be measured with a tachometer

at a standard time, say 30 seconds, after the beginning of a determination.

In the case of the end-point selection in this determination, personal errors have been eliminated by the following means:

A milliammeter is connected in series with the motor, and current consumption is plotted against time from the beginning of the determination. When coagulation sets in, the general tendency of the current consumption will be to increase as the load on the motor is increased by adherence of coagulum to the propeller blade. During the first stages of coagulation, there are frequent large jumps in the current consumption, occasioned by pieces of coagulum which adhere to the blade and are then thrown off, thus causing short periods of alternate labor and racing on the part of the motor. Readings should be continued until there is a steady and rapid rise in current consumption with time, an occurrence caused by complete coagulation of the sample. The time at which this rise starts is taken as the end point.

For purposes of temperature control of the sample under test, the base of the stand on which the motor is mounted should be provided with a water jacket through which water at a standard temperature, say 25° C., can be circulated. This control is of considerable importance, since a difference of 10° in temperature may make a large difference in the stability value obtained.

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Laboratory Distillation and Vacuum Flash Unit

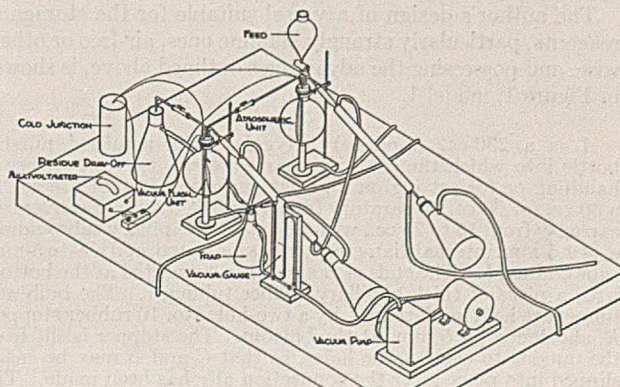
C. E. WINTERS AND J. E. HEDRICK, Kansas State College, Manhattan, Kans.

APPARATUS for the distillation of petroleum, whether used for the evaluation of crudes and distillates or for the preparation of samples for research and development, must be capable of giving sharp fractions in sufficient quantity for refining and analyses. The methods described by Scheumann and Stewart (2) and the elaborate unit developed by Podbielniak (1) are notable examples of what has been done. However, in smaller laboratories, or where crude and distillate fractions are needed only at infrequent intervals, such equipment cannot be used. The need is for a simple, inexpensive unit which can be quickly assembled and dismantled when not in use, yet is capable of giving the desired separations.

A simple and inexpensive combination atmospheric distillation and vacuum flash unit is here described for distilling crudes and for solvent recovery. The apparatus, shown in the diagram, is made from standard laboratory equipment, has a capacity of about 4 liters (1 gallon) per hour, gives sharp cuts, and can be run continuously.

This particular unit was built for running crude oil to lubricating distillate semicontinuously. It consists of two distillation outfits, each using 5-liter flasks for distilling, connected by a

single piece of 0.4-cm. (0.1875-inch) copper tubing. One flask operates at atmospheric pressure at temperatures of 176.67° to 315.56° C. (350° to 600° F.); the other, at 8-mm. vacuum or less and 148.89° to 287.78° C. (300° to 550° F.). Thermocouples, placed in the liquid in each still, were found much more satis-



factory than thermometers, particularly at low distillation rates. Asbestos insulation of both stills was necessary.

The crude oil is fed to the atmospheric still, which serves to preheat the oils for vacuum flashing and removes the gasoline and water. When operation is started, about 1 liter (1 quart) of crude is charged to this still and gradually heated to 232.22° C. (450° F.). Crude is then added continuously, but slowly, through a separatory funnel to the hot charge. With this arrangement, no bumping or foaming occurs, and it is possible to maintain a higher rate of distillation.

The hot bottoms from the topping still are drawn into the vacuum still, being sprayed into it at a high velocity. When operated strictly as a flash unit, there is no difficulty with foaming and entrainment as in ordinary vacuum distillation. If flashing does not remove enough material, a small amount of heat can be applied, making the one flask serve as both a flash chamber and a distillation unit.

Although no attempt was made to obtain sharp cuts of the lighter materials, these could be secured by including fractionating columns in the setup. No difficulty has been experienced in running different crudes. The results were equally satisfactory upon East Texas, Smackover, Mid-continent, Pennsylvania, and California oils. By careful control, fractions of any gravity desired may be obtained. Table I shows the results of rerunning a Texas gas oil fraction to obtain experimental cracking stock, and the separation of a Texas lubricating distillate from heavy residuum.

TABLE I. RERUN OF FRACTIONS TO DESIRED GRAVITY

Charge	Texas Gas Oil Fraction			Texas Residue Fraction		
	°A. P. I.	Temp. °F.	Absolute Pressure Mm.	°A. P. I.	Temp. °F.	Absolute Pressure Mm.
Atmospheric unit	32.2	23.0
distillate	35.0	505	754	..	580	752
Vacuum unit distillate	31.1	310	7	25.2	485	6
Vacuum unit residue	28.8	20.0

The apparatus has been found useful for the vacuum distillation of lubricating distillate to lubricating oils, using the atmospheric still as a preheater for the flashing chamber, and in solvent-extraction work for removing and recovering solvents from the raffinate and extract. Here the first still was used to recover most of the solvent and the oil was then flashed into the second still to remove the last traces.

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RECEIVED January 22, 1937. Contribution 226, Department of Chemistry, Kansas State College.

Vessels for the Storage of Gases and Liquids

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THE vessels described have been satisfactorily used for some time in this laboratory to serve several purposes in the gas analysis of gases and liquids. Requiring no expert glass blowing, they are easily constructed from readily available, inexpensive materials. These advantages, coupled with their sturdiness, flexibility, and convenience in manipulation, constitute an improvement over the accessories hitherto employed for the same purposes.

Storage of Air-Free Reagents over Mercury

It has been found that the reagents or solutions used for manometric analyses (5, 7) can best be kept air-free over mercury. For such storage a modified Hempel pipet (6) and similar vessels have been used. Of late, there have been designed in other laboratories several different one-piece types of vessels, necessitating more or less expert glass blowing in their construction, which have had as their purpose avoidance of the ruinous contact of alkali or other reagents with the glass control stopcock. Such models have been described by Guest and Holmes (2) and by Holmes (3).

The author's design of a vessel suitable for the storage of reagents, particularly strongly alkaline ones, air-free or otherwise, and possessing the advantages outlined above, is shown in Figure 1, model 1.

A is a 236-cc. (8-ounce) "Hygeia" wide-mouthed nursing bottle into which the container parts are set, for convenience in handling or for setting on any flat surface. Into A are set B, a 30-cc. (or 60-cc.) separatory funnel, and C, a bulb of convenient capacity from 15 to 75 cc., with an external capillary tube ending, *a*, of 1.5-mm. internal diameter, bent as indicated, and a 4- to 5-mm. tube ending, *b*. The ends of B and C are connected at the bottom with a piece of thick capillary rubber tubing, *r*. The bulb and funnel are held in place in A by a two-hole No. 10 rubber stopper, R, shortened by 5 mm. at the bottom. The stopper is slit from the outside to each of the holes, so that C and B may be easily slipped into place after the connection at *r* has been made. The

usual rubber adapter tip, *E*, is put on the end of the capillary, *a*. If necessary for greater stability, the bottom of this and the other models may be weighted with either mercury or lead shot, *W*.

The reagent is made air-free by extraction in the manometric apparatus, and is transferred to the storage vessel under pressure, as described by Peters and Van Slyke (4, p. 235). If, for convenience, B is of only 30-cc. capacity, and more than this volume of reagent is to be stored in C, the mercury overflow from B may be caught by the insertion of the stopper and tube, X, into the neck of B. The rubber tube, T, may lead to a beaker or other container. By means of wiring around the indented rim of the bottle, A, this and the other models may be temporarily suspended at a convenient height, so that in any transfer of reagent or gas the operator need only use one hand to hold the capillary, *a*, firmly in the cup of the Van Slyke apparatus. At all times, when not actually delivering reagent, the vessel should stand with tip *E* immersed in a small beaker of mercury. This and models 2 and 3 are more easily taken apart, for cleaning or change of reagent, if the vessel is first emptied of most of the mercury it may contain.

These vessels may be used for any reagent not affected by mercury, and contact between reagent and control stopcock is avoided. Air-free N sodium hydroxide, observed in such a vessel over a period of 18 days, showed an increase in air content of only 4.1 mm. measured in the Van Slyke apparatus at the 0.5-cc. volume, for a 5-cc. sample of solution.

Storage of Blood Samples and Other Gas-Containing Solutions

Model 2, Figure 1, is the same as model 1, with a change in the form of the external capillary ending, *a*, to permit withdrawal of portions of solutions into a pipet, through the rubber connection, *o*. Tube *a*₁ (the ending of which is like that of *a*, model 1) in this model is removable, and is used only to transfer liquid to the vessel. This model may be used in place of the more cumbersome type of apparatus (1, Figure 3, p. 129) for the storage of gas-containing liquids, particularly blood as drawn. It is also useful for the storage of air-free reagents which must be delivered quantitatively, as in method C of Van Slyke and Sendroy (8, pp. 521, 525) for the determination of small amounts of nitrogen in oxygen or carbon dioxide.

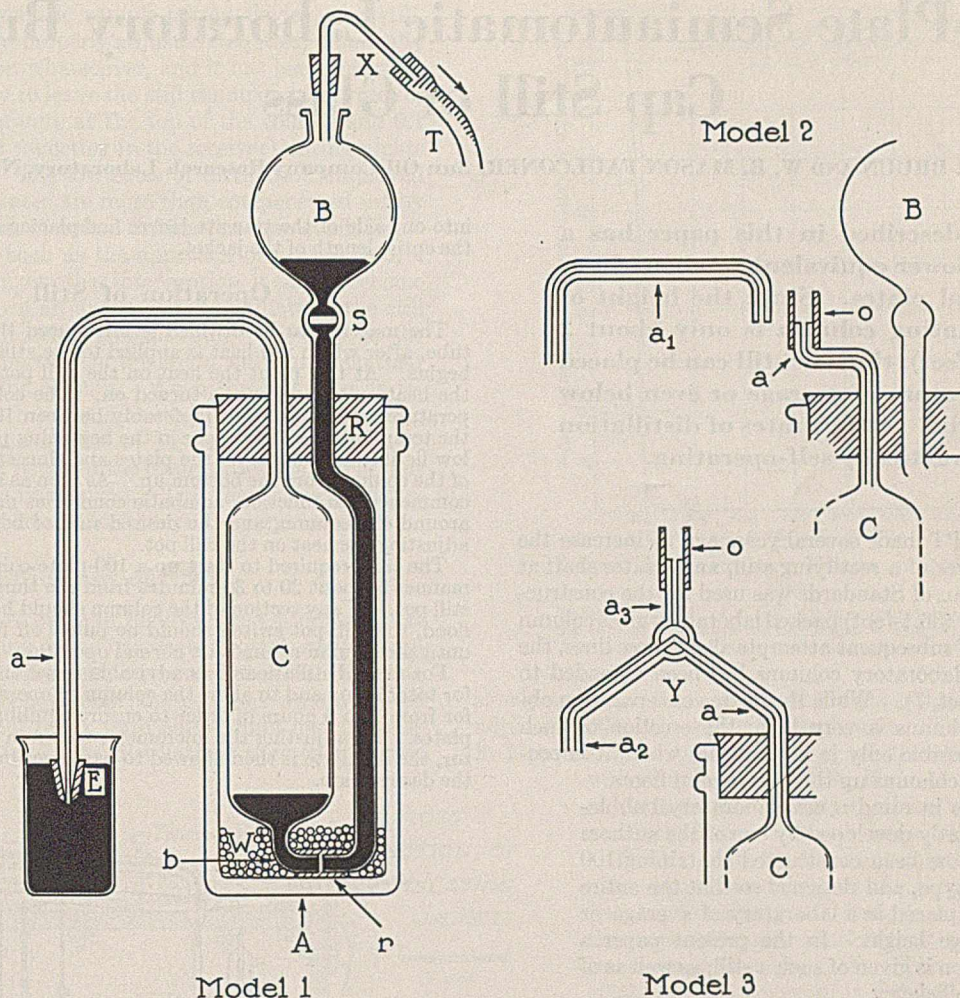


FIGURE 1. STORAGE VESSELS

Model 1, for storage of air-free reagents
 Model 2, for storage of blood samples and other gas-containing solutions
 Model 3, for storage of either gases or liquids

In this, and in the other models of this series, it may more often be necessary to transfer a solution into the vessel under negative pressure, as in the separation of serum from cells, a procedure effected in other systems by the lowering of a free leveling bulb corresponding to *B*. The same result may be attained by the use of the stopper and bent tube, *X*, inserted into the neck of *B*. With the thick-walled capillary rubber tubing, *T*, a connection is made to a 250-cc. suction flask to which suction may be applied. In case neither house nor water pump vacuum is available when the sample is transferred to *C*, as at the bedside, a small Becton and Dickinson "Potain" aspirating syringe, connected to the suction flask, has been found most satisfactory. A few strokes of the plunger are made, the syringe is laid down, and the operator is then free for the manipulations involved in the transfer of material to the container. Depending on the length of glass tubing, *X*, in the rubber stopper in the neck of *B*, the mercury in *B* may be kept at any convenient level, with overflow running into the suction flask, while the sample is taken into *C*. Later, when mercury is needed for displacement, it may be added to *B* through a small funnel. If *B* is large enough, there need be no tube *X* and vacuum may be applied to *B* directly.

Storage of Either Gases or Liquids

By another change in the external ending of bulb *C*, model 3 serves as a very convenient container to take the place of the usual types of gas-sampling tubes (4, Chapter III). The three-way, 120°, Y-form capillary stopcock, *Y*, provides for washing gas through from *a*₂ (the ending of which is like that of *a*₁, model 1) to *a*₃ or vice versa, and then storage of the sample in *C*, through limb *a*. (The 120° stopcock is not an item usually carried in stock by supply houses, but can readily be obtained on order. The usual three-way, 90°, T-form capillary stopcock will do as well, and has been satisfactorily used by the author.

However, one must be very careful in its manipulation, so as to avoid the dangers of simultaneous double connections. When used for gas analysis only, any capillary three-way stopcock may be used in place of *X*.) Gas samples may be taken into the Haldane gas-analysis apparatus by a glass connection from limb *a*₃, or into the manometric apparatus by direct insertion of limb *a*₂ into the cup of the chamber. Obviously, this vessel may also be used as is model 2, for the storage of blood or other gas-containing liquids. If a dry anticoagulant be placed in *C*, blood may be drawn directly into this vessel by the attachment of a needle to a short length of rubber tubing connected to limb *a*₁. The initial flow is wasted through *a*₂, and then the sample is drawn in through *a*, under slight negative pressure.

Model 3 may also be used for the storage of nonalkaline, air-free reagents. For alkaline reagents, however, model 1 is much to be preferred.

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A 100-Plate Semiautomatic Laboratory Bubble-Cap Still of Glass

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The still described in this paper has a separating power equivalent to about 70 to 72 theoretical plates. Since the height of the fractionating column is only about 2 meters (6.5 feet), the new still can be placed in any laboratory of average or even below average height. At low rates of distillation the still is practically self-operating.

IN AN ATTEMPT made several years ago to increase the separating power of a rectifying still, an elevator shaft at the National Bureau of Standards was used for the construction of a 11.0-meter (36.1-foot) packed laboratory glass column (5). As a result of subsequent attempts along these lines, the over-all height of laboratory columns has been extended to 15.85 meters (52 feet, 7). While the degree of separation obtained in these columns is very high, the erection of such columns will be possible only in laboratories where it is possible to extend the columns up through several floors.

With these facts in mind a new laboratory bubble-cap plate was recently developed by one of the authors (4). A still has now been constructed containing 100 plates of the new type, and designed so that the entire still may easily be placed in a laboratory of average or even below average height. In the present paper a complete description is given of such a still, as well as of its operation and efficiency.

Description of Still

An assembly drawing of the 100-plate bubble-cap still is given in Figure 1.

The column, which is made in 20-mm. sections, has a total holdup of about 70 ml. when it is in normal operation. The 100-plate column described in this paper was made by the Otto R. Greiner Company, 55 Plane St., Newark, N. J. The turntable and electric timer were made by the Automatic Temperature Control Company, Inc., 34 East Logan St., Philadelphia, Pa.

The automatic sample-taking device consists of a circular turntable with twelve holes for sample bottles and an electric timer, by means of which cuts can be made at any desired time interval from 10 seconds to 2 hours. The receiver is water-cooled and provided with an intermittent siphon, such as that of a Soxhlet apparatus. The reflux regulator is identical to that reported in an earlier paper (3).

The heating jacket, which is of a greatly improved design, is made of sheet transite with a glass front, so as to provide complete visibility of the column and of the four thermometers which are fastened to the column. The entire jacket is made in a single piece, with a cross section as shown in Figure 2. The heating coils are placed inside the jacket in order to provide immediate response to temperature adjustments of the column. In order to eliminate any effects of wind currents commonly encountered when windows or doors are opened in the laboratory, the transite jacket is insulated on three sides with asbestos paper and with felt pad.

A strong light placed outside the jacket near the top of the column will provide satisfactory illumination at night, although indirect lighting effects are to be preferred. This could be accomplished by building a recess

into one side of the transite jacket and placing a neon tube along the entire length of the jacket.

Operation of Still

The material to be distilled is introduced through the filling tube, after which full heat is applied to the still pot until boiling begins. At this point the heat on the still pot is decreased and the heat on the column is turned on. The column jacket temperatures are maintained preferably between 10° and 20° below the temperature of the vapor in the beginning period, so as to allow liquid to condense on the plates and thus start the operation of the column from the bottom up. As soon as all the plates have commenced to function, adiabatic conditions may be established around the column, and the desired rate of boiling obtained by adjusting the heat on the still pot.

The time required to start up a 100-plate column in the above manner is about 20 to 30 minutes from the time of boiling in the still pot. If any section of the column should have a tendency to flood, the still-pot switch should be pulled off for a few moments until the column resumes its normal operation.

For most distillations it is advisable to set the reflux regulator for total reflux and to allow the column to operate in this manner for from 2 to 6 hours in order to ensure equilibrium on all of the plates. By adjusting the micrometer screw on the reflux regulator, the distillate is then allowed to pass over into the receiver at the desired rate.

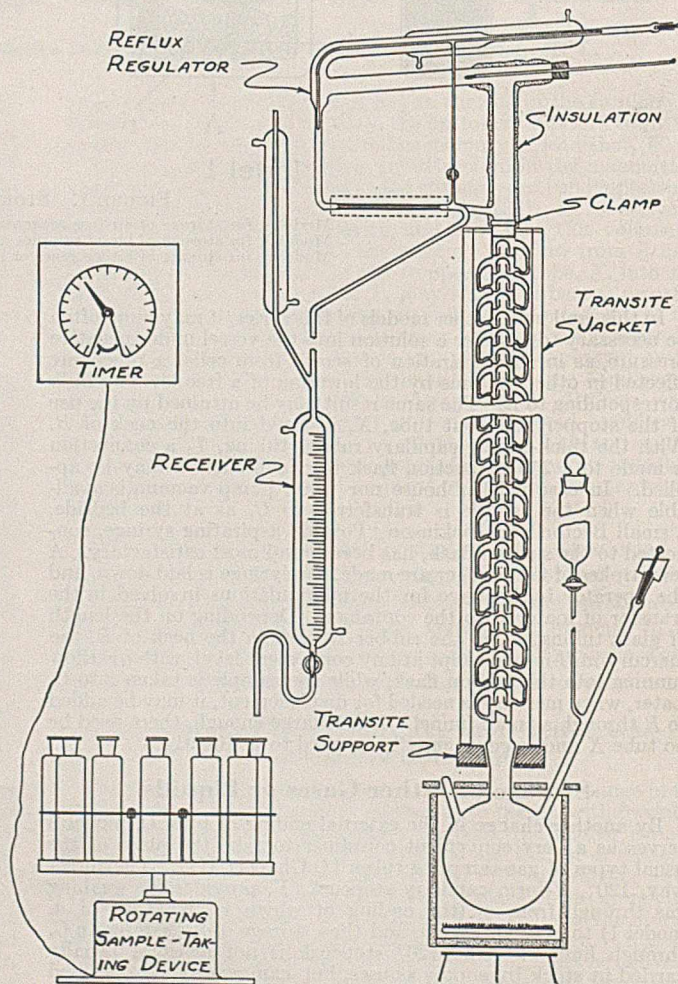


FIGURE 1. ASSEMBLY OF 100-PLATE STILL

By using the automatic sample-taking device, the still, when once started and properly adjusted, requires, practically speaking, no attention whatsoever, and it has been the practice at this laboratory to leave the still running at low rates of boiling (10 ml. per minute at the top of the column and 0.1 to 0.5 ml. per minute collecting in the receiver) during nights as well as Sundays. The low rates of distillation employed under such circumstances are more than compensated for by the 168 hours per week of actual distillation time available.

If for any reason, such as the approach of a week end, a flooding of the column, or other interruption, it should become necessary to shut down an uncompleted distillation, the still has the advantage of being nonsiphoning (2)—that is, the already fractionated portions of the liquid will remain on their respective plates in the column. When the still is to be restarted, the operator has the advantage not only of having liquid on every plate, but also of having the previously established equilibrium between the compositions of the liquids on the various plates unchanged. This feature alone represents a time saving of from 2 to 6 hours at every shutdown.

Efficiency of Still

The efficiency curves given in Figures 3 and 4 indicate that even compounds boiling only a few degrees apart, such as benzene and ethylene chloride, can be separated in the 100-plate still. In these "efficiency runs" the columns were operated under practically total reflux until equilibrium had been established on the plates. The distillations were then started

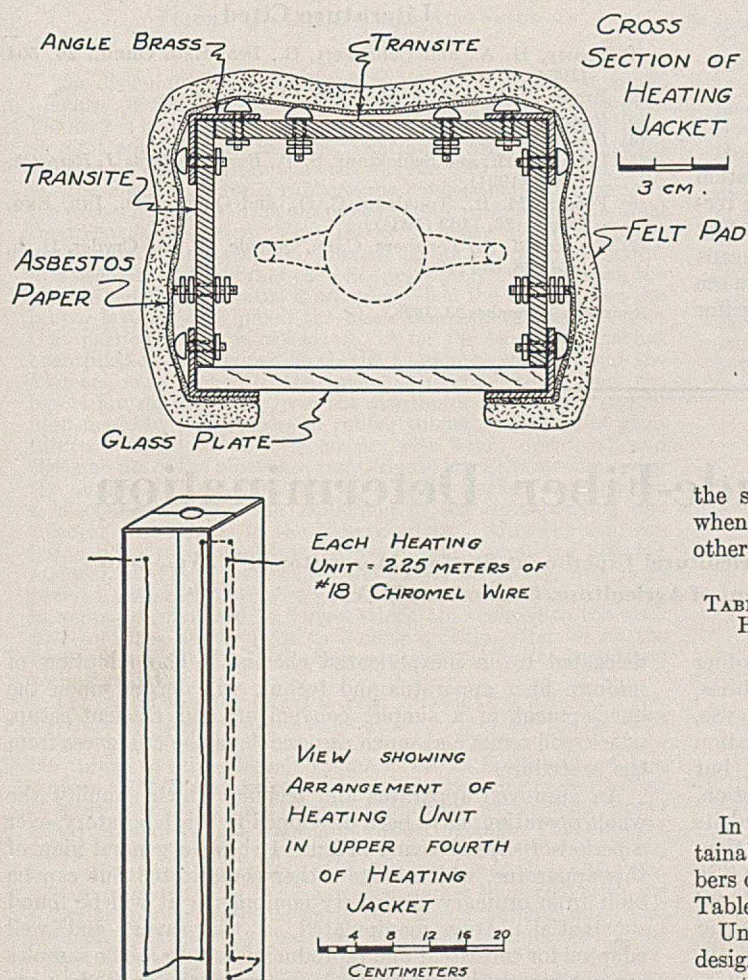


FIGURE 2. HEATING JACKET FOR COLUMN

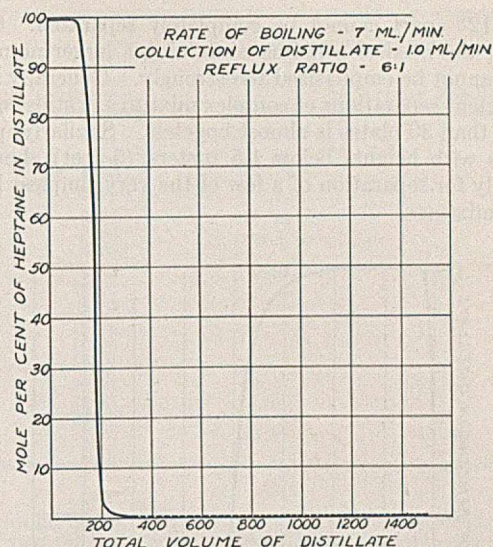


FIGURE 3. EFFICIENCY CURVE OF 100-PLATE STILL

Charge, 1500 ml. of a test mixture containing 10 mole per cent of *n*-heptane (boiling point = 98.4° C.) and 90 mole per cent of toluene (boiling point = 110° C.)

slowly and the rates as well as the reflux ratios were gradually adjusted to the values given in the figures. The results shown in Figure 3 were obtained by manual operation of the still, while the curve shown in Figure 4 is a result of a semiautomatic distillation where manual control was limited to an inspection every 4 to 8 hours.

The 100-plate fractionating column was furthermore tested according to the procedure used by Fenske, Tongberg, and Quiggle (6) and by using the vapor-pressure relationships published by Beatty and Calingaert (1). The results of these efficiency runs are given in Table I.

While the results indicate that the number of theoretical plates in the new column is between 70.6 and 84.2, the experimental errors tend to increase whenever the concentration of *n*-heptane in the still pot becomes small (0.5 mole per cent). For this reason it is believed that 70 to 72 theoretical plates would be a more conservative value for the separating power of the column. This corresponds to a height of the equivalent theoretical plate of about 2.8 cm., as compared with the somewhat lower value of 2.0 cm. which was obtained when a 5-plate column of identical design was tested with other mixtures (4).

TABLE I. EFFICIENCY TEST RUNS USING MIXTURES OF *n*-HEPTANE AND METHYLCYCLOHEXANE (TOTAL REFLUX)

Rate of Boiling at Top of Column ML./min.	Mole Per Cent of <i>n</i> -Heptane Still pot	Mole Per Cent of <i>n</i> -Heptane Top of column	Number of Theoretical Plates
8	0.5	54.1	84.2
10	2.5	76.7	72.6
5	5.8	87.2	70.6

In order to give a more definite idea of the separation obtainable with laboratory columns containing different numbers of plates, a few experimental distillations are included in Table II. |

Unfortunately, the three columns used were not of identical design, but at the rates employed they had been found to have practically the same plate efficiencies (4). It should be particularly noted that with a column containing only 26 plates, the separations to be expected are such that even compounds

boiling 12° apart cannot be completely separated. Consequently, the need of columns containing a larger number of plates cannot be emphasized too strongly. Generally speaking, efficient separations of complex mixtures in stills containing less than 30 plates is almost hopeless. Similarly, packed columns with heights below 1.5 meters (5 feet) should be used only for separation of a few of the very simplest known binary mixtures.

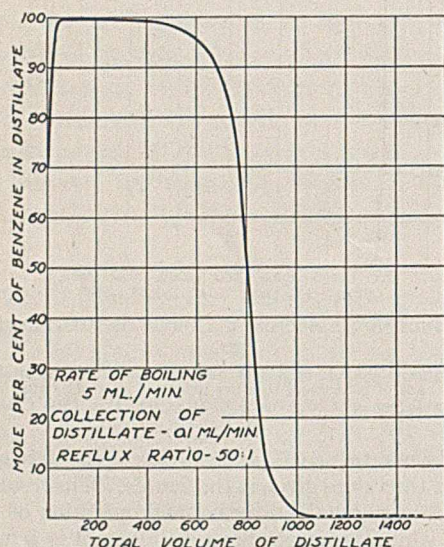


FIGURE 4. EFFICIENCY CURVE OF 100-PLATE STILL

Charge, 1500 ml. of a test mixture containing 50 mole per cent of benzene (boiling point = 80.2° C.) and 50 mole per cent of ethylene chloride (boiling point = 83.7° C.)

For laboratories dealing with more extensive distillation problems, an installation consisting of two stills is to be recommended. The material to be fractionated could then first be subjected to a fast distillation into narrow cuts by means of a 50- to 60-plate column in 40-mm. sections (for design see Figure 2, 4). This column is designed for very much greater

TABLE II. DISTILLATION OF BINARY MIXTURES IN COLUMNS CONTAINING 100, 52, AND 26 PLATES

Test mixture	Conditions of Distillation			Mole Per Cent of Lower-Boiling Constituent in Distillate		
	Rate of boiling ML./min.	Rate of collection distillate ML./min.	Reflux ratio	100-plate column ^a	52-plate column ^b	26-plate column ^c
50:50 mole per cent, benzene-ethylene chloride (difference in boiling points = 3.5° C.)	2	0.1	20:1	99.9	93	80
10:90 mole per cent, <i>n</i> -heptane-toluene (difference in boiling points = 12° C.)	7	0.1	7:1 to 10:1	99.9	99	93

^a Figure 1, 4. ^b Figure 2, 4. ^c Figure 5, 5.

rates of distillation and is even easier to operate than the one used in the present paper. The subsequent redistillation of the cuts thus obtained could be done at a lower rate of distillation in a 100- to 130-plate column consisting of 20-mm. sections, such as those used in the column described in the present paper (for design of the 20-mm. plate sections, see Figure 1, 4).

The maximum permissible vapor velocity for the 100-plate column described in this paper is 31.3 cm. per second (1 foot per second), which corresponds to a rate of boiling of about 30 ml. of benzene per minute.

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RECEIVED November 23, 1936.

Apparatus for Crude-Fiber Determination

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T. B. LEITH, Department of Agriculture, Charleston, W. Va.

IN THE determination of crude fiber in feeds and other plant materials, as carried out in different laboratories, a variety of manipulations and apparatus assemblies is in use, designed to conform with the official method of the Association of Official Agricultural Chemists in general principle, but differing widely in ease of manipulation, time-consumption, and uniformity of the results obtained. It has justified its name through the years by remaining a crude determination, with little concerted attempt to improve and standardize it in spite of its importance in many fields of experimental and regulatory work. The considerable variety in the character of materials to which this apparatus in question must be applied renders the time and accuracy of the difficult filtrations and transfers involved peculiarly subject to the variations of individual technic, in a determination frequently

delegated to an inexperienced chemist. The adoption of uniform fiber apparatus and technic will depend upon the development of a simple, convenient, and efficient setup, which will remove as much as possible of the crudeness from the procedure.

An improved apparatus and technic, which simplify the whole operation, have been developed in this laboratory over a period of several years. Figure 1 shows a general view of this apparatus, which looks rather complicated but can be built from ordinary laboratory equipment; it will be found substantial, easily manipulated, a time-saver, and well adapted for consistent and reproducible results. The samples are not removed from the Erlenmeyer flasks until they are filtered off into the Gooch crucibles. All digestions and washings are completed without previous transfer.

Procedure

The fat-extracted samples are transferred to 1-liter Pyrex Erlenmeyer flasks, which are placed in a row on the table in front of the apparatus. A small amount of fine ignited asbestos is added as an aid to filtration. The 1.25 per cent sulfuric acid, which has been heated to boiling in a 3-liter Pyrex Florence flask, is drawn into the measuring pipets through the distributor by gravity (the Florence flask being placed on the shelf above the pipets), hastened by applying suction to the series of T-tubes connecting the upper ends of the pipets.

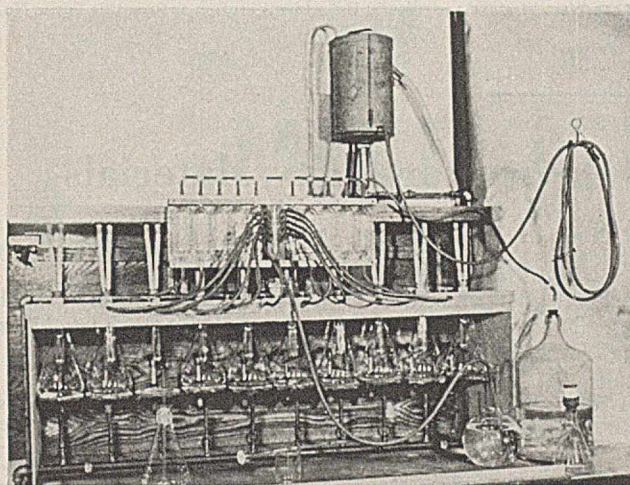


FIGURE 1. CRUDE-FIBER APPARATUS

The distributor (made of Pyrex glass, at moderate cost, by E. Machlett & Son, New York, N. Y.) which is shown in detail in Figure 2 is made with the side arms in two rows, the rows being at right angles to one another. Each side arm has an upward slant of 45 degrees from the central tube which is bent forward (at the lower end) for a rubber-tube connection. This permits the excess liquids to drain out of the system after each individual treatment is completed. Since different lengths of rubber tubing are required to connect the different pipets with the distributor, it is necessary to calibrate each line separately by a mark on the pipet when the apparatus is set up. When the acid reaches the proper level in each pipet, the glass stopcock (3-mm. bore) in that particular line is closed off. After the whole system has been filled to the proper level, the suction is shut off and the Florence flask moved to the table. All rubber tubes from the pipets are disconnected from the distributor (connection having been made by short pieces of rubber tubing and pieces of glass tubing drawn down to form nozzles with 3-mm. openings), and the contents of the pipets are emptied into the Erlenmeyers, using the nozzles to wash down the sides of the flasks. As each line is disconnected, the acid remaining in the corresponding distributor arm returns to the Florence flask. After the acid has been added to all the flasks (the procedure requiring about 1 minute), they are placed over the flames on 13-cm. iron rings covered with nichrome wire gauze, the iron rings being attached to supports connected to flanges which are screwed to the wall. The solutions are brought to boiling quickly, after which the flames are adjusted with the valve in the main line to keep them boiling gently.

The volume of the liquid is kept constant by 2.5×20 cm. test-tube condensers which extend 15 cm. into the flasks. The upper 7 cm. of the test tubes are covered with heavy-walled rubber tubing to fill up loosely the necks of the flasks and act as a cushion when the flasks are shaken. The glass inlets and outlets of these condensers have flexible connection with 6-mm. copper tubes through 20-cm. lengths of rubber tubing. These copper tubes are held rigidly in place by a grooved strip, 5 cm. wide, screwed to the bottom side of the front edge of the shelf. One stream of water cools five condensers and is connected with the water supply by a needle valve for ease of adjustment. This adjustment is made by observing the discharge at the end of the copper overflow pipe.

After boiling gently for 30 minutes, the flasks are removed from the flames and placed on the table in a position slightly tilted by means of a beveled wooden strip in front of the apparatus. Inverted filter tubes (made from straight thistle tubes selected to

TABLE I. COLLABORATIVE RESULTS

West Virginia Results		Average Results of 53 Laboratories
Triplicate determinations	Average	
%	%	%
5.76	5.78	5.84
5.80		
5.79		
6.96	6.99	7.11
7.04		
6.96		
9.82	9.91	9.61
10.01		
9.91		
17.34	17.27	17.02
17.24		
17.24		
29.44	29.57	29.57
29.61		
29.65		
Av. 13.91		13.83

go through the necks of the Erlenmeyers and covered with linen cloth tied on with thread, turned back, and retied with copper wire) are then placed in the Erlenmeyer flasks, the filter tubes having been connected previously to the system through the nozzles described above. Suction is applied, and the filtrate is drawn off quickly and completely. The acid-extracted residue remaining in the flask is washed free from acid with boiling water, each portion being removed to relative dryness by suction through the inverted filter tube. As soon as the last wash water is removed from each flask, the Erlenmeyer and inverted filter are held in a horizontal position above the level of the stopcock, so that the liquid in the inverted filter and rubber tubing will be drawn past the stopcock, which is then closed.

As the filtrations are finished, the nozzles are disconnected from the inverted filters and again connected to the distributor. The suction is then disconnected from the line to the T-tubes above the pipets and connected to the line leading to the bottom of the distributor which formerly was immersed in the acid. The glass stopcocks are opened, air enters the T-tubes, and the system is emptied of the acid wash water. If the washing operation is thorough, no additional rinsing of the system is necessary. The suction is now disconnected from the tube to the bottom of the distributor and connected to the T-tube line, and up to the point of filtration the same procedure is followed for the 1.25 per cent sodium hydroxide solution as for the acid solution, washing the residue from the inverted filters by use of the nozzles as the alkali is delivered from the pipets. After boiling gently for 30 minutes in the alkali solution, the flasks are removed from the flames, the contents are filtered through Gooch crucibles with asbestos pads, and the residues are washed with boiling water until free from alkali. The crucibles are now ready for drying and the determination of loss on ignition.

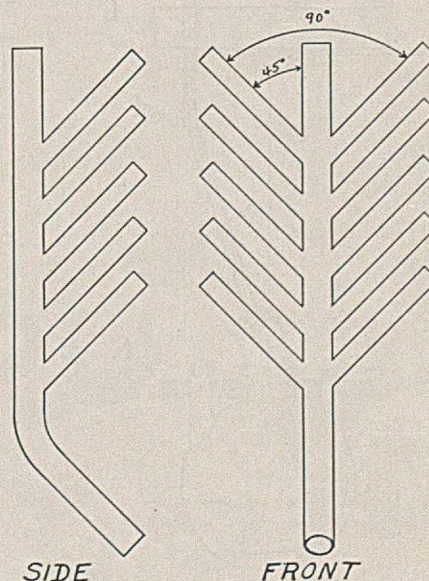


FIGURE 2. DISTRIBUTOR

As soon as the sodium hydroxide digestion is started, a 2-liter vessel of distilled water is connected to the line from the bottom of the distributor, suction is applied to the T-tube line, and the whole distributing system is rinsed and drained by suction from below. This removes the caustic soda and prevents freezing of the glass stopcocks. The inverted filters are also washed thoroughly and soaked in several changes of water. A 12-liter bottle two-fifths full of water is placed in the line to the suction pump to receive the hot acid filtrate and washings, and suction is applied through this reservoir at all times.

An 8-liter tinned copper tank placed over a flame on the shelf above the apparatus supplies hot distilled water by gravity for all washing purposes. This vessel is filled from the storage tank through a block-tin pipe, by either gravity or pressure.

Ordinary 9-mm. glass funnels with cut-off stems are fitted to

the 25-cc. Gooch crucibles by means of No. 7 rubber stoppers to aid in the transfer of material from the Erlenmeyer flasks. By this means the hot extract is removed immediately with two quick pourings.

Table I shows a comparison of the results obtained with this apparatus and the average of the results from 53 feed laboratories throughout the country on check samples sent out by the Association of Feed Control Officials. These samples show a wide variation in fiber content.

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Gas-Tight Laboratory Stirring Device for Pasty Materials

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THE apparatus described below was developed for the purpose of reacting and distilling pasty materials under vacuum. Where materials are of such consistency that ordinary stirring devices fail to give effective mixing, the only alternative types of apparatus known to the author are the kneading machine and the ball mill. These are not available for small charges, of the order of 100 grams, and they have other disadvantages, such as the difficulty of determining changes in weight and of maintaining perfectly vacuum-tight glands, time consumed in opening and closing for charging or discharging, and relatively high cost.

A method of mixing thick masses by affixing wire loops to a stirring rod was described by Hershberg (1), and a method of

making a glandless stirrer for a flask was described by Powell (2). The apparatus now described combines these two ideas and develops them into a form of wide utility.

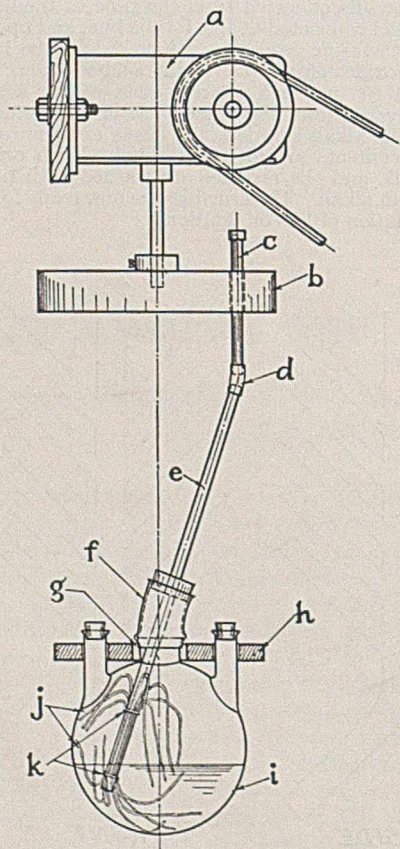


FIGURE 1. APPARATUS

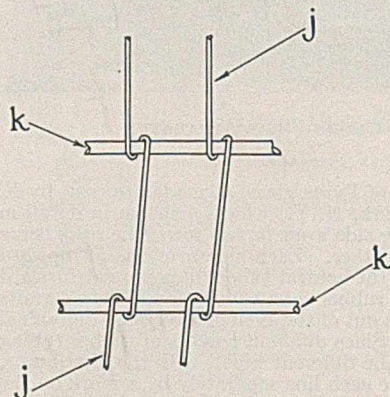


FIGURE 2

rod was 0.9 cm. (0.375 inch) in diameter, very slightly drawn out at the two points where the wires were bound on. After several trials it was found that steel music wire 0.6 mm. (0.024 inch) in diameter (music wire, gage 10) or phosphor bronze wire of about double this thickness was of a suitable springiness and stiffness to stir any paste encountered, yet not to endanger the glass flask. Twenty of these wires, *j*, were attached by twisting them around soft iron wires, *k*, as shown in Figure 2. The iron wires were then twisted around the constricted portions of the glass stirring rod. The steel wires were spread out and cut off to suitable lengths to scrape against the walls of the flask.

The stirrer was driven at 30 revolutions per minute, by a speed-reducing gear, *a*, which was furnished with a disk wheel, *b*, drilled for the floating pin, *c*. Several drill holes were provided to permit adjustment of the width of sweep of the stirrer. As it is necessary to mount the flask very firmly, it was clamped by suitably shaped wooden pieces, *h*, across its three necks. The stirring rod was attached to a heavy rubber tube, *d*, wired in place. All connections to the flask may be cemented with shellac or collodion.

Use of this device reduces to a fine powder a paste which would become a solid hard lump if distilled without stirring.

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RECEIVED January 13, 1937.

A black and white micrograph showing numerous small, angular, and somewhat rounded crystals of Bismuth Cobalticyanide. The crystals are scattered across the field of view, with some appearing in small clusters and others as individual particles. The lighting creates shadows that emphasize their three-dimensional, faceted nature. A white rectangular box is superimposed over the center of the image, containing the title text.

MICROCHEMISTRY

Courtesy, A. A. Benedetti-Pichler

Bismuth Cobalticyanide

Microanalysis of Nitrogen in Certain Pyrimidines by the Dumas Method

DOUGLASS F. HAYMAN AND SOL ADLER, Merck & Co., Inc., Rahway, N. J.

THE micro-Dumas method of Pregl (3) has an enviable reputation for producing accurate results on a variety of substances. Properly handled, it was considered an accurate method for any organic nitrogen-containing compound.

This method was used in this laboratory on a wide range of compounds without any known discrepancy until a certain series of pyrimidines of known purity failed to give the required amount of nitrogen. The nitrogen values obtained were from 0.4 to 2.0 per cent below theory and were reproducible under uniform treatment of the sample. The carbon and hydrogen values for these compounds agreed with the theoretical values within the limits of experimental error.

Several papers have appeared recently in the literature in which references were made to the fact that there were certain types of compounds which could not be analyzed properly by the Dumas method. The nitrogen values obtained were low (1, 2, 4, 5).

The first step in studying this problem was to make the combustions in a quartz tube, employing the hottest flame obtainable from a Tirrill burner. Utilizing this high temperature, the results obtained for nitrogen present were higher but still were below theory. The addition of potassium chlorate to the samples, as advocated by Pregl, together with high heat showed no improvement over the method of burning at a high temperature. Potassium dichromate was tried but with no better results. It was thought that the combustion of this particular type of compound must be abnormal or that the combustion was incomplete.

Mercuric acetate, a slow-burning compound with a high decomposition point, was mixed with the sample to furnish the normal decomposition products over a longer period of time. The results obtained with this compound were very satisfactory. There was an appreciable amount of metallic mercury produced. Because it appeared that the operator might be harmfully affected by the mercury vapor, especially when burning out the temporary filling between analyses, etc., a trial was made with copper acetate, which also gave excellent results. The metallic copper remaining from the combustion of the copper acetate could not be harmful either to the operator or to the analysis.

A finely powdered sample weighing 1.5 to 3.0 mg. was transferred from the weighing bottle to the mixing bottle, a test tube 10 × 75 mm. About five times as much copper acetate was added to the sample, and the whole was thoroughly mixed by rotating the tube. This mixture was then covered with finely powdered copper oxide to a height of 30 mm., and the mixing tube was closed with a tightly fitting cork. In mixing with the copper oxide, the tube was never shaken, but was rotated at an angle of 15° above the horizontal so that some copper oxide was introduced into the original mixture of unknown and copper acetate. This mixture was transferred to the combustion tube.

The first rinsing of the mixing bottle was made with about 6 mg. of copper acetate mixed with the usual amount of copper oxide powder. The second rinsing was made with copper oxide powder alone. The combustion was carried out by using a very hot movable flame, which was brought towards the sample very cautiously, as the large concentration of combustible material might result in too rapid combustion.

Typical analyses before and after using the special method are given in Table I.

Blank runs were made with the copper acetate, but only micro bubbles were produced. Compounds previously ana-

lyzed by the regular Pregl method gave identical results using the special method, showing that it was sound.

It has been found difficult to explain the cause of failure of the Dumas method on these pyrimidines. There was considerable evidence that some nitrogenous compound was left behind, a fact that pointed to incomplete combustion as the most likely source of error. It was a common experience for a very low result to be followed by a higher one, occasionally higher than the theoretical. As a rule, the results on known compounds have run high, following a number of failures with the difficult types. The tube as well as the temporary copper oxide filling required a vigorous and lengthy burning before accurate results on known compounds were again obtained.

TABLE I. TYPICAL ANALYSES

Compound	Regular Micro-Dumas, Quartz Tube and High Heat	Special Method	Theory
2-Thio-4-oxy-6-amino-pyrimidine	26.22	29.53	29.44
	28.28	29.59	
	27.61		
4-Ethoxymethyl-5-methyl-6-oxypyrimidine	16.04	16.86	16.65
	16.19	16.92	
	16.25	16.53	
Vitamin B ₁	16.12	16.69	16.62
	16.07 ^a		
	16.00 ^a		
2-4-Dimethoxy-5-bromo-pyrimidine ^b	15.83 ^a		12.79
	12.36	12.80	
	11.74	12.89	
Cytosine ^b	10.71 ^c		37.84
	11.33 ^c		
	36.57	37.70	
	32.13 ^c	37.74	
	35.05 ^c		

^a Results taken from a paper by Wintersteiner, Williams, and Ruehle (5).
^b Supplied through the courtesy of G. E. Hilbert, Bureau of Chemistry and Soils, U. S. Department of Agriculture.
^c Results taken from a paper by Milner and Sherman (2).

After the copper acetate had been used for some time the results were fairly reasonable if no more copper acetate was used, but the tendency still was for the results to be low so that it did not seem practical to dispense with the new method. Starting with a new combustion tube and an entirely new filling, results will always be low, as shown in the table.

It was also found that if the sample was weighed in a copper boat and burned in the combustion tube in contact with the metallic copper, the results would be higher than normal but erratic. This method was not practical for the analysis of such compounds. It would seem that the copper might have some catalytic property that aids the normal combustion.

It is difficult to make any generalizations as to what type of pyrimidine may give a low nitrogen by the regular Dumas method. Countless pyrimidines have been analyzed successfully, as a study of the literature will show. As more compounds are found which prove hard to analyze, some satisfactory correlation may be found.

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RECEIVED January 13, 1937.

The Determination of Sulfate Ion

The Microvolumetric Chromate Method

GEORGE G. MANOV AND PAUL L. KIRK, University of California Medical School, Berkeley, Calif.

The microvolumetric chromate method for sulfates has been investigated by a separate study of the effect of variables on each step of the procedure.

It has been found that the usual chromate methods contain several errors, notably the co-precipitation of chromate ion with barium sulfate, and the oxygen error in the iodometric determination of dichromate. Procedures have been developed to minimize these errors and to eliminate them completely in some cases.

MICROVOLUMETRIC methods for sulfate determination have been based on the titration with standard barium salts using rhodizonic acid (17) or tetrahydroxyquinone (15, 16) as indicator, and on the chromate method, the original form of which is due to Andrews (2).

Rhodizonic acid has been found by Schroeder (15) and others (3, 9, 14) to be undependable as an indicator, and tetrahydroxyquinone cannot be applied to solutions much below 0.1 *N*, as has been found in this laboratory (unpublished data) and elsewhere (1, 9).

The chromate method has been studied by Bruhns (5), Foster (7), Gibson and Caulfield (9), Kolthoff (11), Morgulis and Hemphill (13), and others, and has been widely used in various forms as a micromethod.

In extended research and class use of micromethods for chromate, constant irregularities have been observed. These could not be definitely traced, because of the large number of possible errors. Results could often be reproduced to within ± 0.3 per cent, but the absolute error was usually -5 per cent or more. There are numerous possible errors in the theory of most of these methods—e. g., co-precipitation of chromate ion with the barium sulfate and barium chromate, oxygen error in the determination of the soluble chromate, reduction of the dichromate by chloride ion in acid solution, and precipitation of other barium salts in alkaline solution—e. g., carbonate, etc. Thus, the published results may have involved counterbalancing of unknown and perhaps large errors.

Micromethods were used in this study in order to make more easily discernible the possible magnitude of errors inherent in the common volumetric chromate methods for sulfate, with a view to their elimination or control.

Bray and Miller (3) found that when sodium thiosulfate solutions were standardized iodometrically against potassium

dichromate, the order of addition of reagents played an important part. If the iodide was added to the acidified dichromate, the liberated iodine corresponded very closely to the theoretical. If, however, the dichromate was added to the acidified iodide, an excess of about 0.4 per cent of iodine was liberated, probably through oxidation of the iodide ion by dissolved oxygen of the air. Bray and Ramsey (4) found the same effect in the reduction of vanadic acid by iodide and, by systematic investigation, were able to magnify the errors up to 1200 per cent in the initial stages of the reaction.

Experimental

All solutions are made up from freshly boiled distilled water and stored under an atmosphere of nitrogen (99.5 per cent purity) to eliminate the effect of dissolved oxygen. All titrations were performed in glass-stoppered flasks, the atmosphere within being altered at will. Potassium dichromate was used directly for preparation of a 0.01000 *N* solution. That the pure compound can serve as a primary standard has been shown by Bray and Miller (3) and many others, and has been amply cross-checked in this laboratory by standardization of the same thiosulfate solution against pure potassium iodate from two sources. Six normal sulfuric acid was boiled for a few minutes, cooled, and bottled. Fifty per cent aqueous potassium iodide was prepared from the chemically pure salt. Sodium thiosulfate solution was prepared approximately 0.01 *N* from the pure salt.

OXYGEN ERROR. The thiosulfate solution was standardized in various ways, using 0.01000 *N* dichromate solution as the primary standard. Ten milliliters of the dichromate, 2 ml. of the iodide, and 2 ml. of the 6 *N* sulfuric acid were added in various orders, and the liberated iodine was titrated with the thiosulfate, using 1 ml. of freshly prepared starch solution as indicator.

In Table I is shown the effect of order of addition of reagents on the oxygen error. The operations were performed rapidly, the total time required for a run being approximately 4 minutes. These results indicate that, if all the operations are performed rapidly, the order of addition of reagents plays no part when the atmosphere is either nitrogen or air. With an oxygen atmosphere, there is a distinct increase in the quantity of the iodine liberated.

The data of Table II show that time and the order of addition of reagents definitely affect the oxygen error. If dichromate is added last in air, 10 minutes' standing will introduce up to 2 per cent, and 30 minutes up to 4 per cent error. This definitely indicates the probability of measurable errors in the usual iodometric procedure. The tabulated results form only a portion of the confirmatory observations which were made. Bruhns (5) found that atmospheric oxidation played no role. Kolthoff (12) confirmed this finding with proper experimental conditions, but found that increased

TABLE I. EFFECT OF ORDER OF ADDITION OF REAGENTS UPON THE OXYGEN ERROR

Order of Addition	Normality of Thiosulfate		
	N ₂ atmosphere	Air	O ₂ atmosphere
Dichromate, iodide, acid	0.00988	0.00986	0.00980
	0.00988	0.00988	0.00978
Iodide, acid, dichromate	0.00988	0.00987	0.00979
			0.00976
Acid, iodide, dichromate	0.00988	0.00988	0.00977
			0.00977
Dichromate, acid, iodide	0.00987	0.00988	0.00979
	0.00989		0.00977
Acid, dichromate, iodide	0.00989	0.00989	0.00977
			0.00976

TABLE II. EFFECT OF TIME AND ORDER OF ADDITION OF REAGENTS UPON THE OXYGEN ERROR^a

Order of Addition	N ₂ Atmosphere		Air Atmosphere		O ₂ Atmosphere	
	Time	<i>N</i>	Time	<i>N</i>	Time	<i>N</i>
	Min.		Min.		Min.	
Dichromate, acid, iodide	0.5	0.00987	0.5	0.00988	0.5	0.00978
	30	0.00988	10	0.00986	45	0.00941
Acid, iodide, dichromate	0.5	0.00988	0.5	0.00988	0.5	0.00977
	45	0.00987	10	0.00972	45	0.00916
			30	0.00942		

^a The first two reagents were mixed and allowed to stand various lengths of time as indicated. The third reagent was added, allowed to stand 5 minutes, and the solution titrated rapidly with thiosulfate.

TABLE III. PRECIPITATION OF BARIUM CHROMATE

Time of Digestion Min.	Blank, ml. of 0.01081 N Thiosulfate
Series 1, Ammonia Made from c. p. Ammonium Hydroxide	
5	0.233
15	0.293
60	1.053
Series 2, Carbonate-Free Ammonia	
5	0.228
15	0.248
60	0.218

acidity caused an appreciable oxygen error. These correct conditions have not been used in many of the published sulfate methods. In all subsequent titrations reported, the dichromate has been determined by adding iodide ion to acidified dichromate always in an atmosphere of nitrogen. This will henceforth be termed the "nitrogen method."

Many unreported determinations were also made using standard ferrous ammonium sulfate (Mohr salt) solution to titrate the dichromate directly to the end point of barium diphenylamine sulfonate. These values checked very closely with the data of the nitrogen method, and no oxygen error was found, thus confirming Bray and Ramsey (4).

PRECIPITATION OF BARIUM CHROMATE. Experiments were performed to determine the digestion time required for the complete precipitation of barium chromate from a faintly ammoniacal solution. Ten milliliters of water and 5 ml. of acidified barium chromate (0.06 mole dissolved in 1 liter of 0.4 N hydrochloric acid) were pipetted into a 25-ml. volumetric flask and brought to boiling, and 2 ml. of 6 N ammonium hydroxide were carefully added. The precipitates were digested for various lengths of time, the contents of the flask cooled, made up to volume, and filtered, and a 10-ml. aliquot was taken for titration of the chromate. This method gave the blank due to the reagents, shown in Table III, series 1.

Lengthened digestion time should have decreased the blanks because of more complete precipitation of barium chromate. The results found were due to carbonate ion contained in the ammonium hydroxide as shown in series 2. Carbonate caused the reaction, $\text{BaCrO}_4(s) + \text{CO}_3^{--} = \text{BaCO}_3(s) + \text{CrO}_4^{--}$ to approach equilibrium. The approximate equilibrium constant of this reaction is $K = (\text{CrO}_4^{--})/(\text{CO}_3^{--}) = 0.126$ at 100° C. The effect of carbonate ion was eliminated by use of carbonate-free ammonium hydroxide, prepared by distillation of the commercial product from barium chloride. The data of series 1 were obtained by use of a fresh bottle of ammonia which probably contained little carbonate. The authors find no reference to this point in the literature.

ADSORPTION OF CHROMATE ION ON BARIUM CHROMATE. In most volumetric chromate methods for sulfate, the excess barium is precipitated as chromate from a faintly alkaline solution. The question of adsorption of chromate ion on this precipitate was studied separately by the following experiment:

An accurate 0.01 N solution of barium chloride was prepared by weight and found by standardization against silver nitrate to be 0.01002 N. Into a 25-ml. volumetric flask, immersed in a boiling water bath, were pipetted 4.988 ml. of this barium chloride solution and 14.950 ml. of the standard 0.01000 N potassium dichromate. After several minutes, the solution was made faintly alkaline with carbonate-free ammonium hydroxide, and digestion continued for 15 minutes. The flask was cooled, and the solution was made up to volume and then filtered through a dry No. 40 Whatman's paper. Ten-milliliter aliquots were titrated using the nitrogen procedure. The theoretical normality was calculated on the assumption that the formula of the precipitate was BaCrO_4 , and that no adsorption had occurred. The data are shown in Table IV.

TABLE IV. ADSORPTION OF CHROMATE ION BY BARIUM CHROMATE IN FAINTLY AMMONIACAL SOLUTION

Normality of Chromate in Filtrate	Adsorption %
0.00298 (theoretical)	None
0.00298	0.0
0.00299	-0.3
0.00296	0.6
0.00298	0.0
0.00297	0.3
0.00298	0.0
	Av. 0.1

It is seen that chromate ion is not adsorbed on barium chromate within experimental limits.

PRECIPITATION OF BARIUM SULFATE. Experiments were performed to determine the digestion time necessary for the complete precipitation of barium sulfate from barium chromate solution. Several 9.978-ml. portions of 0.00985 M potassium sulfate were pipetted into different 25-ml. volumetric flasks which were placed in boiling water. After a few minutes, 5 ml. of acid barium chromate were added dropwise, and the barium sulfate was digested for various lengths of time. The subsequent neutralization, digestion, filtration, and titration were performed as described above.

Digestion for 5, 15, and 60 minutes gave the same results within a variation of ± 0.3 per cent, indicating that the precipitation of barium sulfate was independent of the time of digestion, within the limits stated. It did not necessarily indicate that all of the barium sulfate had been precipitated, for it was first necessary to show that the reaction, $\text{BaSO}_4(s) + \text{CrO}_4^{--} = \text{BaCrO}_4(s) + \text{SO}_4^{--}$, did not take place. Small portions of the filtrates above described were acidified and tested for sulfate ion with barium chloride. None was found, indicating that the reaction did not reverse during one hour's digestion.

Another experiment was performed as follows:

Barium sulfate was precipitated as in the preceding section, and digested for 15 minutes to ensure complete precipitation. Then 2 ml. of 6 N carbonate-free ammonium hydroxide and 3 grams of pure potassium dichromate were added, giving 1.3 M chromate ion, about 125 times that ordinarily liberated by the sulfate. This solution was digested for 5 hours, cooled, filtered, acidified with hydrochloric acid, and tested with barium ion. Only a very faint opalescence was observed. It may be stated that, under the conditions of the ordinary sulfate determination, the reaction, $\text{BaSO}_4(s) + \text{CrO}_4^{--} = \text{BaCrO}_4(s) + \text{SO}_4^{--}$, does not proceed. This confirms the results of Kolthoff (11). At this stage of the investigation, twelve analyses were run by the method described under "precipitation of barium sulfate." The results were reproducible to within 0.4 per cent but the absolute error was -5.5 per cent.

The effect of neglecting the volume of the precipitated barium sulfate and barium chromate in the 25-ml. volumetric flask amounted to 0.02 per cent and 0.07 per cent, respectively, and from the change in solubility of barium sulfate with ionic strength in faintly alkaline solutions it was calculated that all but a negligible fraction of the barium sulfate was precipitated in the presence of excess barium ion.

CO-PRECIPITATION OF CHROMATE ION WITH BARIUM SULFATE. In the usual chromate procedure, barium sulfate is precipitated in the presence of chromate ion, and co-precipitation of the latter is likely to occur. The effect has been studied by Kolthoff (11), but his interpretation appears to be doubtful, owing to the possible reduction of the dichromate ion by acidified chloride ion. At the suggestion of W. C. Bray, perchloric acid was used to reinvestigate the co-precipitation effect. Solutions of 0.1 N potassium sulfate and 0.1 N barium perchlorate were prepared, and the procedure was carried out as follows:

One milliliter of the sulfate solution was pipetted into a 25-ml. flask and various amounts of 60 per cent c. p. perchloric acid and 9.962 ml. of 0.01000 *N* potassium dichromate were added. The flask was placed in a beaker of boiling water and, after a few minutes, 0.9 ml. of the barium perchlorate solution was added. Digestion was continued for 15 minutes, and the subsequent operations were performed as previously described.

TABLE V. EFFECT OF ACID CONCENTRATION ON CO-PRECIPITATION OF CHROMATE ION WITH BARIUM SULFATE

Acidity after Precipitation of All BaSO ₄	Co-precipitation %
<i>N</i>	
Series 1, Perchloric Acid	
1.0 (no Ba ⁺⁺ added)	None
0.01	29.7
0.1	4.4
1.0	1.5
Series 2, Hydrochloric Acid	
	(Apparent)
0.1	6
0.8	7
1.4	10.5

TABLE VI. ADSORPTION OF CHROMATE IONS ON PREFORMED BARIUM SULFATE

Normality of Chromate	Adsorption %
0.00591 (no Ba ⁺⁺ added)	None
0.00591	0.0
0.00589	0.3
0.00591	0.0
0.00589	0.3
0.00588	0.5
	Av. 0.3

The results in series 1 showed that chromate ions co-precipitated with barium sulfate even at concentrations as low as 4×10^{-4} *N*. While barium chromate might have precipitated at the lowest acidity, there was still marked co-precipitation even in approximately normal acid. This, then, was the cause of the low results which the authors had always observed in the application of the chromate method.

As is well known, chloride ion in acid solution reduces dichromate ion, and the acid barium chromate solution should be made up with perchloric, not hydrochloric acid. Failure to observe this precaution resulted in large errors, as shown in series 2. The increased acidity decreased the co-precipitation, but increased the reduction of dichromate ion, yielding the "apparent" values listed in the table. Chloride ion is evidently a definite interfering factor in the usual chromate method.

ADSORPTION OF CHROMATE ION ON PREFORMED BARIUM SULFATE. The experiments described under "co-precipitation of chromate ion with barium sulfate" were repeated, except that the standard dichromate solution was added after precipitating barium sulfate and making the contents of the flask alkaline. Within the limit of experimental error, chromate ions were not adsorbed on preformed barium sulfate.

Other possible sources of error investigated and found to have no effect (± 0.2 per cent) were filtration of standard potassium dichromate through Whatman's No. 40 filter paper, and addition of solid ammonium chloride to the cold dichromate to the extent of 10 per cent, since it was thought that ammonium dichromate might spontaneously decompose. Boiling 0.01 *N* potassium dichromate solutions in air for 1 hour entailed 0.7 per cent loss of hexavalent chromium, but boiling 10 per cent ammonium chloride solutions of potassium dichromate under the same conditions gave no increased loss of hexavalent chromium. Hydrochloric acid rapidly reduced hexavalent chromium at approximately 100° C., but

the reaction was not autocatalyzed by the presence of large amounts of trivalent chromium ion.

Discussion of Results

From the results of the above experiments, it is evident that most of the published methods contain errors in the theory of their application. High results for sulfate and the methods in which they are obtained may be given by oxygen error (2, 5, 7, 11, 13), reduction of dichromate ion by chloride ion (9), and carbonate in the added base (all methods). The causes of low results are oxygen error (9), co-precipitation of chromate ion with barium sulfate (2, 6, 7, 9, 11, 13), and reduction of dichromate ion by acidified chloride ion (2, 6, 7, 11, 13).

The objection to the presence of counterbalancing errors is raised not because they exist *per se*, but because variations in the technic of individual workers on the same method yield results whose reproducibility may be satisfactory, but whose absolute accuracy may vary significantly.

Of the existing methods, the procedure of Gibson and Caulfield (9), of which only the barest details have been published, appears to be the most promising. With certain modifications, it should be possible to avoid most or all of the systematic errors. In their procedure, if the precipitation of the barium sulfate is carried out in about 0.1 *N* perchloric acid and carbonate-free ammonia added, the excess chromate which is subsequently added will not be co-precipitated or adsorbed by either the barium sulfate or barium chromate. Neither will it be reduced by chloride ion in hot alkaline solution, since the chloride is later removed in the filtration. If the Emich filter stick or a sintered glass filtered stick (10) is warmed in dilute (2 *N*) perchloric acid and the chromate determined by the "nitrogen method" or by titration with standard Mohr salt, which involves no oxygen error (4 and unpublished data), such a procedure should be a distinct improvement on the existing methods. Preliminary work indicates this to be the case, and further work is in progress on such a revised method. The authors have been forced to the conclusion that there exists at present no entirely satisfactory microvolumetric chromate method for sulfates.

Acknowledgment

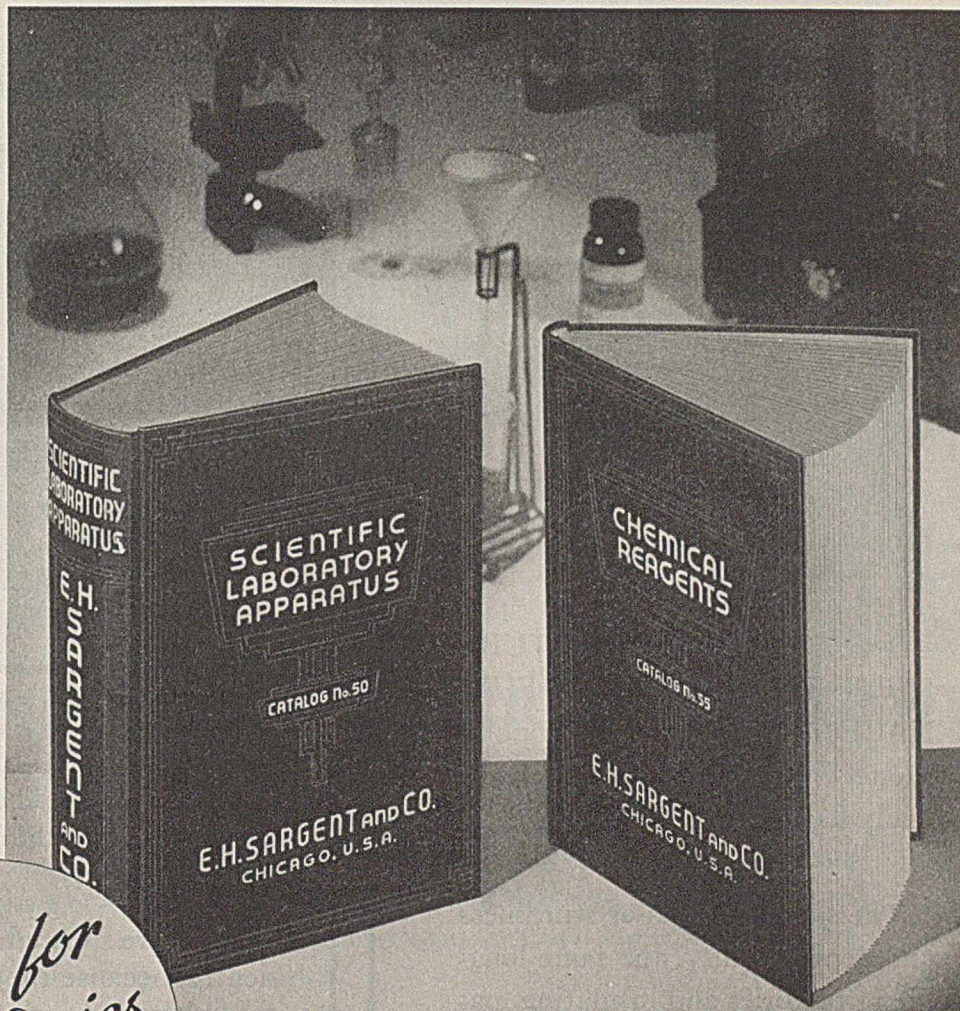
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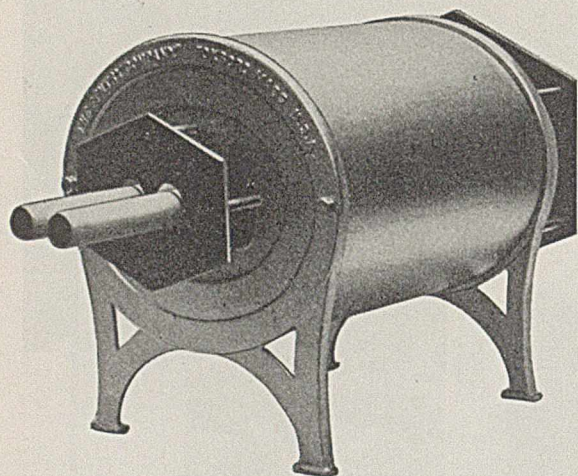
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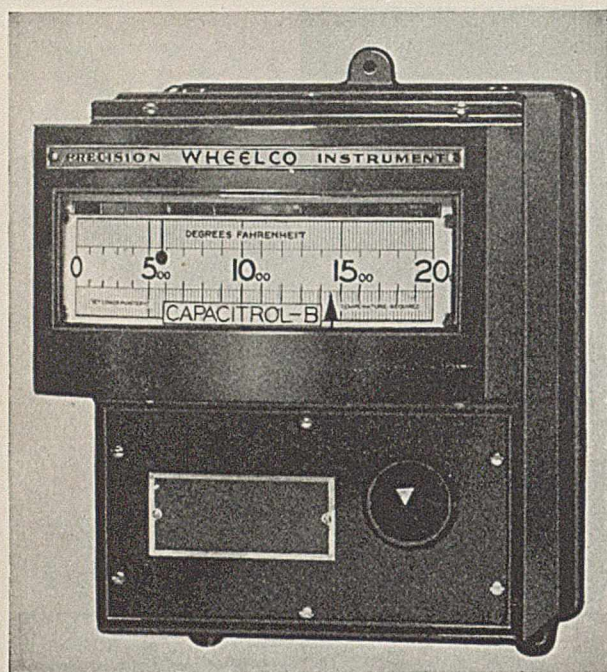
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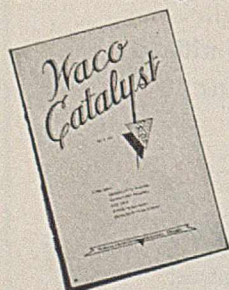
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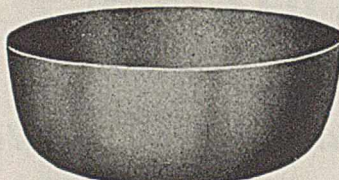
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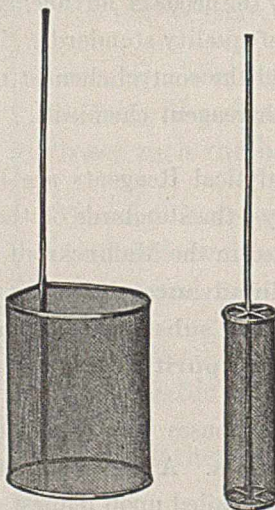
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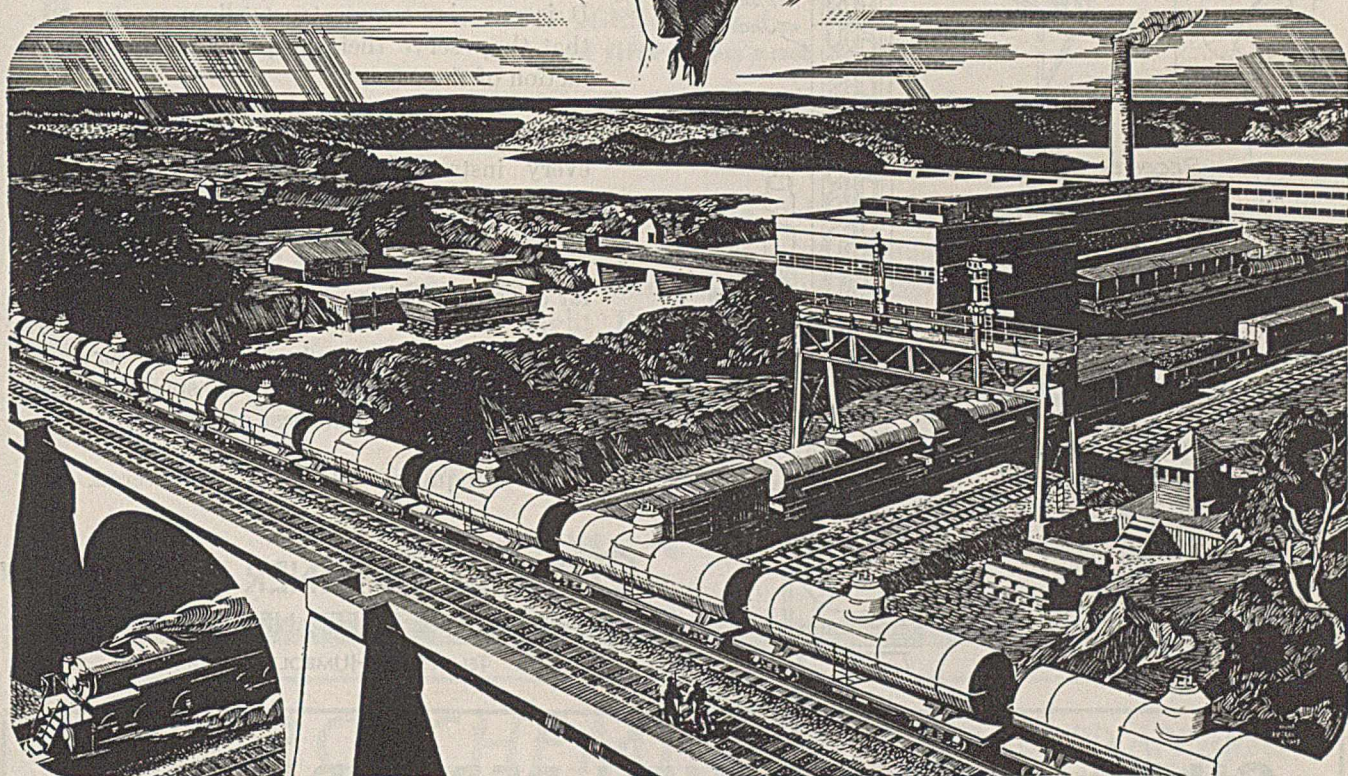
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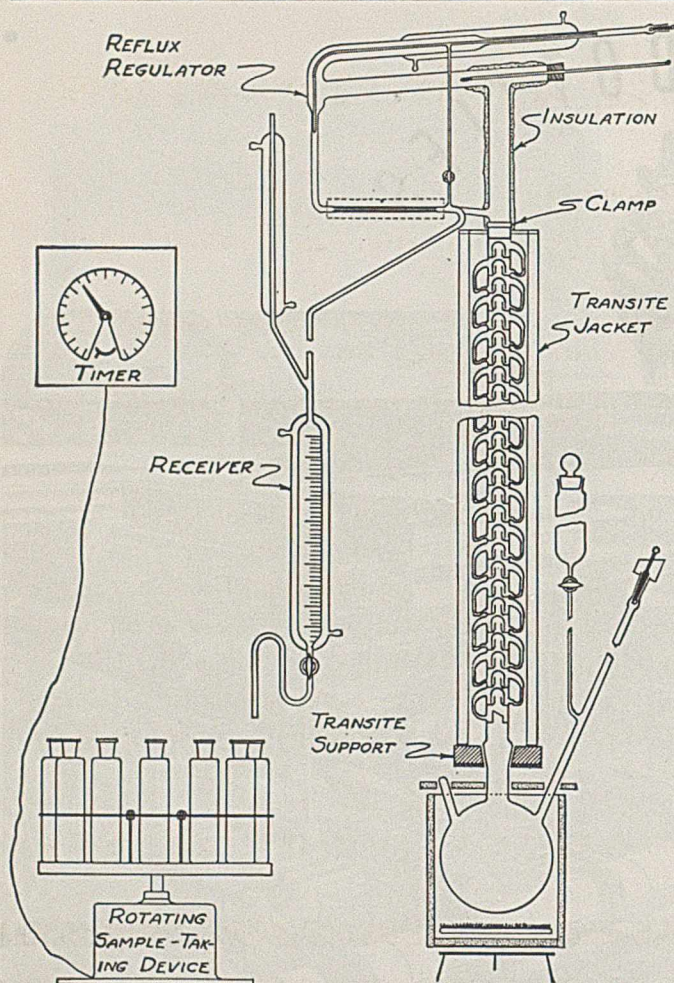
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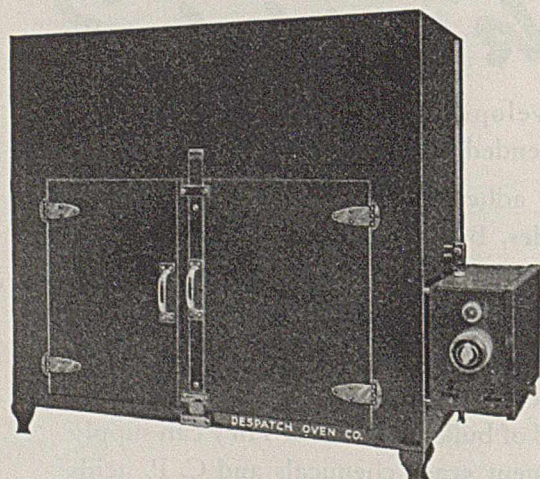
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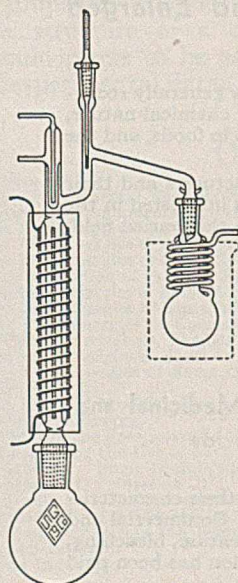
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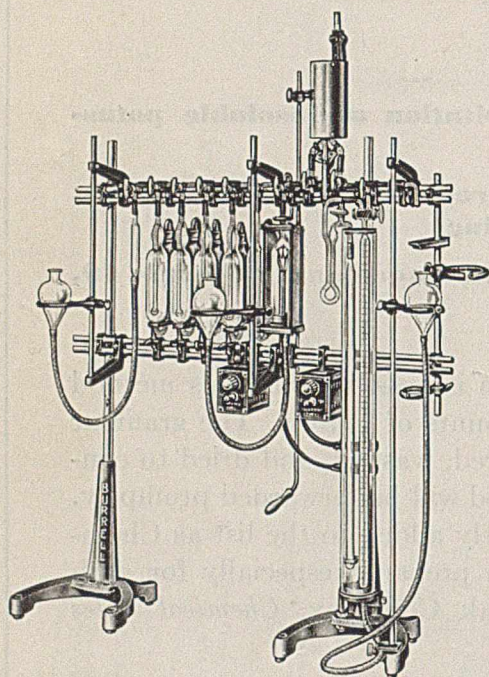
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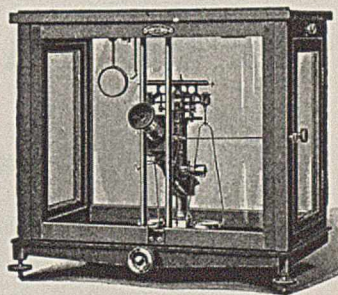
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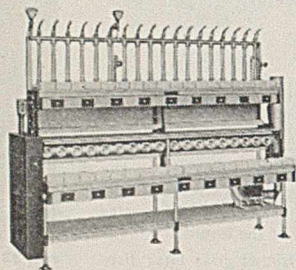
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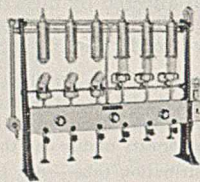
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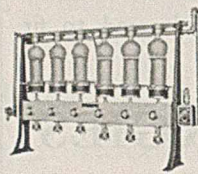
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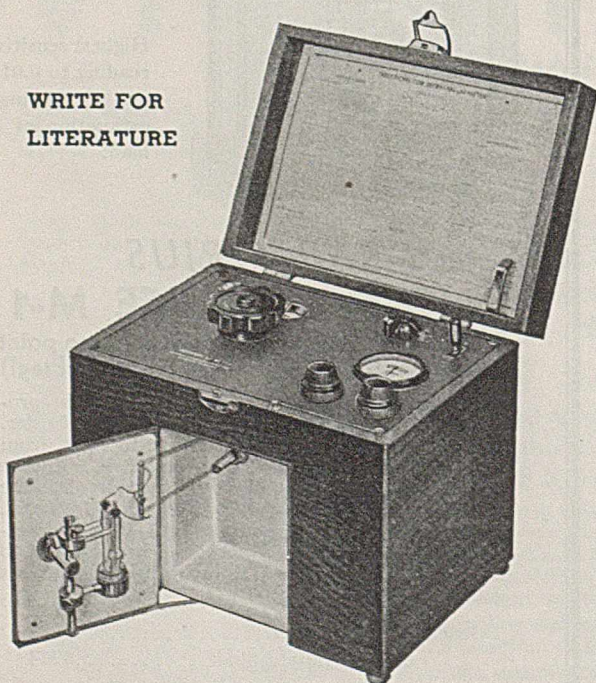
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