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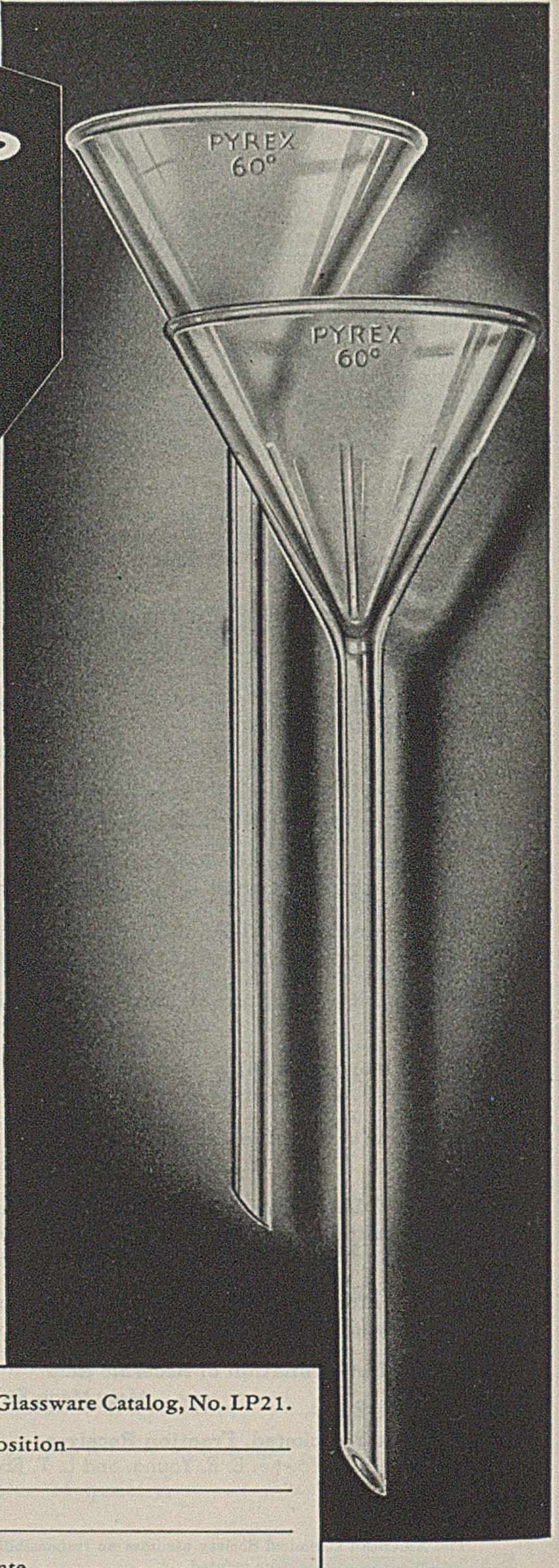
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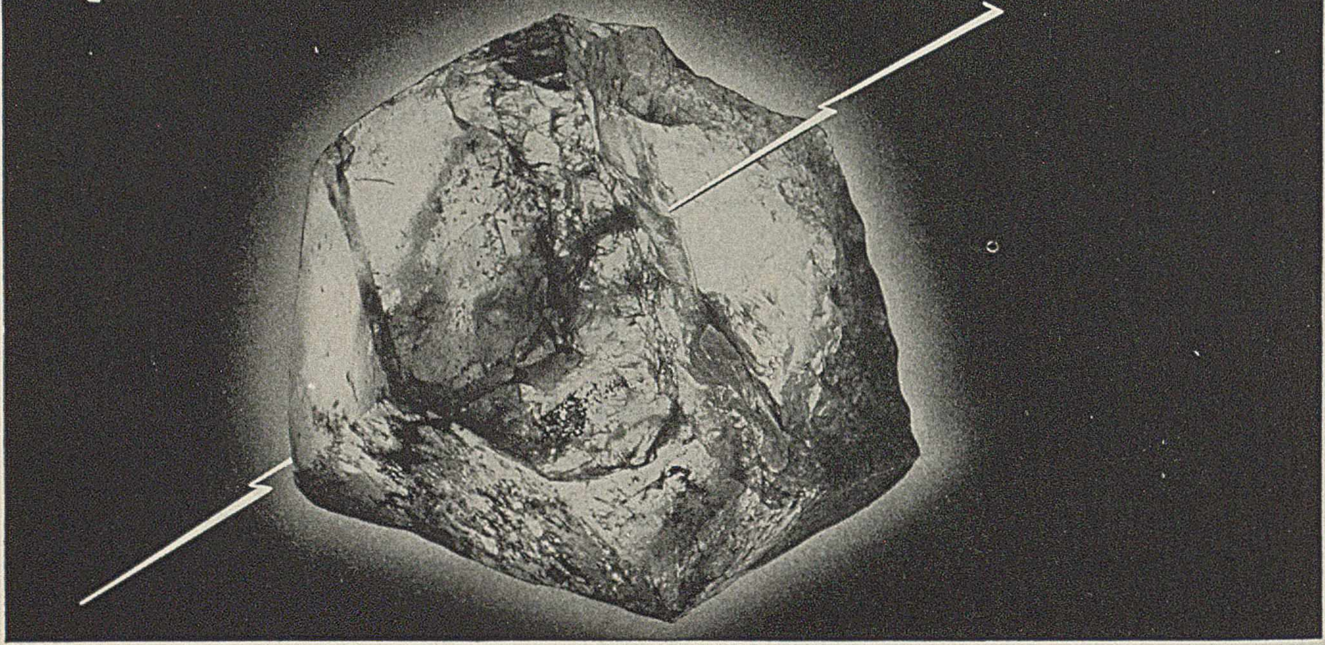

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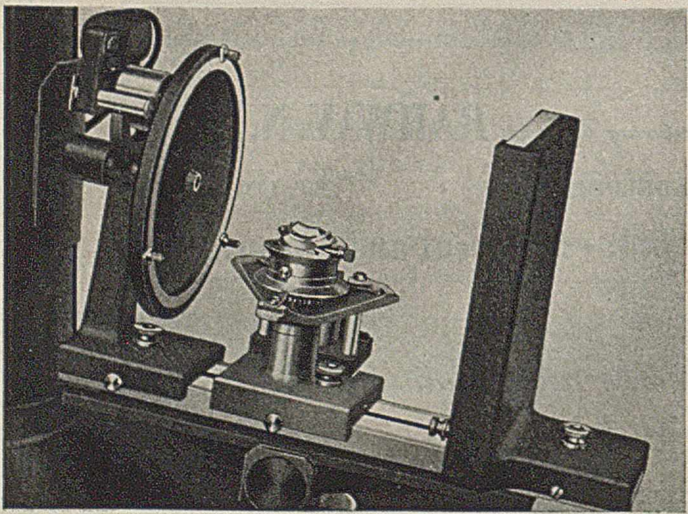

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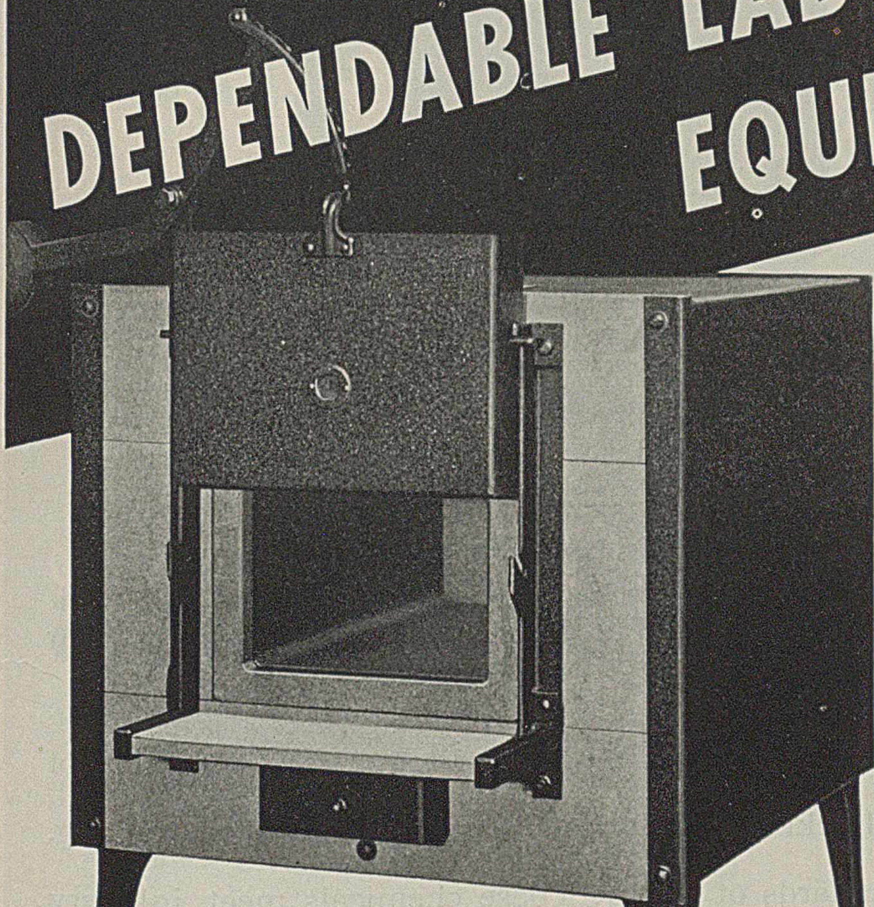

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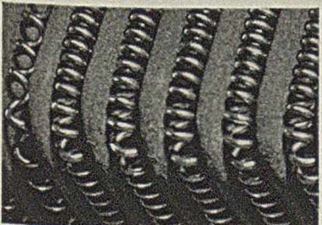

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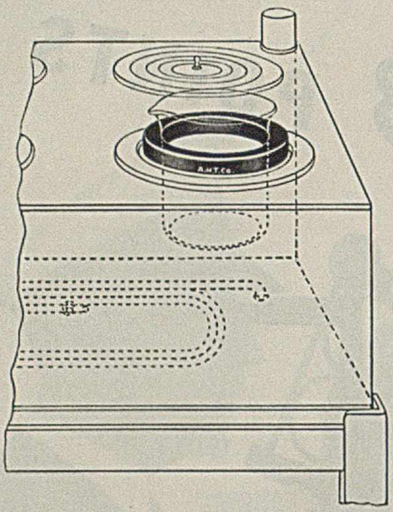

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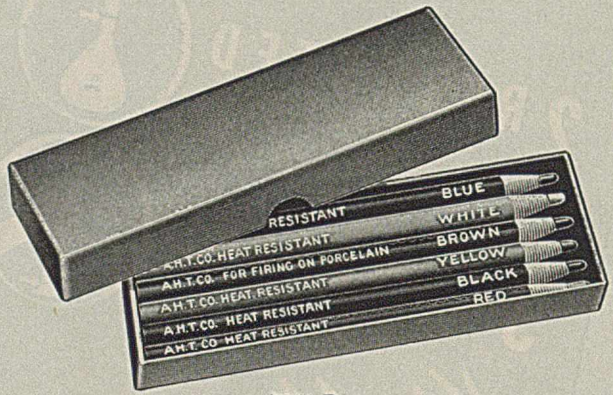

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Chemical Factors in the Determination of Water in Insulating Oil

A New Electrical Method

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Consolidated Edison Company of New York, Inc., Brooklyn, N. Y.

The presence of small quantities of water in insulating oil seriously impairs its usefulness in electrical equipment. The need for an accurate as well as rapid method for its determination cannot be overemphasized. The present paper describes the experimental modifications of the combustion procedure directed toward lowering the hydrocarbon correction. The influence of temperature in the removal of the water from oil and the limitations of the Grignard procedure are experimentally demonstrated. An electrical method is briefly described and its application to a field determination of water is pointed out.

IN RECENT years several chemical procedures have been advanced which claim specificity for the estimation of water in organic liquids.

The Fischer method (*6*), worked on extensively in this country by Smith, Bryant, and Mitchell (*12*), depends on the oxidation of sulfur dioxide by iodine in the presence of water. The latter authors first worked out the estimation of water by acetyl chloride, which was adapted by Clark to the determination of water in transformer oil. Because of the color of an insulating oil and the probable presence of interfering substances in the original oil sample, it appears likely that in any chemical procedure the water first must be removed from the oil, as, for example, in the procedure described by the authors (*4*). The chief difficulties with the Fischer method and the acetyl chloride method in their application to oils are the estimation of peroxides in the former method and the estimation of volatile acidity in the latter. Two additional methods involve the use of α-naphthoxydichlorophosphine (*9*), which is not specific to the OH group of water, and of benzoic anhydride (*11*). The Grignard reagent has also been suggested by Larsen (*7*) as a possibility for determination of traces of water in oils.

In the method (*4*) which the authors have described, the volatile carbonaceous material and the free water, after being trapped out by the use of a Dewar flask containing solid carbon dioxide, were carried into a combustion furnace. The products of combustion and the free water were absorbed in microchemical absorption tubes and weighed as carbon dioxide and gross water. The net water was obtained by applying an empirical correction ratio of water to carbon dioxide.

The accuracy of the method depends on the use of the correct ratio of water to carbon dioxide and the weight of carbon dioxide obtained in each experiment. Some knowledge of the former was obtained by continuing the experiment for 1 liter of nitrogen after the water weight had fallen to a minimum. The latter factor was greatly reduced by a change in procedure which is described in this paper. The ratio adopted for the mineral oil type of transformer oil was 0.3 and for the noninflammable synthetic oil 0.2. Carbonaceous material vaporized from a mineral oil which would be retained by the solid–carbon dioxide trap would be expected theoretically to have a water–carbon dioxide ratio of between 0.2 and 0.5. The higher than theoretical ratio (0.1) for the synthetic noninflammable oils may be due to partially chlorinated compounds below $C_{2n}H_nCl_n$ or to organic impurities absorbed in the operation of the transformer.

Apparatus

The modifications in the apparatus were directed toward the reduction of the amount of carbonaceous material entering the combustion furnace. It was found that the magnitude of the correction was greatly reduced by means of an oil scrubber in the train where preferential solution of the oil vapors took place. The change in procedure for the determination of water in oil is apparent from a description of the new section of the apparatus as shown in Figure 1. This section replaces *D* and *F* in Figure 1 of (*4*). (In *5*, page 301, in the description of the apparatus, "cell *E*" should read "cell *D*").

One hundred milliliters of oil were introduced into *C* through the serum rubber stopper and stopcock *D* after the residual water in the train had been removed. Approximately 10 ml. of Apiezon oil (an oil of low volatility used in high vacuum practice) were also added to cell *B*. Purified nitrogen gas in small bubbles formed by the porous fritted disk, *A*, carried the water from the oil sample into the solid carbon dioxide trap, *E*. During this period, scrubber *B* was maintained at a temperature of 100° C. When the removal of water was complete, the Dewar flask was removed and the nitrogen was directed around the oil sample cell by means of the three-way stopcock *G*. In this manner the

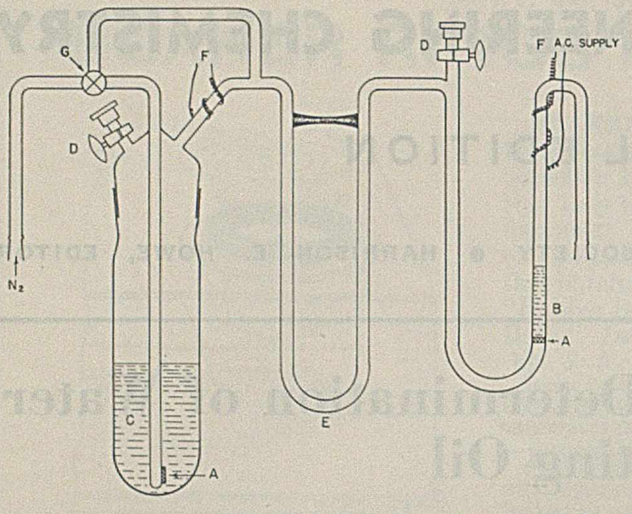

Figure 1. Interchangeable Apparatus for Determining Water in Insulating Oil

A. Porous fritted disks
B. Apiezon oil cell
C. Oil sample flask
D. Serum rubber stopper and stopcock
E. Dry ice trap
F. External spiral coiled heater
G. Three-way stopcock

trapped water in *E*, together with any volatile products, was carried through scrubber *B*, which was maintained at room temperature, into the combustion furnace. An external coiled heater, *F*, prevented frothing in either *B* or *C*. When the oil was of the halogenated type a spiral tube containing silver oxide maintained at a temperature of 400° C. was put in place at the exit end of the combustion furance. As is shown below, the temperature of the oil sample must be considered in connection with the removal of water. A safe maximum temperature would appear to be the average operating temperature of the oil. One may also be guided by the condition of the oil as revealed by chemical tests. Unless otherwise stated, a new mineral oil or the average nonflammable synthetic oil was heated to 105° C. during the passage of 2 liters of nitrogen, whereas for a used mineral oil the passage of 5 liters of nitrogen was carried out at 50° C. or at room temperature.

Efficiency of Apiezon Scrubber in Diminishing Carbon Dioxide Correction

In Table I is illustrated the reduction of the carbon dioxide correction by the use of the Apiezon-oil scrubber. When the oil scrubber was maintained at an elevated temperature, it was apparently ineffective in retaining carbonaceous material (experiments 3 and 3A). However, when the scrubber was maintained at room temperature it lowered greatly the quantity of oil vapor entering the combustion furnace. The adopted carbon dioxide–water correction apparently would have enabled one to obtain the correct results (experiments 3, 3A, A-16, and A-1) without the scrubber even where large amounts of carbon dioxide were obtained. The correction due to the solubility of water in the Apiezon oil is negligible, as was indicated by continuing the experiment until an additional liter of nitrogen had passed through the train (experiment 3A).

Table I. Efficiency of Apiezon Scrubber in Diminishing the Carbon Dioxide Correction

Expt. No.	Oil Type	Temperature Oil scrubber	Temperature Oil sample	H_2O	CO_2	Gross H_2O	Gross CO_2	Net, H_2O
		° *C.*	° *C.*	*Mg.*	*Mg.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
3	Used 10C[a]	25	125	3.58	1.35	33	13	29
3A	Used 10C	110	125	4.75	8.00	62	105	31
3A (continued)	1 additional liter N_2	...	...	0.14	0.43	...	...	..
A-15	New 10C	Absent	25	3.34	5.80	108	187	52
A-15-A	New 10C	25	25	2.14	0.91	50	21	43
A-1	N. S. O.[b]	Absent	125	11.57	9.55	116	96	97
A-16	N. S. O.	25	125	3.87	0.58	102	15	99

[a] Mineral oil type of transformer oil.
[b] Nonflammable synthetic oil.

Table II. Effect of Time of Heating and Temperature on Removal of Water from Sample 6 (10C Oil)[a]

Expt. No.	Oil Sample Temperature	Weight of Sample	N_2	Gross H_2O	Gross CO_2	Net, H_2O
	° *C.*	*Grams*	*Liters*	*P. p. m.*	*P. p. m.*	*P. p. m.*
1	125	56	1	59	26	51
2	125	87	1.5	99	31	90
3	25	87	4	29	20	23
4	25	87	17	34	17	29
4 (continued)	125	..	4 additional	112	17	107
4 (continued)	125	..	18 additional	34	11	31
					Total water found in Expt. 4	167

[a] Scrubber of Apiezon oil at room temperature.

Effect of Temperature on Removal of Water from Oil

The experimental results on many oil samples indicated that if an oil sample were heated while the water was being removed into the solid carbon dioxide trap high results were obtained which depended in magnitude on the time of heating. This effect was more evident in the mineral oil than in the nonflammable synthetic oil. Furthermore, the used transformer oils exhibited this effect to a greater degree than the new oils. In Table II, the results on a sample of used transformer oil (mineral oil type) are given. When experiments 1 and 2 are compared with experiment 3 (Table II, last column) the magnitude of the error involved is clearly illustrated. Thermal decomposition of oxygenated compounds was responsible for the formation of the additional water, although the residual dissolved oxygen gas in the sample might have played a minor part. In experiment 4 after 17 liters of nitrogen had passed through the oil sample at room temperature a very large increase in water content occurred when the temperature of the oil sample was raised to 125° C. Further heating yielded comparatively little additional water, indicating that oxygenated compounds were present in a limited amount. The completeness of removal of water at room temperature was indicated by the fact that the 4-liter run (experiment 3) yielded very little less than the 17-liter run (experiment 4). Thus by continued heating at 125° C. for a period involving the passage of 22 liters of nitrogen, an oil sample actually containing 30 p. p. m. of water was shown to behave as if 165 p. p. m. of water were present.

Behavior of Grignard Reagent in Determination of Water in Oil

The application of Grignard reagent to the determination of water in oils showed that after making allowance for the acid content determined on a duplicate oil sample the residual active hydrogen content of the oil sample is too large to be neglected. The term "residual active hydrogen" may be conveniently applied to the active hydrogen other than that of water and acids. Alcohols, amines, phenols, and acids too weak to be titrated may be considered to be the source of the residual active hydrogen.

Table III. Comparison of Results of Grignard and Combustion Methods

(Single oil sample at 25° and 125° C.)

Temperature of Oil Sample		Neutralization Number	Grignard: Methane Evolved Found	Grignard: Methane Evolved Corr.[b]	Grignard: Calculated[a] Water	Combustion: Water	Combustion: Equivalent methane
° C.			P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
25		0.36	226[c]	123	69	16	21
125	Distillate	0.04	95	67	38	..	..
	Residue	0.31	175	92	52	..	..
	Total			159	90	30	54

[a] $1H_2O = 2CH_4$. Acidity deducted using relation $1(H) = 1CH_4$.
[b] Blank deducted. Acidity deducted using relation $1(H) = 1CH_4$.
[c] Grignard reaction carried out in a mixture of 30% ether and 70% 10C oil.

It was first observed that the character of the oil sample (petroleum origin or chlorinated aromatic) influenced greatly the yield of the reaction. This phenomenon has been described by Hibbert and co-workers (*8*). It could be minimized by maintaining a large ratio of isoamyl ether to the oil sample. An attempt was made to analyze with the Grignard reagent the two fractions formed in the combustion procedure. The material which was condensed in the solid carbon dioxide trap (cell 2) is referred to in Table III as the distillate and that which remained in the oil cell (cell 1) as the residue. In a separate experiment, the acidity of the distillate and residue was determined by titration by means of a capillary syringe without removing either from the analytical train. The results bring out several points of interest. The large increase in water resulting from its removal from the oil sample at an elevated temperature (30 p. p. m. as compared to 16 p. p. m.) confirmed the results reported in Table II.

The major portion of the acid for this particular mineral oil sample was nonvolatile. In experiments with nonflammable synthetic oil carried out in a similar manner, the entire acid content remained in the residue. The residual active hydrogen appeared to a limited extent in the distillate (cf. 54 and 67 p. p. m. methane). After due allowance was made for the influence of the solvent and after the methane equivalent to the acid had been deducted, there was an apparent increase in the active hydrogen content of the oil sample as a result of heating to 125° C. (cf. 123 with 67 + 92 = 159 p. p. m. methane). This discrepancy (159 − 123 = 36 p. p. m.) was in good agreement with the difference between the calculated methane from the water obtained at 125° and 25° C. (54 − 21 = 33 p. p. m.). Except for the possibility of oxidation at the elevated temperature due to dissolved oxygen initially present in the oil sample, a probable explanation of the anomaly was related to the facts that ketones may enolize at the elevated temperature and that alcohols may split off water which under optimum conditions would yield two moles of methane as compared to a yield of but one mole of methane from the original alcohol.

It was concluded that the results of the Grignard test when expressed as evolved methane may be used only as an index of the stage of oxidation of an insulating oil. Based on experimental results with the microgravimetric procedure developed in this laboratory, it was considered extremely uncertain to ascribe the evolved methane to any particular chemical reactive group or compound after an acidity correction had been applied. Results of even greater uncertainty may be expected in the estimation of the Grignard added. The establishment of an oxygen balance by means of the results of the Grignard test did not appear to be of general application in the light of experimental work.

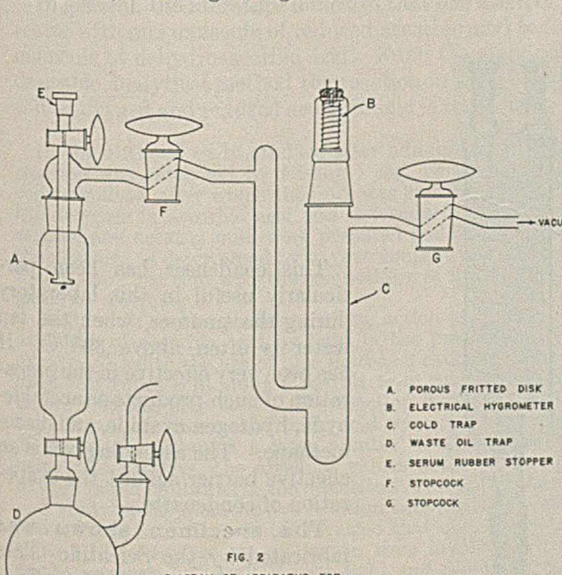

FIG. 2
DIAGRAM OF APPARATUS FOR ELECTRICAL DETERMINATION OF WATER IN INSULATING OIL

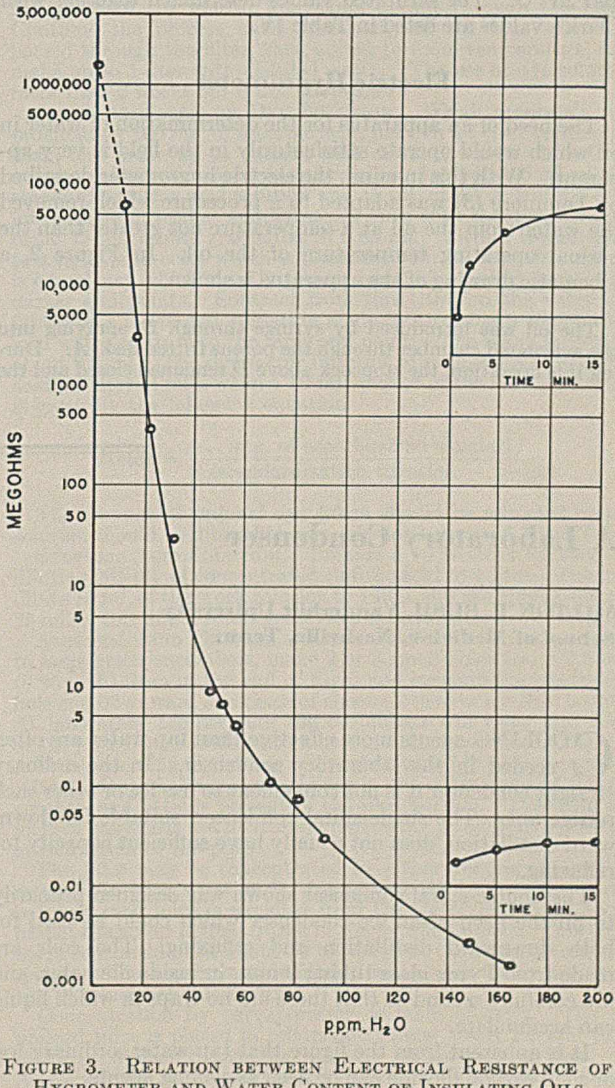

Figure 3. Relation between Electrical Resistance of Hygrometer and Water Content of Insulating Oils

Table IV. Solubility of Water in New Insulating Oils at Room Temperature

Expt No.	Oil Type	Temperature of Oil Sample	CO₂	H₂O		
				Gross	Net	Clark's values at 25° C.
		° *C.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
A-17	10C	25	7	46	44	...
A-15-a	10C	25	21	50	43	75
A-15-b	10C	125	32	57	47	...
A-16-a	N. S. O.	25	6	103	102	120 (Pyranol)
A-16-b	N. S. O.	125	15	102	99	...
A-12	5314[a]	125	7	54	52	70

[a] Mineral oil type of high-voltage cable oil.

Oil samples were prepared by shaking with an excess of water at 50° C. and cooling to room temperature. The saturated 10C oil was repeatedly decanted, the N. S. O. was repeatedly drawn off in a separatory funnel, and the 5314 oil was centrifuged.

Solubility of Water in Insulating Oils at Room Temperature

In a paper by Clark (*2*) the solubility of water in new Pyranol, transformer oil, and high-voltage cable oil was given. In connection with checking the precision of analytical trains, the authors prepared stock saturated solutions of the oils with respect to water at room temperature, which for purposes of comparison may be considered to be between 20° and 25° C. The saturated values determined together with Clark's values are listed in Table IV.

Electric Hygrometer

The need of an apparatus for the determination of water in oil which would operate satisfactorily in the field is very apparent. With this in mind, the electric hygrometer described by Dunmore (*3*) was adapted to a procedure which removed the water from the oil at a temperature not greater than the normal operating temperature of the oil. In Figure 2, a schematic drawing of the apparatus is shown.

The oil was introduced by syringe through *E*, spraying into the evacuated chamber through the porous fritted disk, *A*. During this operation, the stopcock above *D* remained closed and the cold trap, *C*, was surrounded by a bath of dry ice. Stopcocks *F* and *G* were then closed and the contents of the trap and coil raised to some convenient temperature. The resistance of the film was measured either by a General Radio megohm bridge, as extended by Balsbaugh *et al.* (*1*), or a modified Jones and Joseph bridge (*10*) with a cathode ray tube as a null detector with three stages of amplification.

In Figure 3 is shown a plot of the logarithm of the resistance against the water content of the oils as determined by the combustion procedure. The drift in the resistance readings is illustrated by the insert curves. The change in resistance with time, although of a larger magnitude at the higher measured resistance, in terms of water content, is approximately the same as at the lower measured resistance. The resistance readings on the main curve were taken in each case after a 5-minute delay period.

Experiments are in progress on the simplification of the hygrometer construction and the selection of a more rugged alternating current resistance bridge of a suitable range. The method shows every promise of working out satisfactorily in the field.

Acknowledgment

The electrical bridges described in this paper were constructed in this laboratory under the direction of W. F. Davidson, director of research.

Literature Cited

(1) Balsbaugh and Oncley, Ind. Eng. Chem., **31**, 318 (1939).
(2) Clark, *Elec. Engr.*, **59**, 433 (1940).
(3) Dunmore, *Bur. Standards J. Research*, **23**, 701 (1939).
(4) Evans, Davenport, and Revukas, Ind. Eng. Chem., Anal. Ed., **11**, 553 (1939).
(5) *Ibid.*, **12**, 301 (1940).
(6) Fischer, *Angew. Chem.*, **48**, 394 (1935).
(7) Larsen, Ind. Eng. Chem., Anal. Ed., **10**, 195 (1938).
(8) Lieff, Wright, and Hibbert, *J. Am. Chem. Soc.*, **61**, 865 (1939).
(9) Lindner, *Z. anal. Chem.*, **86**, 141 (1931).
(10) Luder, *J. Am. Chem. Soc.*, **62**, 89 (1940).
(11) Ross, *J. Soc. Chem. Ind.*, **51**, 121T (1932).
(12) Smith, Bryant, and Mitchell, *J. Am. Chem. Soc.*, **57**, 841 (1935); **61**, 2407 (1939); **62**, 1, 3504 (1940).

Presented before the Conference on Electrical Insulation, Washington, D. C.

A Laboratory Condenser

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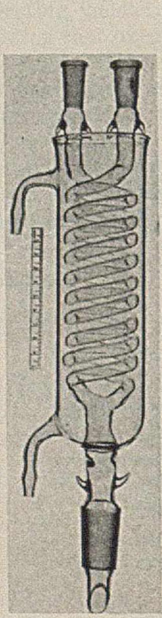
COOLING agents more effective than tap water are often needed in the laboratory condenser. In the ordinary straight condenser it is not convenient to use ice or other such refrigerant. The single-spiral condenser, suitable for downward distillation, does not usually have sufficient capacity for refluxing.

The double-spiral condenser shown was designed primarily to fill the need of an ice condenser which could be used for both downward distillation and refluxing. The coils are made from Pyrex glass tubing 9 mm. in inside diameter, and are carefully wound so that there are no traps in which liquid can accumulate.

It is apparent from the figure that tap water, ordinary ice, or solid carbon dioxide can be used as cooling agents.



This condenser has been particularly useful in this laboratory during the summer, when the tap water is often above 30° C. It has been very effective in the preparation of such products as acetaldehyde, hydrogen cyanide, and diazomethane. The ascending coil is an effective barrier against the evaporation of condensate.

The specimen shown was fabricated by the Scientific Glass Apparatus Company, Bloomfield, N. J.

Quantitative Determination of Dissolved Oxygen

Ascorbic Acid Oxidase Method

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DISSOLVED oxygen exerts the controlling role in many processes occurring in biological fluids. That this is true of milk has been amply demonstrated (*4, 8, 13, 14*). It is evident that to understand and control these oxidations a knowledge of the dissolved oxygen content is highly important. A simple rapid method for the determination of dissolved oxygen in milk is needed, especially at the present time, in view of the possibility of commercially deaerating pasteurized milk to preserve its vitamin C content and prevent the development of the oxidized flavor.

Methods for determining dissolved oxygen fall into several general classes.

The dissolved gases may be removed, the volume of mixed gases measured, and the mixture analyzed for carbon dioxide, oxygen, nitrogen, and water vapor. Complete removal of the dissolved gases is difficult and heating of the liquid in conjunction with reduced pressure is recommended (*10*). During the time required for removal at the temperatures recommended, some of the oxygen may react with other constituents of the biological fluid. This method is time-consuming and requires rather elaborate apparatus.

The amount of dissolved oxygen present in water low in organic matter, and from which certain interfering inorganic substances are absent, can be determined by adding to the water reagents that react quantitatively with the dissolved oxygen (*3, 17*). The well-known Winkler (*1, 17*) method is of this type. These methods are not applicable to biological fluids because the reagents are relatively strong, are not specific for oxygen, and react with organic material.

Methods have been described based on the reaction between dissolved oxygen and any one of a series of reducing agents to produce a colored compound, the amount of which is determined colorimetrically (*9, 11, 18*). Alkalies or acids are used to accelerate the reaction.

A quantitative method for dissolved oxygen, based on its reaction with reduced ascorbic acid added to the liquid, is reported in this paper. The reaction is completed in 5 to 15 minutes at 25° C., within the pH range 5.0 to 7.5.

In general, the literature indicates that one atom of oxygen reacts with one molecule of reduced ascorbic acid to form one molecule of dehydroascorbic acid. From the standpoint of a desirable analytical method the reaction in milk between dissolved oxygen and reduced ascorbic acid is too slow.

In the authors' early studies, after adding ascorbic acid, the reaction was catalyzed by adding 1 mg. per liter of copper as copper sulfate, after which the milk was kept cold for 2 days and the decrease in ascorbic acid was determined. Mixtures of deaerated and aerated milk were prepared and the composition of the mixtures as determined by oxygen content was found to agree within 1 to 2 per cent with the composition of the mixtures as prepared by weighing.

Next, work on the photosensitizing action of riboflavin on the oxidation of ascorbic acid by light in the presence of dissolved oxygen (*6*) led to the use of blue light as a catalyst. Completely filled test tubes containing a marble were rotated end over end before a strong blue light. The reaction between the dissolved oxygen and the reduced ascorbic acid was complete in less than 30 minutes. Although a large number of analyses were made using this catalyst, the absolute values obtained for dissolved oxygen raised doubts as to the quantitative nature of the reaction.

A study of the quantitative reaction between dissolved oxygen and reduced ascorbic acid (*5*) revealed that under various conditions 1.19 to 1.67 atoms of oxygen were involved with copper as the catalyst, 1.57 to 2.04 with light and riboflavin, 2.00 with alkali, and 1.00 with ascorbic acid oxidase (from cucumber juice or cabbage juice).

As a result of this study ascorbic acid oxidase was adopted as the catalyst and with a 10 to 1 concentrate of the enzyme the reaction was found to be complete in milk in 5 minutes at 25° C.

This general method for the determination of dissolved oxygen has been under investigation for 3 years and the method using cucumber juice as a catalyst has been in use for more than a year, during which time several thousand oxygen determinations have been made on milk, water, buffer solutions, bacteriological culture media, etc. With plenty of equipment conveniently arranged one person can make 30 determinations in a half day.

Reagents and Apparatus

PREPARATION OF DYE SOLUTION. Grind about 0.135 gram of 2,6-dichlorophenolindophenol in a mortar, add about 50 ml. of hot distilled water, grind further, and decant through a filter into a 1-liter volumetric flask. Add more hot water to the residue remaining in the mortar and again decant through the filter. Continue the process until practically all the blue color has passed through the filter, then adjust to room temperature, and make up to 1 liter with distilled water. The use of dye solution more than 2 weeks old is not advisable.

STANDARDIZATION OF DYE SOLUTION. Weigh accurately approximately 100 mg. of ascorbic acid, place in a 1-liter volumetric flask, and make up to volume with distilled water. Mix thoroughly and use at once for standardizing. Introduce 5 ml. of this standard ascorbic acid solution and 15 ml. of 0.1 *N* sulfuric acid into a 200-ml. beaker and titrate at once with the dye solution, using 15-ml. burets graduated to 0.05 ml. Titrate the solution to a light pink color which is permanent for 30 seconds. There is a tendency which must be guarded against to select darker and darker end points. Subtract from this titration the value obtained on a blank determination made by titrating a comparable acid water mixture to the same end point. The blank is usually about 0.3 ml. The dye factor in terms of milligrams of ascorbic acid per liter of milk when a 10-ml. aliquot of the milk is titrated is given by the following equation

$$\text{Factor} = \frac{\text{mg. of ascorbic acid weighed}}{2\ (\text{standardization titration} - \text{blank})}$$

The amount of original dye taken should be adjusted or the solution should be diluted to give a factor between 6.5 and 7.0.

SULFURIC ACID SOLUTION. Prepare a 10 *N* stock solution by diluting 285 ml. of concentrated sulfuric acid to 1 liter. For use, dilute 10 ml. of the stock solution to 1 liter and use approximately 25 ml. of this dilute solution for each determination.

ASCORBIC ACID OXIDASE. Freeze solid two to four medium to large green cucumbers, make 2 or 3 small holes about 0.6 cm. (0.25 inch) deep in the end of each, and suspend the cucumbers hole end downward in a piece of cheesecloth over a 1-liter beaker. At laboratory temperature the cucumbers will thaw and most of the juice (about 500 to 800 ml.) will drain out in 8 to 12 hours. A little squeezing of the bag will express an additional amount of juice. Most of the enzyme resides in the outer layer of the cucumber, and little is present in the seed portion. Therefore the yield of enzyme is not increased appreciably by excessive pressure or extraction of the pulp.

The juice may be concentrated by either freezing or pervaporation. In concentration by freezing about half of the water is frozen, the juice is expelled from the ice crystals, and about half of the water is then frozen in the expelled liquid. This process is continued until about 30 to 50 ml. of the juice concentrate remain. The concentrate is filtered and preserved by a drop or two of toluene or chloroform.

Concentration by pervaporation is more efficient. The expressed juice is placed in cellophane tubing about 1.8 cm. (0.75 inch) in diameter and the tube is looped over a glass rod. An electric fan is directed toward the loops. Evaporation to one

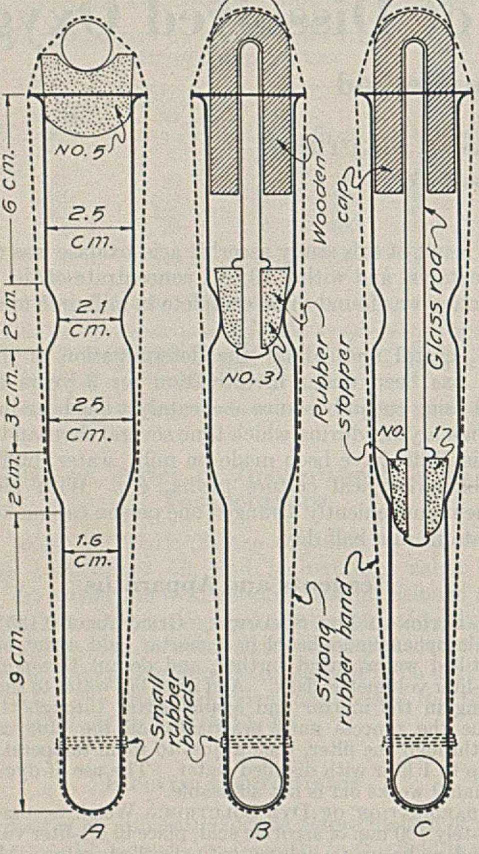

Figure 1. Special Tube for Determining Dissolved Oxygen by Ascorbic Acid–Ascorbic Acid Oxidase Method

tenth to one fourteenth of the original volume will take about 8 hours. The temperature of the juice remains considerably below room temperature, owing to the cooling effect of evaporation. The concentrate is filtered and preserved by a drop or two of toluene or chloroform. For each determination 0.1 ml. of the concentrated juice is used.

The concentrate preserved in this way in the dark at 20° to 25° C. will maintain its activity for about 1 month; if kept cold it remains active for 2 months or more. The enzyme is destroyed very rapidly by shaking. Mercuric chloride, sodium chloride, and glycerol ($^{1}/_{2}$ volume), when used in bactericidal concentration, rapidly inactivate the enzyme. One-half saturation with ammonium sulfate can be used as a preservative, but it is not so satisfactory as toluene or chloroform. The enzyme can be precipitated with an equal volume of acetone and the dried precipitate possesses activity.

Concentrated Ascorbic Acid Solution. Weigh 3.0 grams of *l*-ascorbic acid and 10 grams of sodium chloride and make up to 50-ml. volume with water. For each determination use 0.1 ml. of the solution.

Special Tubes for Oxygen Analysis. The tubes used for the oxygen determination are illustrated in Figure 1, which is largely self-explanatory.

The tube is so made that it can be closed at three levels, leaving no air trapped under the stopper after filling and after removing portions for titration. The filled tube with a No. 5 stopper in position *A* holds about 70 ml., with No. 3 stopper on a glass rod in position *B* about 45 ml., and with No. 1 stopper on a rod in position *C* about 20 ml. A large rubber band held over the small end of the tube by a small band holds the stoppers tightly in place. A round piece of wood partly drilled through is used to center and press downward on the glass rods. The upper end of this wooden cap is grooved, so that the band will not slip off.

In preparation for the taking of the sample the tube arranged as in *A* is used. A glass marble is used for mixing and is held in place in a depression cut on the top of the No. 5 stopper. The marble is mounted on the stopper of each tube, so that it will be in the hand while taking the sample and thus will not be forgotten after the sample is taken. The sample should not be taken with the marble in the tube, because air may be trapped between the marble and the bottom of the tube.

The authors have over 100 of these analysis tubes which were made by a glass blower. A large number of tubes was needed in studies of the oxygen content of milk which were carried out in commercial milk plants, and for studies on the rate of disappearance of oxygen from milk on holding.

Time-Saving Devices. The authors' work has required so many oxygen determinations that it has been found advisable to construct a number of devices to simplify and shorten the time required for the manipulation. These devices include a battery of 8 buret holders, beaker holders with pipet drainage support, oxygen analysis tube holder for shaking with spring clamps to hold in stoppers and tubes, a drainage rack, and various racks for holding the analysis tubes.

Method

Collection of Sample. The special oxygen-analysis tube as illustrated in Figure 1, *A*, is used for collecting the sample.

Preferably the milk is made to flow from the vat by a glass or rubber-tube siphon or from a milk line by a petcock and rubber or glass tube. Hot milk can be siphoned or passed through a cold water–jacketed coil and thus discharged cold without exposure to air. The marble and stopper are removed from tube *A*, the end of the siphon is inserted to the bottom of the tube, the milk is made to flow steadily with undisturbed surface into the sampling tube, and one to two volumes are allowed to overflow. The siphon is then removed and the marble is placed gently on the surface of the milk in the analysis tube and released. If the marble is dropped into the milk a row of bubbles of air will follow in its wake. The rounded No. 5 stopper is then inserted. The rounding of the stopper aids in preventing the trapping of air and in expelling the surface milk. The rubber band placed over the stopper holds it under tension, so that if the milk is cooled further the stopper will follow the surface down and not permit air to be drawn in between the wall and the stopper. The sample is now ready for analysis.

Samples can be taken satisfactorily by means of a specially constructed pipet of about 250-ml. capacity. The pipet should be rather long and narrow, with a stem that is long enough to reach to the bottom of the special oxygen-analysis tubes. In sampling, the pipet is slowly drawn full of milk, the end is inserted to the bottom of the oxygen-analysis tube, and about two tube volumes of milk are allowed to overflow slowly; the pipet is then withdrawn, the marble added, and the stopper placed in the tube.

Determination of Reduced Ascorbic Acid in Milk. The analysis tube is inverted several times to mix the sample by causing the marble to fall from one end to the other.

Pipet 10 ml. of milk from the upper compartment of the tube into a 200-ml. beaker to which 25 ml. of dilute sulfuric acid have previously been added. Duplicate aliquots may be taken if desired. Titrate with the dye solution, using a 15-ml. buret calibrated in 0.05-ml. divisions. In titrating it will be found that after a small amount of dye is added the solution will assume a pink color. If this color fades on standing, more dye is added. Continue the addition of dye in portions until a light but definite pink color remains for 30 seconds. This is taken as the end point of the titration. Before calculating the original ascorbic acid in the milk a blank of about 0.4 ml. (*12*) should be subtracted.

In order to save the time which may be required for the pink color to fade it is convenient to have 6 or 8 burets and titrate 6 to 8 samples at one time. If one is interested only in the oxygen content, determination of the reduced ascorbic acid present in the original milk may be omitted.

Additional Ascorbic Acid Added. Fresh milk contains only about one third enough ascorbic acid to react with the dissolved oxygen present in ordinary milk; therefore ascorbic acid must be added in amount to be amply sufficient to react with all the oxygen which may be dissolved in the milk.

Add 0.1 ml. of the concentrated ascorbic acid solution, using a 1-ml. buret pipet graduated to 0.01 ml. To the end of this pipet a small glass tube 25 cm. long and 3 mm. or less in outer diameter is attached by means of a short piece of rubber tubing 3 mm. in outer diameter and 1 mm. in internal diameter. The flow is controlled by a spring pinchclamp. Insert the glass tube to the bottom of the analysis tube and add 0.1 ml., making this addition to the bottom of the tube, so that none of the solution will be expelled with the overflow when the stopper is inserted later. If this buret is held in the hands ascorbic acid can be added rapidly to a number of tubes in succession.

The tube is stoppered according to the arrangement in Figure 1, *B*. The volumes have been so worked out that the surface milk is displaced in seating the stopper. Discard this excess milk and invert the tube continuously for 1.5 minutes to ensure complete mixing of the added ascorbic acid with the milk. Then remove the stopper and titrate an accurately measured 5-ml. portion, and a duplicate if desired, for ascorbic acid according to the procedure described above. The buret reading should be between 13 and 15 ml.

ADDITION OF ASCORBIC ACID OXIDASE. After removal of the sample to determine the original plus added ascorbic acid, add to the bottom of the analysis tube 0.1 ml. of the concentrated cucumber ascorbic acid oxidase, using a 1-ml. buret graduated to 0.01 ml., similar to that used for adding the ascorbic acid. The same buret should not be used, however, because great care should be taken to prevent contamination of the other burets and equipment with the ascorbic acid oxidase concentrate. Close the tube with the stopper according to the arrangement in Figure 1, *C*. Mix the contents of the tube by repeated inversion for 1 minute, and allow the tube to stand for 15 minutes, during which time the enzyme causes all the dissolved oxygen to react with the reduced ascorbic acid. Pipet 5 ml. and a duplicate, if desired, from the lowest compartment of the tube directly into 24 to 26 ml. of 0.1 *N* sulfuric acid previously placed in the beaker in preparation for the titration. The acid inactivates the enzyme and prevents further fast reaction between the air to which the aliquot is now exposed and the remaining ascorbic acid.

It is very necessary to make this titration immediately after pipetting out the sample. Although tests indicate that the enzyme is inactivated, nevertheless the rate of ascorbic acid oxidation is fairly rapid. Enough ascorbic acid should be present at the start so that this final titration does not fall below 2 ml. The 5-ml. pipet used in removing samples for this final titration should be reserved for the measurements involving this step only, because of the danger of producing errors in other titrations as a result of contamination with ascorbic acid oxidase.

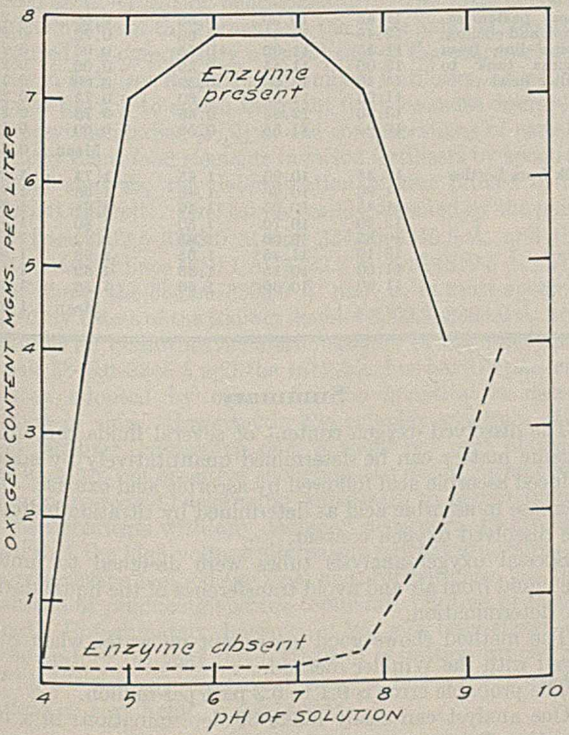

FIGURE 2. ACTIVITY-pH RANGE OF CUCUMBER JUICE ASCORBIC ACID OXIDASE

CALCULATION. The dye is standardized against pure ascorbic acid, so that when 10 ml. of milk are titrated, the milliliters of dye used less the blank times the factor gives the milligrams per liter of ascorbic acid in the milk.

The oxygen content in milligrams per liter of milk is obtained by multiplying the difference in dye titration before and after adding the ascorbic acid oxidase by twice the dye factor divided by 11. The dye factor is multiplied by 2 because only 5 ml. of milk were titrated and divided by 11 because the molecular weight of ascorbic acid is eleven times the atomic weight of oxygen.

From the oxygen content in milligrams per liter as calculated above subtract 0.45 mg. per liter for the blank resulting from the small contaminations with oxygen which occur during manipulation.

Evidence for Reliability of the Method

TITRATION BLANK ON ENZYME ADDED. The possibility of the enzyme's possessing dye-reacting properties, the ability of the sulfuric acid to stop enzyme action, and the duplicability of titrations were indicated by results obtained in a series of experiments carried out in conjunction with some routine oxygen determinations.

Two 5-ml. aliquots were removed from the middle compartment of each tube after incorporating the ascorbic acid, and were added directly to 25-ml. portions of the 0.1 *N* sulfuric acid in the 200-ml. beakers. To one beaker was then added 0.1 ml. of the ascorbic acid oxidase concentrate. Both beakers were titrated about 2 minutes later.

In all, 80 pairs were titrated and in 42 the difference was 0.1 ml. of dye or less. The greatest difference was 0.55 ml., the next greatest 0.45 ml. The average deviation was 0.14 ml. with signs disregarded and 0.04 ml. with signs considered. Since 0.1 ml. of the enzyme extract was titrated in this case, whereas only about one fourth of this amount would be present in the 5-ml. aliquot removed in the oxygen determination, the amount of dye reacting with the constituents of the enzyme extract is negligible. This was confirmed by titrating 5 ml. of the enzyme extract directly. These results also indicate the agreement expected in duplicate titrations.

pH RANGE OF ASCORBIC ACID OXIDASE ACTIVITY. The pH range over which solutions could be analyzed for oxygen without pH adjustment was determined by adding limited amounts of ascorbic acid oxidase to aerated buffer solutions. An average composite curve was constructed and is presented in Figure 2. Blank determinations for the decrease in ascorbic acid in the buffer solutions in the absence of added oxidase were also made. The kind and dilution of the buffer influenced the blank in the range from pH 4 to 7. At pH 8 the enzyme was inactivated, but the alkali in the absence of enzyme caused a decrease in the amount of ascorbic acid. The enzyme was almost completely inactive at pH 4. The enzyme in the pH range of 5 to 7.5 has sufficient activity to complete the reaction in the allotted 15 minutes.

The optimum pH range for the action of ascorbic acid oxidase from various sources is reported as follows: Tauber, Kleiner, and Mishkind (*16*) 5.56 to 5.93 and 5.38 to 5.57 for Hubbard squash; Srinivasan (*15*) 4.6 to 5.6 and 5.3 to 5.6 for *Moringa pterygosperina;* Ito (*7*) 6.0 for cucumber juice; and Ebihara (*2*) 6.0 to 6.5 for cucumber juice. The values reported for cucumber juice agree well with those in Figure 2. Since several buffers as well as milk and whey were used, the authors believe Figure 2 indicates the activity range of ascorbic acid oxidase from cucumber juice.

EFFECT OF AMOUNT OF ENZYME ADDED. Numerous experiments indicate that an excess of enzyme exerts no influence on the oxygen determination. Only one such experiment is cited here as an example.

TABLE I. COMPARISON OF OXYGEN DETERMINATIONS ON WATER

Oxygen Content		Oxygen Content	
Winkler	Ascorbic acid oxidase	Winkler	Ascorbic acid oxidase
Mg./l.	*Mg./l.*	*Mg./l.*	*Mg./l.*
0.00	0.01	5.2	5.2
0.00	0.07	5.8	6.0
0.00	0.08	6.1	6.0
0.02	0.00	8.2	8.0
1.6	1.6	9.8	9.7
2.0	1.9	10.1	10.3
2.9	2.7	10.8	10.6
4.1	4.1	10.9	10.7

Enzyme in the following amounts was added to a series of tubes of milk: 0.05, 0.10, 0.20, 0.30, 0.50, and 1.00 ml. The amounts of oxygen obtained were 8.24, 8.40, 8.18, 8.32, 8.41, and 8.45 mg. per liter, after corrections were made for the oxygen content of the enzyme concentrate.

BLANK ON BOILED OXYGEN-FREE WATER. A 5-liter short-necked round-bottomed Pyrex flask, three fourths full of water, was made to boil vigorously. After about one fifth and in some cases as much as one third of the water had been evaporated, samples were removed for oxygen determination by siphoning without interrupting the boiling. The siphon tube reached to the bottom of the boiling flask. The outer end of the siphon tube was made of coiled aluminum tubing surrounded by a cooling bath; thus cooled oxygen-free water was delivered at the lower end of the siphon. Three volumes of water were allowed to flow through the siphon and overflow the oxygen-analysis tube before the sample was taken for analysis. At various times 48 such samples were taken. The results obtained indicated a blank of 0.44 mg. per liter for oxygen-free water. Similar samples analyzed by the Winkler method gave a blank of 0.10 mg. per liter, including the blank on the reagents.

BLANK ON OXYGEN-FREE MILK. Milk was deaerated by a process which involved subjecting milk to a pressure sufficiently low to make the milk boil and thus convert some of its water into vapor, which was used as the agent to sweep out the dissolved oxygen. For these tests the pressure utilized was sufficiently low to decrease the temperature of the milk about 20° C. Determinations were made on 123 samples prepared in this way.

The average blank was 0.45 mg. of oxygen per liter of milk. The mean deviation from the average blank was 0.14, the range from 0.05 to 0.80, while 64 samples were found to deviate by 0.1 mg. or less from the average blank. These deviations are about those that would be encountered in duplicate titrations. The blank on milk agrees well with the average value of 0.44 obtained with water.

A few blank determinations should be run on each lot of enzyme, because occasionally for some unknown reason the blanks are higher.

COMPARISON BETWEEN WINKLER AND OXIDASE METHOD. A series of samples of water was analyzed for oxygen by both the Winkler and the ascorbic acid oxidase methods. The results obtained are presented in Table I. The difference between the results by the two methods is not significant. A blank of 0.10 mg. was subtracted from the results by the Winkler method and of 0.44 from the results by the ascorbic acid oxidase method.

EXAMPLE. As an example of the variations in results which might be expected when the determinations are made by one conversant with the method and particularly by one trained in determining the end point of the dye titration, Table II is presented. This gives results obtained with samples taken to test a particular run made on a commercial milk deaerator. Conversion factor for dye used was 1.20. Blank on method and reagents was 0.45 mg. per liter of oxygen.

Milk from the cans received from the dairy barn was dumped directly into the raw milk vat, the milk was gently agitated, and the samples were removed. Most raw milk at the time it enters the pasteurization process is much higher in oxygen than the raw milk of Table II because of passage through weigh tanks, pumps, storage vats, etc. The milk from the raw-milk storage vat was sucked into a milk deaerator and deaerated (*13*). The milk was pumped out of the deaerator and samples were taken from the line leading from the pump. The analyses of these samples represent the extent of deaeration.

By means of this pump the milk was forced through a plate heater, by which the milk was heated to 71.6° C. (161° F.) through a holding pipe (16 seconds), through a plate cooler, and finally into a surge tank, the surface of which was protected from air by a float which rested on the surface of the milk and rose and fell with the variations in the amount of milk in the surge tank. The milk passed to the filler bowl tank on the bottler by gravity. The third set of samples was taken from this line and represents the amount of air incorporated in the series of steps following deaeration.

The final set of samples was taken from the filled quart bottles and represents the amount of air incorporated in filling the bottles, using conventional valves but with a protecting float on the surface of the milk in the filler bowl.

Errors in the end point of the dye titration can be reduced by duplicate determinations on each tube. The results in Table II represent only single titrations on the various portions in each tube. Table II indicates the variations which might be expected in applying this method to samples taken at intervals during the run of a milk deaerator.

TABLE II. OXYGEN CONTENT OF MILK

(Samples taken at various time intervals during operation of a continuous commercial market milk deaerator)

	Dye Titration			Oxygen Content	
Stage of Sampling	Start	After enzyme	Difference	Difference, ml. × 1.2	After blank, 0.45
	Ml.	*Ml.*	*Ml.*	*Mg./l.*	*Mg./l.*
Raw milk in vat	11.25	6.45	4.80	5.76	5.31
	11.15	6.25	4.90	5.88	5.43
	12.05	7.15	4.90	5.88	5.43
	11.40	6.55	4.85	5.82	5.37
	11.75	7.80	3.95	(4.74)	..
	12.00	6.95	5.05	6.06	5.61
				Mean	5.43
After deaeration, sample following deaerator pump	13.90	13.35	0.55	0.66	0.21
	11.60	11.00	0.60	0.72	0.27
	11.60	10.90	0.70	0.84	0.39
	13.25	12.85	0.40	0.48	0.03
	12.55	12.10	0.45	0.54	0.09
	12.10	11.65	0.45	0.54	0.09
	13.00	12.60	0.40	0.48	0.03
	13.00	12.55	0.45	0.54	0.09
				Mean	0.15
After pasteurization and cooling, pipe line from surge tank to filler bowl	11.45	10.90	0.55	0.66	0.21
	12.45	11.85	0.60	0.72	0.27
	11.55	11.00	0.55	0.66	0.21
	12.00	11.45	0.55	0.66	0.21
	14.40	13.90	0.50	0.60	0.15
	11.95	11.35	0.60	0.72	0.27
	13.30	12.65	0.65	0.78	0.33
	12.05	11.55	0.50	0.60	0.15
				Mean	0.23
Milk from bottles	12.35	10.90	1.45	1.74	1.29
	11.80	10.40	1.40	1.68	1.23
	11.45	10.05	1.40	1.68	1.23
	12.20	10.70	1.50	1.80	1.35
	10.85	9.00	1.85	2.22	1.77
	13.10	11.45	1.65	1.98	1.53
	11.50	10.15	1.35	1.62	1.17
	11.90	10.60	1.30	1.56	1.11
				Mean	1.33

Summary

The dissolved oxygen content of several fluids containing organic matter can be determined quantitatively by adding reduced ascorbic acid followed by ascorbic acid oxidase. The decrease in ascorbic acid as determined by titration indicates the dissolved oxygen content.

Special oxygen-analysis tubes were designed to protect the liquid from air and avoid transference of the liquid during the determination.

The method shows good agreement on water when compared with the Winkler method.

The probable error is 0.1 to 0.2 part per million.

One analyst can easily make 30 determinations in a half day if sufficient conveniently arranged equipment is available.

Literature Cited

(1) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, 5th ed., pp. 531–2 (1940).

(2) Ebihara, T., *Japan. J. Biochem.*, 29, 199–215 (1939).

(3) Frankforter, G. B., Walker, G. W., and Wilhoit, A. D., *J. Am. Chem. Soc.*, 31, 35–43 (1909).

(4) Guthrie, E. S., Hand, D. B., and Sharp, P. F., 12th Ann. Rept., N. Y. State Assoc. Dairy and Milk Inspectors, pp. 101–10, 1938.

(5) Hand, D. B., and Chase, E. C., "Oxidation and Reduction of Vitamin C", Division of Biological Chemistry, Cincinnati Meeting, American Chemical Society.

(6) Hand, D. B., Guthrie, E. S., and Sharp, P. F., *Science* 87, 439–41 (1938).

(7) Ito, N., *J. Agr. Chem. Soc. Japan*, 14, 140–8 (1938).

(8) Leeder, J. G., and Herreid, E. O., Vermont Agr. Expt. Sta., *Bull.* 457 (1940).

(9) Linossier, G., *Bull. soc. chim.*, (3) 5, 63–6 (1891).

(10) Pulley, G. N., and Von Loesecke, H. W., Ind. Eng. Chem., 31, 1275–8 (1939).

(11) Rothchild, H., and Stone, I. M., *J. Inst. Brewing*, 44, 425–31 (1938).

(12) Sharp, P. F., *J. Dairy Sci.*, 21, 85–8 (1938).

(13) Sharp, P. F., Guthrie, E. S., and Hand, D. B., Proc. 33rd Ann. Convention, International Assoc. Milk Dealers, Laboratory Section, *Bull.* 20, 523–50 (1940).

(14) Sharp, P. F., Hand, D. B., and Guthrie, E. S., 13th Ann. Rept., N. Y. State Assoc. Dairy and Milk Inspectors, pp. 95–104 (1939).

(15) Srinivasan, M., *Biochem. J.*, 30, 2077–84 (1936).

(16) Tauber, H., Kleiner, I. S., and Mishkind, D., *J. Biol. Chem.*, 110, 211–18 (1935).

(17) Winkler, L. W., *Ber.*, 21, 2843–54 (1888).

(18) Winkler, L. W., *Z. angew. Chem.*, 24, 341–3 (1911).

Spectrochemical Analysis of Trace Elements in Fertilizers

ZINC

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FROM year to year an increasing number of plant nutrition experiments have shown that many serious deficiency diseases are due solely to an inadequate supply in the soil of minor plant food elements that are essential for normal plant growth. In a list of such elements—the so-called secondary plant nutrients—zinc has been accorded a prominent place. Thus, the white bud of corn, pecan rosette, bronzing of the tung-tree leaf, citrus little leaf, and leaf wilt of tobacco have all been ascribed to zinc deficiencies (*3*). The toxic effect of large quantities of the element, on the other hand, is also well recognized. Consequently a knowledge of the concentration of zinc in fertilizer materials and mixed fertilizers, added directly to the soil to enrich the plant food, becomes desirable.

In previous studies (*5*, *6*) of the concentrations of certain secondary plant food elements in mixed fertilizers by spectrochemical analysis, the determination of zinc proved to be somewhat difficult. Zinc can be readily detected by the pairs of arc lines 3302.6–3303.0 Å. and 3345.0–3345.5 Å. and the three persistent lines 4680.1 Å., 4722.2 Å., and 4810.5 Å. The first of these, the 3302.6–3303.0 Å. pair, is, in most spectra, masked by traces of the sodium doublet 3302.3–3303.0 Å. and unsuitable for quantitative determination. Of the other lines the pair 3345.0–3345.5 and the 4810.5 Å. line have in particular been adopted by others for the quantitative determination of zinc. However, in the complex spectrum of a mixed fertilizer, containing only a small per cent of zinc, these lines are not sensitive enough in the direct current arc source to overcome background sufficiently to permit intensity measurements with any degree of accuracy. Study has shown that the high-voltage alternating current arc source is a more sensitive method for zinc, and, furthermore, has the advantage of producing spectra comparatively free of background. Unfortunately, however, it has also been shown in this laboratory (*6*) that this method of excitation cannot be used for the analysis of fertilizer samples, but is restricted to solutions or very homogeneous solids.

Consequently, it has been necessary to abandon an attempt to determine zinc simultaneously with the other important secondary nutrients, boron, manganese, and copper in the fertilizer samples, and an effort has been made to find or devise a spectrochemical method for the quantitative determination of zinc that could be applied to a mixed fertilizer sample. The purpose of this paper is to describe: (1) the modifications in the spectrochemical procedure that have been adopted for the quantitative determination of zinc in mixed fertilizers and (2) the application of this method to the analysis of 44 representative mixed fertilizer samples whose complete composition has previously been determined by chemical methods in this laboratory (*2*).

Apparatus and General Procedure

The apparatus used, a large Hilger Littrow quartz spectrograph, a water-cooled arc stand operated by means of a direct current at a 220-line voltage, and a Bausch & Lomb nonrecording densitometer, have been described (*5*, *6*). The only modification in the apparatus has been the addition of two Nichrome wire resistance boards, inserted in the electrical circuit in parallel with the water-cooled rheostat, to permit the use of higher currents. With this arrangement any desired current from 5.0 to 25.0 amperes can be conveniently obtained.

As in the analyses for boron, manganese, and copper the direct current arc method of excitation using a cupped graphite anode and a pointed graphite cathode was selected. The well-known logarithmic step-sector method of Scheibe in conjunction with the internal standard method of Gerlach was retained and the samples were again analyzed without any preliminary chemical treatment.

Modified Experimental Procedure for Zinc

A method satisfactory for an accurate spectrochemical determination of zinc in a mixed fertilizer would include the measurement of a zinc line of greater sensitivity than those ordinarily used, and/or photographing under conditions where the background produced is considerably less. Rogers (*8*) investigated the use of the zinc line at 2138.6 Å. in order to avoid preliminary chemical treatment in the analysis of

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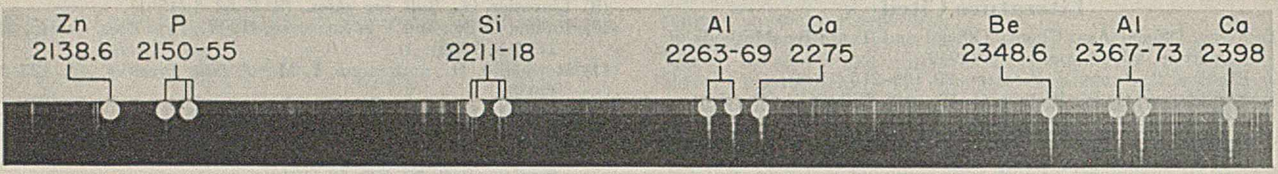

FIGURE 1. SPECTROGRAM OF MIXED FERTILIZER SAMPLE FOR QUANTITATIVE DETERMINATION OF ZINC

various plant materials. Using photographic plates treated with a special ultraviolet sensitizing material, this line can be photographed at appreciably higher intensities than any of the zinc lines in the near ultraviolet, and, except with very long exposures, the background in this region is practically negligible.

Several investigators have shown that when a rapidly volatilizing material is consumed in a direct current arc more intense lines can be obtained by the use of higher currents. Consequently, the effect of current on the rapidly volatilizing zinc was studied. These studies showed that for the volatilization of a given amount of sample the sensitivity of the zinc line at 2138.6 Å. does not change appreciably with increasing current. However, the higher current permits the complete volatilization of a larger sample without increasing the exposure time and when a larger sample and higher current are used, the arc strikes more directly to the sample, completely volatilizing it while consuming relatively less of the graphite holder. This results in effectively increasing the blackness of the zinc line over its background. For this reason throughout the zinc analyses a current of 20 amperes and a sample of 20 mg. were adopted.

When duplicate analyses of the fertilizer samples for zinc were first attempted under these conditions, inconsistently high results were encountered at irregular intervals. Further investigation showed that certain samples, in particular when the silicon content was high, did not completely volatilize before the graphite cup was consumed. Consequently, last traces of the sample, presumably containing some of the slowly volatilizing beryllium, added to the fertilizer sample as the constant internal standard, were lost. This would mean that the intensity of the beryllium line would be weakened. Consequently, the ratio of the intensity of the zinc line to the intensity of the beryllium line and the resulting value for the concentration of the zinc would be too high.

This difficulty is most readily overcome by increasing the depth of the graphite cup to assure complete volatilization of the sample. Mannkopff and Peters (*4*) have studied the effect of cup depth best suited for various substances when they have different melting points, and Pierce, Torres, and Marshall (*7*) reached the conclusion that with readily volatile elements higher intensity may be obtained if the sample is placed in a deep cup. This conclusion was confirmed in the present investigations with zinc. When the cup depth was increased from 6 to 10 mm., not only was complete volatilization of the sample assured, but the sensitivity of the zinc line was increased. If the sensitivity of a spectrum line can be sufficiently increased, it can be photographed, by use of shorter exposure time, entirely free from background. In the present case, where a stepped sector is used during each exposure, this means that if the sensitivity can be sufficiently increased, the line can be measured at a step where it is free from background. When the fertilizer samples were volatilized from deep cups, the zinc line was increased in sensitivity, so that measurements entirely free from background could be made even in those cases where the zinc concentration in the fertilizer was extremely small.

The conditions finally adopted for the analysis of zinc were: a direct current arc maintained by a 220-line voltage at 20 amperes current, an electrode separation of 4 mm., and a slit 7 mm. high and 0.06 mm. wide. The cathode is a pointed graphite rod 0.47 cm. (0.19 inch) in diameter and the anode a graphite rod 1.25 cm. (0.25 inch) in diameter into which a flat-bottomed cup 10 mm. deep, 4.3 mm. in diameter, and with a wall 0.5 mm. thick, has been cut. A 20-mg. sample of the mixed fertilizer is placed in this cup, the spectrograph is adjusted to photograph the region 2000 to 2450 Å., and the sample is arced for 2.5 minutes. The intensities of the zinc line at 2138.6 Å. and the beryllium line at 2348.6 Å. are measured and the ratio of these intensities is used to determine the zinc concentration from the working curve. Eastman 1-0 spectroscopic ultraviolet sensitive plates were selected as the fastest obtainable. The plates were constantly brushed during development in Eastman developer D-76c for 5.5 minutes at 18° C. Figure 1 shows a section of the spectrum of a fertilizer sample when photographed under these conditions.

TABLE I. COMPARISON OF SPECTROCHEMICAL ANALYSIS FOR ZINC WITH CHEMICAL VALUES

Fertilizer Grade[a]	Source	Year Sampled	Spectrochemical[b]	Chemical[c]	Ratio Chemical/ Spectrochemical
			Av. %	%	
1*-9-4	N. Y.	1929	0.0415	0.032	0.77
2*-8-10	N. Y.	1929	0.0144	0.012	0.83
2-12-6	Ohio	1929	0.0084	0.033	3.81
7-5-4	Md.	1926	0.0092	0.0080	0.87
4*-8-4	Va.	1930	0.092	0.0080	0.09
3-8-3	Va.	1930	0.012	0.0080	0.67
4*-8-4	N. C.	1925	0.015	0.0080	0.53
4*-8-4	Va.	1926	0.0261	0.060	2.30
3-8-5	Md.	1930	0.036	0.0080	0.22
4*-12-4	Va.	1930	0.0185	0.048	2.59
5*-8-5	Penna.	1929	0.0100	0.032	3.20
5*-8-7	Va.	1930	0.062	0.048	0.77
7*-6-5	Va.	1930	0.059	0.004	0.07
2-9-5	Md.	1935	0.00495	0.0080	1.62
2-12-2	Ind.	1935	0.014	0.012	0.86
2-12-4	Md.	1935	0.014	0.0080	0.57
3*-9-3	Ga.	1935	0.00385	0.0080	2.08
4*-8-4	Ga.	1935	0.0255	0.032	1.25
3-8-6	N. C.	1935	0.047	0.000	–
4*-8-6	S. C.	1935	0.00375	0.0016	0.43
4-8-4	La.	1935	0.0255	0.000	–
4-8-5	Md.	1935	0.031	0.016	0.52
4-8-7	N. Y.	1935	0.065	0.016	0.25
4-10-7	Va.	1935	0.0088	0.008	0.91
4-12-4	Ark.	1935	0.014	0.014	1.00
6-6-5	Va.	1935	0.018	0.024	1.33
6*-8-6	Mass.	1935	0.0099	0.008	0.81
3-21-6	Ohio	1929	0.108	0.064	0.59
4-16-4	N. Y.	1935	0.0445	0.020	0.45
4*-16-10	Penna.	1930	0.045	0.016	0.36
4-24-12	Ind.	1934	0.031	0.032	1.03
8-12-20	Maine	1935	0.253	0.012	0.05
8*-16-8	Ga.	1927	0.033	0.144	4.36
8-16-12	Minn.	1933	0.049	0.045	0.92
8*-16-16	Mass.	1935	0.080	0.040	0.50
9*-27-9	Va.	1928	0.0233	0.072	3.09
12-24-12	Germany	1930	0.0125	0.008	0.64
10-30-10	N. J.	1929	0.0185	0.004	0.22
17-34-17	Ala.	1932	0.0275	0.028	1.02
0-10-4	Tenn.	1935	0.0241	0.036	1.49
0-10-10	N. Y.	1929	0.034	0.004	0.12
0-12-5	Md.	1935	0.030	0.012	0.40
0-12-12	Ind.	1934	0.030	0.008	0.27
0-14-6	Ohio	1926	0.036	0.008	0.22

[a] Grade formulas stand for percentages of N, P_2O_5, and K_2O in this order except that numbers indicated by asterisk stand for percentages of NH_3.

[b] Values expressed as element in accordance with recommendation adopted by the Association of Official Agricultural Chemists.

[c] Chemical results from Lundstrum and Mehring are converted to per cent of element (Zn) to facilitate comparisons.

Table II. Precision of Spectrochemical Analysis of Zinc

Trial	Concentration	Deviation from Mean
	%	%
1	0.015	0.0006
2	0.013	0.0014
3	0.015	0.0006
4	0.017	0.0026
5	0.014	0.0004
6	0.012	0.0024
7	0.016	0.0016
8	0.013	0.0014
	Av. 0.0144	0.00138

Table III. Accuracy of Spectrochemical Analysis of Zinc

Fertilizer Grade[a]	Source	Year Sampled	Zn Added	Original Spectrochemical Analyses	Subsequent Spectrochemical Analyses
			%	*Av.* %	%
1*-9-4	N. Y.	1929	0.032	0.0415	0.0758
4*-8-4	Va.	1926	0.032	0.0265	0.0496
4*-8-4	Ga.	1935	0.016	0.0255	0.0386
6*-8-6	Mass.	1935	0.016	0.0099	0.0268
12-24-12	Germany	1930	0.048	0.0125	0.0569
0-14-6	Ohio	1926	0.048	0.0360	0.0819

[a] Grade formulas stand for percentages of N, P_2O_5, and K_2O in this order, except that numbers indicated by asterisk stand for percentages of NH_3.

A series of standards prepared by duplicating as closely as possible the average composition of the 44 mixed fertilizers as determined chemically was available from previous analyses of the fertilizer samples. As these standards had been found to be entirely satisfactory for the analyses of boron, manganese, and copper and as they contained zinc in concentration from 0.0008 to 0.4 per cent and 0.05 per cent beryllium as an internal standard, they were used to prepare a working curve for the zinc analyses, although the choice of an element as an internal standard which volatilizes at a rate closer to that of the rapidly volatilizing zinc than does the slow-volatilizing beryllium would have been more advantageous. Figure 2 shows the straight-line working curve obtained by plotting the intensity ratios against the known zinc concentrations, the circular and triangular symbols representing two different sets of standards photographed on separate plates.

Discussion of Results

The results obtained from duplicate analyses of the fertilizer samples are listed in Table I. The average deviation from the mean of the duplicate determinations of the 44 samples is ±4.88 per cent. The deviations range from a minimum of 0.0 per cent to a maximum of ±12.0 per cent and with but three exceptions are within ±10.0 per cent.

As with the boron, manganese, and copper determinations, precision and accuracy tests have been made during the zinc analyses. Table II lists the results obtained from repeated analyses of the same fertilizer sample from time to time during the course of the zinc analyses. The arithmetical mean and the average deviation from the mean are given at the bottom of the second and third columns, respectively. From the data in this table the probable error of the mean, $0.6745 \sqrt{\frac{\Sigma(d^2)}{\eta(\eta - 1)}}$, is found to be 0.000402. Table III lists the results obtained from repeated analyses of six fertilizer samples, selected at random, after known amounts of zinc had been added to each. These results, while insufficient for any statistical analysis, show that the accuracy is of the same order as the precision.

Thus, the method devised for the analysis of zinc is shown to be capable of a precision and accuracy equal to those obtained in the analysis of boron, manganese, and copper. The use of plates which are treated with a special sensitizing material, which must subsequently be removed, for accurate quantitative work is thereby justified. With measurements entirely free from background a somewhat higher precision might have been expected (*5*). However, the use of faster plates which never appear to be as clear and as free from chemical fog as the slower process plates used for the boron, manganese, and copper determinations, as well as possible slight variations in the sensitizing material, may counterbalance this advantage.

Table I also gives a comparison between the average spectrochemical values and the chemical values obtained by Lundstrom and Mehring (*2*). In general, the chemical values tend to be somewhat lower than the spectrochemical. This same tendency was found by Rogers and Gall in a comparison of spectrochemical and chemical methods for the determination of zinc in plant ash (*9*). The mean of their spectrochemical values was usually appreciably higher than the corresponding average of the chemical values. In the results compared in Table I, the difference between the values obtained by the two methods is usually within a twofold factor—i. e., the ratio of chemical to spectrochemical is within a variation of 0.50 to 2.00. When the average of the spectrochemical values is particularly high, approaching or exceeding 0.1 per cent (the chemical values with but a single exception never exceeding 0.09 per cent), and when the chemical value is reported as 0.000 per cent, the agreement becomes particularly poor.

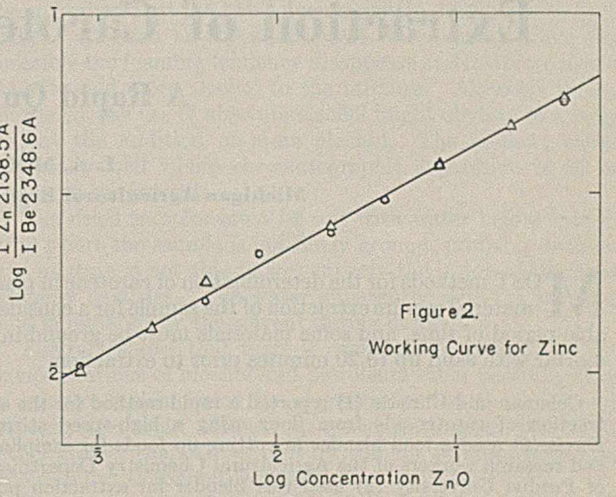

Figure 2. Working Curve for Zinc

From the working curve, Figure 2, concentrations of zinc from 0.0008 per cent (8 parts per million) to 0.4 per cent (4000 parts per million) can be determined. These values represent only the limits established for the analysis of the 44 fertilizer samples, where the concentrations always fall well within these limits. The upper limit of the method has not been investigated but, as pointed out by Rogers (*8*), is probably not much greater than 1 per cent where reversal of the 2138.6 Å. zinc line would be encountered. However, when concentrations of this magnitude are reached, the objection to the lines in the near ultraviolet would no longer be valid.

Tests have been made which show that the lower limit of the method cannot be extended below about 0.0002 per cent (2 parts per million).

Possible interference of an iron line at 2138.6 Å. has been suggested by Rogers (*8*). Harrison (*1*) assigned this line a relative intensity in the arc source of only 8, as compared to the zinc line 800; hence interference would not be expected until the iron concentration became relatively high. However, tests were made concerning the possible interference of this line and a copper line at 2138.5 Å. to which Harrison assigns an intensity value of 25. These tests show that, under the conditions of the zinc analyses, 3.0 per cent iron and 1.0 per cent copper, values in excess of those ever found in the fertilizer samples by previous chemical and spectrochemical analyses, give no measurable densities of the lines at 2138.6 and 2138.5 Å., respectively.

Summary

A method has been described for the spectrochemical determination of zinc in mixed fertilizers and the method applied to the analysis of 44 representative mixed fertilizers of known chemical composition. The method is capable of determining zinc within the limits of 0.0002 per cent (2 parts per million) to approximately 1 per cent (1 part per hundred) with an accuracy within ±5 per cent, thus equaling methods previously described for the analysis of boron, manganese, and copper. As the method involves the use of plates which have been treated with a special sensitized coating, the accuracy obtained confirms the fact that these plates are sufficiently consistent to permit quantitative determinations without appreciable sacrifice of accuracy. Comparison of the values obtained by the spectrochemical method with those obtained by chemical analysis show that in general the chemical values are lower than the spectrochemical values, a discrepancy previously noted elsewhere in similar comparisons.

The method described augments the number of essential trace elements whose concentrations could be guaranteed by supplemental spectrochemical analysis following the usual chemical determinations of the primary plant nutrients. The determinations when the concentration of zinc exceeds 1 per cent can be readily achieved by use of the zinc lines at 3345.0 or 4810.5 Å.

Literature Cited

(1) Harrison, G. R., "Wavelength Tables", New York, John Wiley & Sons, 1939.
(2) Lundstrom, F. O., and Mehring, A. L., Ind. Eng. Chem., 31, 354 (1939).
(3) McMurtrey, J. E., Jr., and Robinson, W. O., Yearbook U. S. Dept. Agr., p. 807, 1938.
(4) Mannkopff, R., and Peters, C., *Z. Physik.*, 70, 444 (1931).
(5) Melvin, E. H., and O'Connor, R. T., Ind. Eng. Chem., Anal. Ed., 13, 520 (1941).
(6) Melvin, E. H., and O'Connor, R. T., "Proceedings of Seventh Summer Conference on Spectroscopy and Its Application", p. 42, New York, John Wiley & Sons, 1940.
(7) Pierce, W. C., Torres, O. R., and Marshall, W. W., Ind. Eng. Chem., Anal. Ed., 12, 41 (1940).
(8) Rogers, L. H., *Ibid.*, 7, 421 (1935).
(9) Rogers, L. H., and Gall, O. E., *Ibid.*, 9, 42 (1937).

Extraction of Carotene from Plant Material

A Rapid Quantitative Method

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MOST methods for the determination of carotene in plant material require extraction of the sample for a considerable period of time, and some materials must be ground in a mortar with sand up to 20 minutes prior to extraction.

Coleman and Christie (*1*) reported a rapid method for the extraction of carotenoids from flour using a high-speed stirrer. Davis (*2*) used a food blender in cutting up foods for sampling, and research workers of the Agricultural Chemistry Department of Purdue University (*4*) used this blender for extraction purposes. It consists of a quart heavy glass container of cloverleaf design in cross section, at the bottom of which is an assembly consisting of knives turned by a motor at a speed of about 10,000 r. p. m. Thus the material is subjected not only to considerable maceration by the knives but also to agitation.

This paper presents a rapid quantitative method for the extraction of carotene from certain plant materials, using the food blender (manufactured by the Waring Corporation, New York, N. Y.) in conjunction with a foaming solvent.

Experimental

Several solvents were tried in extracting the carotene from plant material but because of the high speed of the blades and an attempt to use as small an amount of solvent as possible, there was considerable splashing and jumping of the solvent. Quantitative results were therefore not attainable unless loss of the solvent from the top of the container could be prevented. By experimentation it was found that a certain mixture of 95 per cent ethyl alcohol and petroleum ether (Skelly-solve B used throughout this work) produced a foam which prevented this splashing and jumping of the solvent. In order to study the limitations of concentration of the two constituents of the foaming solvent the following experiment was performed.

A total of 200 ml. of varying concentrations of 95 per cent ethyl alcohol and petroleum ether were made up in 250-ml. Erlenmeyer flasks, which were placed in a water bath at 27° C. The various mixtures were then successively placed in the container of the blender and the time in seconds was noted for the last bubble of the foam to disappear after the motor had been turned off. Both constituents had an initial 3-second period for the last bubble to disappear, which in reality was the time required for the knives to stop after the motor had been turned off. The results are shown in Figure 1.

Fresh green samples were cut up with scissors sufficiently fine for accurate sampling. Silage samples were ground through a food chopper preparatory to sampling. One to 4 grams of the prepared sample were weighed out and transferred to the container of the blender.

The foaming mixture used in this study was approximately 57 per cent of 95 per cent ethyl alcohol by volume. It consisted of 100 ml. of 95 per cent ethyl alcohol and 75 ml. of petroleum ether which was added to the blender containing the sample. The blender was then run for 5 minutes, which was sufficient time for macerating the sample and extracting the carotene. Sometimes it was necessary to add more alcohol to the mixture to induce foaming. The lack of foaming is due to the water contained in the sample.

The residue was permitted to settle, and the supernatant liquid was transferred to a separatory funnel with the aid of a glass rod and a small funnel. Sufficient water was added to make the alcohol concentration equal to about 80 per cent, after which the hypophase was separated from the epiphase. The residue was then washed with 30 ml. of petroleum ether, which in turn was used to extract the alcohol layer. The residue and alcohol layer were again twice treated with 30 ml. of petroleum ether. The combined petroleum ether extracts were washed with tap water six or seven times to remove all the alcohol. The extract was concentrated under vacuum in an Erlenmeyer flask to about 25 ml., the process being hastened by running hot water over the flask. The carotene was then separated from the other pigments by passing the extract through a column of dicalcium phosphate (*3*). The filtrate was made up to volume and the carotene concentration evaluated with a photoelectric colorimeter.

With dried samples some difficulty was encountered in obtaining quantitative extraction. Commercial dehydrated alfalfa-leaf meals could be extracted quantitatively without any difficulty. However, the carotene was not extracted quantitatively from hay samples that were put through the 1-mm. screen of a Wiley mill. This difficulty was overcome by placing the weighed sample (2 grams) on a filter paper in a funnel and washing with 25 ml. of hot tap water (60 to 70° C.). The excess water was drawn off by light application of vacuum, the sample was then transferred, and the same procedure was followed as with the green material.

In order to determine whether the treatment had extracted the carotene quantitatively, the values obtained were checked against those secured by a recently published method (*3*) which consisted mainly of grinding the sample in a mortar with sand and refluxing for one hour with alcohol. The remaining part of the procedure was identical with that outlined above. The results of these comparisons are shown in Table I.

Discussion

The blender with the foaming mixture extracted the carotene as effectively in 5 minutes as refluxing the sample with alcohol for 1 hour. The extraction method has another advantage in that it is not necessary to grind the silage or green samples in a mortar previous to extraction, and furthermore, in the case of fresh green material enzyme destruction of the carotene is minimized because of the short time required to macerate the sample.

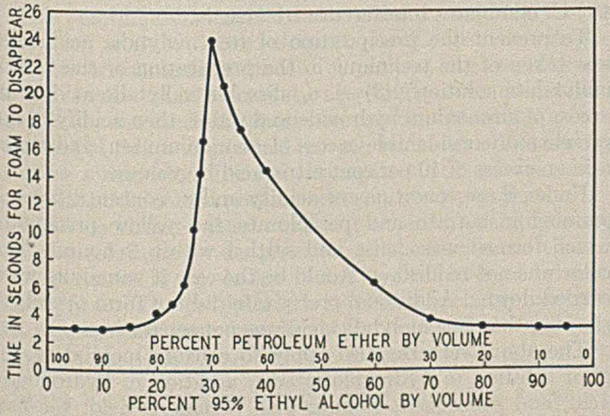

Figure 1. Relationship between Stability of Foam and Concentration of 95 Per Cent Ethyl Alcohol and Petroleum Ether

Table I. Carotene Values

(Obtained by refluxing with alcohol for 1 hour or extracting in the blender for 5 minutes)

Sample	Alcohol Extraction	Blender Extraction
	Micrograms per gram	
Fresh green material		
June grass	153.0	158.0
Clover	195.0	202.5
Oats	130.0	130.0
Alfalfa leaves	97.0	105.0
Rye	100.0	102.0
Dock leaves	135.0	130.0
Dandelion leaves	80.0	75.0
Carrot tops	135.0	141.0
Cabbage-weed leaves	131.0	135.0
Plantain leaves	100.0	100.0
Clover leaves	169.0	170.0
Carrot root	103.0	109.0
Silages		
Alfalfa-brome grass	42.5	40.5
	30.3	31.0
Sweet clover	5.5	5.0
	5.3	5.0
Corn	4.5	4.8
	1.0	1.3
Alfalfa	42.3	36.8
	32.5	31.0
	25.0	24.5
Hays		
Alfalfa	11.3	12.0
	5.5	6.0
	7.5	7.8
	24.5	25.0
	7.5	8.0
	13.0	14.5
	1.8	2.1
Soybean	30.0	30.5
	82.0	82.0
	62.5	62.5
	51.0	54.0
	53.0	54.0
Dehydrated alfalfa-leaf meal	61.0	61.0
	64.0	63.0

In making carotene determinations by this method certain precautions are necessary. The concentration of water must be so limited that the two solvents remain miscible with each other. As soon as the addition of water makes them immiscible the foaming tendency disappears and it is often necessary to add more alcohol to the mixture. Although it was not tried, the use of absolute alcohol might obviate to a large extent the addition of more alcohol. The method works especially well where chromatographic separation is to be made on the extract.

The dried samples must be wet with water before extraction where the sample is not finely ground, probably because the mixture is not able to wet entirely the inside of the large stemmy particles. The water apparently wets the particles and is replaced by the solvent during extraction.

Figure 1 shows that there is considerable latitude in the concentrations of alcohol and petroleum ether possible, since a mixture which foams for a greater period than 4 to 4.5 seconds is usable. However, concentrations of petroleum ether greater than 43 per cent by volume were not tested for their ability to extract carotene.

There is some indication that the mixture of the two solvents is a better solvent than alcohol by itself—for instance, only small amounts of lycopene were extracted from tomatoes with alcohol, while the mixture was quite effective.

Experiments with mixtures of other solvents indicated that the foaming tendency was largely limited to these two solvents.

Literature Cited

(1) Coleman, D. A., and Christie, A., *Cereal Chem.*, 3, 84 (1926).
(2) Davis, W. B., *News Ed.* (*Am. Chem. Soc.*), 17, 752 (1939).
(3) Moore, L. A., Ind. Eng. Chem., Anal. Ed., 12, 726 (1940).
(4) Purdue University, personal communication.

Journal article 510 (N. S.).

Rapid Determination of Phosphorus in Ferromolybdenum and in Calcium Molybdate

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Phosphorus in ferromolybdenum and in calcium molybdate is determined (without previously filtering off any compounds) as the yellow phosphomolybdate.

TWO methods have been given for the determination of phosphorus in ferromolybdenum (*2*).

In the first method, the solution of the alloy is treated with ammonium or sodium hydroxide, to remove most of the molybdenum. Two separations are usually suggested; if only one separation is used a long process of washing is required. With the bulk of the molybdenum removed, the iron precipitate can be dissolved and the phosphorus precipitated with ammonium molybdate, as in steels. In a second method, the phosphorus is separated as magnesium ammonium phosphate in the presence of citric acid. This method is no more satisfactory for phosphorus than is the separation of magnesium under the same conditions. Precipitation is slow (overnight) and not always complete.

With calcium molybdate, ferric chloride can be added to the solution of molybdate with subsequent separation by ammonium hydroxide, as in the ferromolybdenum method.

This paper presents a more rapid routine method for the determination of phosphorus in ferromolybdenum and in calcium molybdate.

Experimental

FERROMOLYBDENUM. A 1-gram sample was transferred to a tall form 300-cc. beaker, 10 cc. of $(1 + 2)$ nitric acid were added, and the beaker was immediately covered with a watch glass. After the first rapid reaction, the beaker was placed on a warm plate to complete solution of the alloy, then removed from the plate and hydrofluoric acid was added (10 drops for low and 20 drops for high-silicon alloys). Then 10 cc. of perchloric acid (70 per cent technical) were added, and the beaker was set in a "no-bump beaker" holder on the hot plate. The cover was removed to distill out the nitric and hydrofluoric acids, then replaced. Heating was continued until considerable amounts of molybdenum trioxide separated. Poor results were obtained on those samples which were not fumed well.

The beaker was cooled, and about 25 cc. of water were added. From a graduate, ammonium hydroxide (specific gravity 0.9) was added. A volume of 15 cc. was found satisfactory to dissolve all the trioxide and precipitate ferric hydroxide. Another 25-cc. portion of water was added to cool the mixture. A thermometer was placed in the beaker, and in order to keep the temperature below 40° C. the reaction beaker was placed in a larger beaker containing cold water. Nitric acid (specific gravity 1.42) was added from a buret, and the amount of acid required to dissolve the ferric hydroxide was noted. Measured excess portions of nitric acid (6, 8, 10, and 12 cc.) were added to a series of beakers to determine the optimum volume of nitric acid, 50 cc. of molybdate solution were added at once, and the mixture was stirred several minutes, or put in a shaking device. The cooling bath, which was now warm, was not removed (for hand stirring) because it accelerated separation of the yellow precipitate. The time of settling and the character of the precipitate were noted. The precipitate was filtered and titrated as usual by the alkalimetric method.

Since no standard ferromolybdenum was available, a synthetic mixture of 0.5 gram of standard steel and 1 gram of ammonium molybdate was used to check the composition of the precipitate.

CALCIUM MOLYBDATE. A 1-gram sample was used. The solvent was 2 to 1 hydrochloric acid (*3*) plus one drop of nitric acid. Heat was applied till only a small residue was left. From this point, the same procedure was followed as for ferromolybdenum.

Procedure

FERROMOLYBDENUM. Transfer a 1-gram sample to a tall 300-cc. beaker, add 10 cc. of 1 to 2 concentrated nitric acid, cover with a watch glass, and heat, if necessary, to effect complete solution. Remove from the hot plate, add about 10 drops of hydrofluoric acid (20 drops for high silicas) and 10 cc. of 70 per cent (technical) perchloric acid, place in a no-bump beaker, heat to heavy fumes, and maintain for about 5 minutes.

Cool, add 25 cc. of water, shake, add 25 cc. of ammonium hydroxide (specific gravity 0.9), and stir to dissolve all yellow precipitate. Add 25 cc. more of cold water, place the reaction beaker in a larger beaker of water, add concentrated nitric acid (sp. gr. 1.42) until the ferric hydroxide is dissolved (approximately 20 cc.), and add just 10 cc. excess of acid. While adding the acid, the temperature of the solution should not pass 45° C. At once, add 50 cc. of molybdate solution (*2*), stir or shake, let stand 2 hours, filter, wash, and titrate as usual with standard acid and alkali ($0.148\ N$). 1 cc. = 0.02% P on a 1-gram sample.

CALCIUM MOLYBDATE. Transfer a 1-gram sample to a tall 300-cc. beaker, add a mixture of 15 cc. of 2 to 1 hydrochloric acid and 1 drop of nitric acid, and heat to nearly complete solution. Remove from the hot plate, add about 20 drops of hydrofluoric acid and 12 cc. of 70 per cent (technical) perchloric acid, place in a no-bump beaker, and heat to heavy fumes.

Complete as in the second paragraph for ferromolybdenum, noting that ammonium hydroxide yields a white precipitate with calcium molybdate instead of the red iron precipitate with ferromolybdenum.

Discussion

The obvious way to determine phosphorus in ferromolybdenum is to dissolve the sample in nitric acid and precipitate with molybdate. The fact that standard texts do not present this method indicates that it has not been entirely successful.

The problems are: to take care of interfering elements, to prevent the separation of free molybdic acid, and to form the easily filterable "yellow precipitate".

Of the interfering elements, silica and insoluble silicates are taken care of by hydrofluoric acid. Organic matter is oxidized by nitric and perchloric acids. Vanadium, present in only small amounts, is taken care of by the relatively high nitric acid content (*1*). Likewise, the small amounts of tungsten are converted to ammonium tungstate by the excess ammonium hydroxide, and upon acidification neither retard precipitation of phosphorus nor precipitate as tungstic acid in this large volume of solution (150 cc.). Precipitation at 40° C. eliminates interference by arsenic.

To prevent the precipitation of free molybdic acid, note was taken of the technique in the preparation of the "stock molybdate solution" (*3*)—i. e., dissolve molybdic acid in an excess of ammonium hydroxide and water, then acidify in the presence of considerable excess of ammonium ion, and maintain an excess of 10 per cent nitric acid by volume.

Under these conditions of acidity and of concentrations of ammonium nitrate and perchlorate the yellow precipitate which formed was dense and settled within 2 hours. The color was not reddish, as would be the case if vanadium were carried down. Additional precipitate did not form overnight showing that free molybdic acid was not separating.

The above remarks also apply to calcium molybdate, for after solution in hydrochloric acid, addition of hydrofluoric acid, and subsequent fuming with perchloric acid, the material is found in the same state as the ferromolybdenum.

One precaution must be emphasized. After the sample has been fumed with perchloric acid, the beaker is removed

Table I. Determination of Phosphorus in Synthetic Samples

Ferromolybdenum	
0.025, 0.026, 0.028%	(Si 0.64%)
0.026, 0.027, 0.028%	
0.025, 0.027, 0.027%	
0.028, 0.030%[a]	(Si 0.77%)
0.036, 0.038%	(Si 0.90%)
Calcium Molybdate	
0.014, 0.015, 0.017%	

[a] Manufacturer's analysis: P 0.028%, Si 0.74%.

from the hot plate and cooled, and 25 cc. of water are added, followed by 25 cc. of ammonium hydroxide. The mixture must be stirred to dissolve all the molybdic acid. Failure to do so leads to high results. Previously, solid ammonium nitrate had been used (because of its cooling effect) in conjunction with less ammonium hydroxide, but the technique was changed to include 25 cc. of ammonium hydroxide to be certain that no deposits of oxide remained.

The purpose of the "synthetic sample" is to check the yellow precipitate, and to show that the standard sodium hyhroxide–hydrochloric acid solutions should be 0.148 *N* as with the usual precipitations for phosphorus at 40° C. Ordinary yellow precipitate, $(NH_4)_3PO_4.12MoO_3$, requires 23 moles of sodium hydroxide for each mole of phosphorus P; but when precipitation takes place at about 80° C. the yellow precipitate is $(NH_4)_3PO_4.12MoO_3.HNO_3$, which requires 24 moles of sodium hydroxide per mole of phosphorus. Thus, the fact that there exists more than one yellow precipitate requires proof as to whether or not a new yellow precipitate forms under the new conditions of precipitation. The results indicate that the familiar $(NH_4)_3PO_4.12MoO_3$ forms.

Two previous papers (*4*) have discussed the determination of sulfur and copper in ferromolybdenum.

Results

The first synthetic sample was 1 gram of ammonium molybdate plus 0.5 gram of Bureau of Standards No. 82 (0.102% P, 2.78% C, 2.09% Si), planned to represent a high-silicon high-carbon ferromolybdenum. This represented 0.051 per cent phosphorus. The recovery was 0.051 and 0.051 per cent. A second synthetic sample used Bureau of Standards No. 19c (0.049% P, 0.21% C, 0.20% Si). This represented 0.025 per cent phosphorus. The recovery was 0.023 and 0.026 per cent phosphorus.

Results for routine determinations are found in Table I.

Literature Cited

(1) Johnson, C. M., "Chemical Analysis of Special Steels", 3rd ed., p. 42, New York, John Wiley & Sons, 1920.
(2) Lundell, G. F., "Chemical Analysis of Iron and Steel", Chapter 11, New York, John Wiley & Sons, 1931.
(3) *Ibid.*, Chapter 36.
(4) Silverman, Louis, Ind. Eng. Chem., Anal. Ed., 10, 433 (1938); 12, 343 (1940).

Determination of Zirconium in Steel

A Rapid Colorimetric Method

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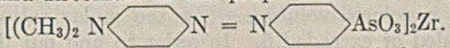
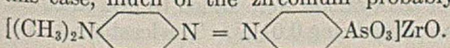
THE authors, needing a rapid routine method for the determination of zirconium in steel and finding none that was completely satisfactory, made a search of the general literature on zirconium determinations. After investigation of several methods, the precipitation of zirconium by *p*-dimethylaminoazophenylarsonic acid described by Feigl (*1*), together with the colorimetric measurement of the precipitated reagent as reported by Nazarenko (*2*), was selected as the most satisfactory approach.

This determination can be made without preliminary separation of iron or other elements, although considerable amounts of manganese, silicon, chromium, etc., are present in the steel. This, however, necessitates standardization against similar steel of known zirconium content. The importance of this is shown in Figure 1, which was obtained by plotting milligrams of zirconium against the readings of a Cenco-Sheard-Sanford photelometer on semilog paper.

When no considerable amount of other metals is present, and the solutions to be precipitated contain more than 5 micrograms in 10 ml. or less of 2 *N* hydrochloric acid, line *C* is obtained. The precipitate in this case probably contains the reagent and zirconium in the proportions of 2 to 1, as indicated by .

When the solutions contain the same amount of zirconium in 50 ml. of 2 *N* hydrochloric acid, line *B* is obtained. In this case, much of the zirconium probably precipitates as . Line *A*, which is used with the proposed method, was obtained by precipitating the zirconium from 50 ml. of solution containing 0.1 gram of steel, which had been analyzed for zirconium by the selenious acid method. If extreme accuracy were desired, a preliminary separation of zirconium by means of a mercury cathode or other suitable method would make it possible to use line *C*, giving about twice as many scale divisions for the same amount of zirconium.

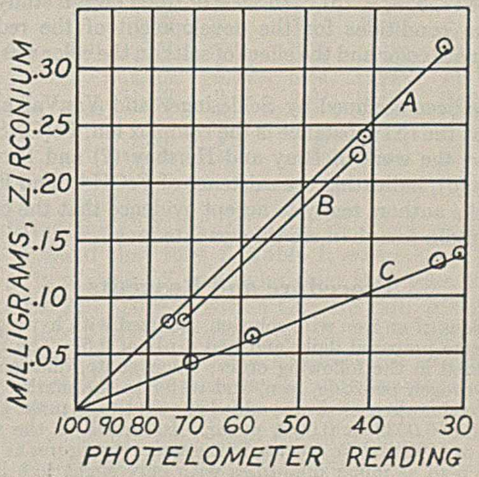


Figure 1

Reagents Required

Hydrochloric acid, 1 part to 1 part of water. Crystalline potassium hydrogen sulfate. Ammonium hydroxide, specific gravity 0.90. Hydrochloric acid wash, 10 ml. of concentrated hydrochloric acid per liter of water. Ammonium hydroxide wash, 333 ml. diluted to 1 liter with water. *p*-Dimethylaminoazophenylarsonic acid, 0.250 gram of dye, 10 ml. of concentrated hydrochloric acid, diluted to 250 ml. with ethyl alcohol.

Method

Dissolve 1 gram of sample in 50 ml. of 1 to 1 hydrochloric acid. When solution is complete, dilute to 75 ml. with water and filter. Save the filtrate. Wash the residue 3 times with hot water, 3 times with hot 1 to 1 hydrochloric acid, and 3 times with hot water. Ignite paper and residue in a platinum crucible, fuse ash with as little potassium hydrogen sulfate as needed, dissolve cooled melt by heating the crucible, and melt in a beaker containing 100 ml. of water and a few drops of sulfuric acid. Now remove the crucible, washing well with hot water, and to the solution of dissolved melt add 2 drops of methyl orange indicator and a slight excess of ammonium hydroxide; boil a minute, filter, and wash the precipitate with cold water. Put paper and precipitate back into the beaker, add 50 ml. of 1 to 1 hydrochloric acid, break paper into pulp, and heat to boiling. Boil a minute and filter into original filtrate saved from first filtration.

Wash well with hot water, transfer to a 500-ml. volumetric flask, cool, and dilute to the mark with water. Mix well and pipet 50 ml. of the combined filtrates into a 250-ml. beaker. Bring the measured 50 ml. of solution to the boiling point, add 15 ml. of dye solution, cover with a watch glass, boil 1 minute, and remove from plate. Let stand at room temperature for at least 30 minutes. Filter through 3 close-texture filter papers, wash excess dye from papers, and precipitate with hydrochloric acid wash solution. After washings are absolutely colorless, set the funnel containing washed paper and precipitate into the neck of a 100-ml. volumetric flask. Now remove dye combined with zirconium by washing with ammonium hydroxide wash, about 3 to 4 washes. Dilute to the mark with water, mix well, and fill absorption cell by filtering through cotton. Photoelectric reading is read in milligrams of zirconium on plotted curve. In this case, weight in grams × 10 × 100 = per cent zirconium. The solution of dye which is colorimetered is yellow. A blue filter is used in the photelometer.

In the authors' laboratory this determination is made in less than 2 hours. The results do not deviate by more than 0.005 per cent from those obtained by the selenious acid method.

This method is subject to the same necessity for fusion of the insoluble zirconium with potassium pyrosulfate that is met in all other methods. It is possible, however, to eliminate the usual sodium carbonate fusion when working with steel containing less than 0.05 per cent of phosphorus. The authors have added phosphorus to the original solution of the steel in amounts equivalent to 0.170 per cent without producing any significant change in the results for zirconium. However, with some steels a sodium carbonate fusion of the residue should be made before fusion with potassium pyrosulfate.

Titanium interferes with this method by reacting in the same manner as zirconium, but this can be prevented by adding 3 drops of 3 per cent hydrogen peroxide before the precipitation, if the titanium is not more than 10 times the zirconium content.

The *p*-dimethylaminoazophenylarsonic acid obtained from the Paragon Testing Laboratories, Orange, N. J., has been found very satisfactory.

The authors were handicapped in their work by the fact that there is no Bureau of Standards steel sample of certified zirconium content.

Literature Cited

(1) Feigl, F., Krumholz, P., and Rajman, E., *Mikrochemie*, 9, 395 (1931).
(2) Nazarenko, V. A., *J. Applied Chem.* (*U. S. S. R.*), 10, 1696–9 (1937).

A Study of the Ferric Thiocyanate Reaction

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THE thiocyanate method for iron is much used. However, it has some disadvantages. Nitrates generally intensify the color, although small amounts may be tolerated with some concentrations of thiocyanate (*14*, *16*). Phosphates change and decrease the color (*4*, *5*) and salts may interfere (*1*, *3*, *5*, *9*, *13*). In view of these facts a study of the optimum conditions for the development of the red ferric thiocyanate color and the effect of salts on the color was undertaken.

It has been assumed by Schlesinger and VanValkenburgh (*12*) that the red substance is the complex ion, $Fe(CNS)_6^{---}$; however, the work of Bray and Hershey (*2*) and Lamb and Jacques (*6*), indicating the existence of $FeOH^{++}$ and $FeCl^{++}$, leaves the authors ready to accept evidence that the complex may contain less than six thiocyanate ions.

Procedure and Reagents

Dilutions of an iron wire solution, oxidized with hydrogen peroxide, were prepared daily and had a pH of 2.5. The reagents were added in the following order: thiocyanate, dilution water, acid, hydrogen peroxide, iron, and water to the mark. Hydrogen peroxide, when used, was added in quantity to make the solution either 0.0032 or 0.0064 molar. Inasmuch as the formula weights of CNS and Fe are nearly the same, the figures as p. p. m. may be read as molar quantities with only slight loss in accuracy.

Interfering Substances

Nitric acid intensifies the color with thiocyanate in the presence of iron. Experiments in the absence of iron showed that solutions 0.1 *N* with nitric acid also developed a color when the thiocyanate concentration exceeded 0.1 *N* and, if the acid were changed to hydrochloric, solutions 1.26 *N* with this acid developed a color when the thiocyanate exceeded 0.05 *N;* when the hydrochloric acid was weaker, 0.1 *N*, the thiocyanate had to be 0.4 *N* to develop color.

In a previous article (*11*) the amounts of hydrogen peroxide necessary to make a colored substance from thiocyanate were given, but no limit for a safe maximum was set. Further work showed that the peroxide could be increased to 0.0064 *M* without significant error, but greater concentrations intensified the yellow color produced.

Thiocyanate–Iron Influence on Color

From the formula $Fe(CNS)_6^{---}$ one would expect to obtain a colored solution when the molar ratio of CNS/Fe equaled or exceeded 6. In order to find out if the amount of thiocyanate necessary to produce a color bore any relation to this ratio, several experiments were performed in which various amounts of thiocyanate were added to iron in 50-ml. Nessler tubes, the acidity being 0.01 *N*. The least amount of thiocyanate necessary to develop a color was measured. The results are used to make Figure 1. The experiment was repeated in the presence of hydrogen peroxide, but the findings were not significantly different. It appears that when the ferric ion is 0.1 p. p. m. the thiocyanate must be 60 p. p. m. to show a color; when the iron is 1.0 p. p. m. only 4.5 p. p. m. of thiocyanate are necessary. Apparently, with the higher concentration of iron, only part is active in producing color or else there is a colored substance with less thiocyanate than the postulated $Fe(CNS)_6^{---}$. It is evident that the presence of six ions of thiocyanate to one of iron does not necessarily mean that a colored substance is formed.

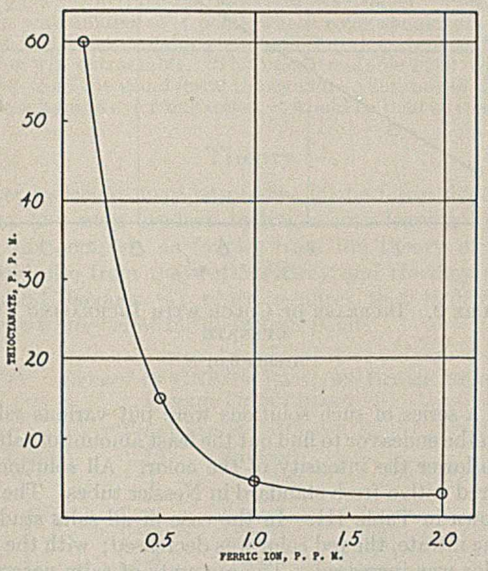

Figure 1. Amounts of Thiocyanate and Iron Necessary to Show Color

Effect of Hydrochloric Acid

In the next series of experiments the effect of varying amounts of hydrochloric acid on the production of the red color was observed. In the first set the iron was 0.5 p. p. m., the thiocyanate 3.0 p. p. m. (ratio 6), and the acid concentration varied from 0.002 to 0.010 *N* in ten tubes; no color was evident. In the second set the iron and thiocyanate were not changed, but the acid concentration was varied from 0.02 to 0.10 *N* in nine tubes; a slight color was present in all experiments, but no difference could be detected between the individual tubes. In the third set the thiocyanate was increased ten times to 30 p. p. m. (ratio 60), and the acid concentration varied from 0.002 to 0.40 *N*. A slight color appeared in all tubes, the strongest being at an acidity of 0.01 *N*. It is evident that most color appears when the acid concentration is 0.005 to 0.010 *N* and that the color decreases when the acid is either less than 0.005 *N* or greater than 0.01 *N*. The data also show that when the CNS/Fe ratio was 6 color first appeared when the hydrochloric acid was 0.02 *N*, while when the CNS/Fe ratio was 60 color first appeared when the hydrochloric acid was 0.002–0.005 and the maximum color appeared at 0.01 *N*. Thus at higher thiocyanate concentrations less acid is required to bring out the color.

It is possible that a change in the amount of iron would cause a change in the acidity requirements. Accordingly the iron was increased to 5.0 p. p. m., and the thiocyanate to 150 p. p. m. (ratio 30). Again most color appeared at an acid concentration of 0.01 *N*, decreasing as the acidity decreased or increased from this figure. The acidity 0.01 *N* thus appears to be the optimum for iron determinations when hydrochloric acid is present. This concentration seems just about enough acid to prevent hydrolysis of the ferric ion; however, the slowness of this reaction, as noted by Lamb and Jacques (*6*), would have the same effect as the presence of more acid. Calculation of the amount of $FeOH^{++}$ existing at a pH of 2, using 3×10^{-3} as the equilibrium constant (*6*, p. 1219), shows that an appreciable amount exists at that pH under equilibrium conditions.

Effect of Acid Counteracted by Thiocyanate. The previous results showed that the red color was less intense as the acid concentration was increased beyond 0.01 *N* when the CNS/Fe ratio was 60. To see if this relationship held at higher concentrations of thiocyanate, varying amounts of thiocyanate were added to Nessler tubes containing different amounts of acid at two iron levels and the color intensities were compared. The time from mixing to reading was about 7 minutes. Table I gives the data. It seems that at high thiocyanate concentrations the influence of the acid in decreasing the red color is lessened—for example, changing the acid from 0.01 to 0.60 *N*, when the concentration of thiocyanate was 240 p. p. m. and the CNS/Fe ratio was 2400, resulted in less color in the more acid solution. This held also for a thiocyanate concentration of 1200 p. p. m., CNS/Fe ratio 12,000, but when the concentration of thiocyanate reached 2400 p. p. m. no difference in color was noticed with increased acid. In other words, with a small amount of iron (0.1 p. p. m.), a thiocyanate concentration of 0.040 *N* (2400 p. p. m.) produces the same color whether the acid is 0.01 or 0.60 *N*. When the amount of iron is increased five times to 0.5 p. p. m. it is necessary to increase the thiocyanate concentration to over 11,000 p. p. m., CNS/Fe ratio 22,400, before the effect of the stronger acid is overcome. However, at the two different iron levels at the point where the effect of acid is overcome by thiocyanate, the CNS/Fe ratios are essentially the same. The usual analytical practice is to use a thiocyanate concentration of approximately 0.3 *N* which is, according to this work, high enough to minimize the effect of the acid in lessening color.

Table I. Effect on Red Color of Varying Thiocyanate Concentration at Different Acidities

Tube No.	Fe	HCl	CNS	Cl/CNS		CNS/Fe	Color Intensity
	P. p. m.	*N*	*P. p. m.*	*M*	*P. p. m.*	*P. p. m.*	
1	0.1	0.01	240	2.4	1.5	2,400	<2 but >4
2			1,200	0.48	0.30	12,000	<3 but >5
3			2,400	0.24	0.15	24,000	Same as 6
4	0.1	0.60	240	150	91	2,400	<5 and <1
5			1,200	29	18	12,000	<6 and <2
6			2,400	15	9.1	24,000	Same as 3
7	0.5	0.01	561	1.0	0.65	1,122	<8 but >11
8			1,122	0.52	0.33	2,244	<9 but >12
9			5,610	0.10	0.06	11,220	<10 but >13
10			11,220	0.05	0.03	22,440	Same as 14
11	0.5	0.60	561	62	3.9	1,122	<12 and <7
12			1,122	31	2.0	2,244	<13 and <8
13			5,610	6.2	0.39	11,220	<14 and <9
14			11,220	3.1	0.20	22,440	Same as 10

Considering the Cl/CNS ratio and its effect on the red color, it is found that tube 1, Table I, where the Cl/CNS ratio in p. p. m. was 1.5, had more color than tube 4 where the ratio was 91. Tube 2, with a Cl/CNS ratio of 0.30 had more than tube 5 where the ratio was 18, but in tube 3 with a Cl/CNS ratio of 0.15 the color was identical with that of tube 6 where the Cl/CNS ratio was 9.1 and the amount of acid increased 60 times. It may be concluded that when the thiocyanate concentration is high the chloride ion is less destructive to the red color. Much the same conclusion was reached in the previous paragraph.

Color Increase with Thiocyanate Concentration

The effect of an excess of thiocyanate on the color intensity was next investigated. In the first experiment the solution was 0.01 *N* in hydrochloric acid, the iron was 20 p. p. m., and the CNS/Fe ratio was varied from 1 to 12. The intensity of ratio 6 was taken as standard on the colorimeter. The results are shown in Figure 2. It is evident that color increases linearly as the CNS/Fe ratio increases.

TABLE II. EFFECT OF LARGE EXCESS OF THIOCYANATE ON RED COLOR

Tube No.	Fe	HCl	CNS	CNS	$\frac{CNS}{Fe}$	Color Intensity
	P. p. m.	*N*	*P. p. m.*	*N*	*P. p. m.*	
1	1.0	0.01	60	0.001	60	Color increases with increase in CNS concentration
2			120	0.002	120	
3			240	0.004	240	
4			360	0.006	360	
5			480	0.008	480	
6			600	0.010	600	
7			1,200	0.020	1,200	
8			1,800	0.030	1,800	
9			2,400	0.040	2,400	
10	0.1	0.01	240	0.004	2,400	Color increases with CNS
11			360	0.006	3,600	
12			480	0.008	4,800	
13			600	0.010	6,000	
14			720	0.012	7,200	
15			840	0.014	8,400	
16			960	0.016	9,600	
17			1,080	0.018	10,800	
18			1,200	0.020	12,000	
19			1,800	0.030	18,000	
20			2,400	0.040	24,000	
21	0.1	0.5	28,880	0.5	288,800	Color increases with CNS
22			57,760	1.0	577,600	
23			86,640	1.5	866,400	
24			115,520	2.0	1,155,200	
25			144,440	2.5	1,444,000	

In the next series of experiments (Table II) the thiocyanate concentrations were increased progressively at different iron and acid concentrations. The color increases with increased thiocyanate concentration in each unit of the series and there seems to be no limit of color intensity that may not come from increasing concentrations of thiocyanate.

Experiments with Acids and Anions

In order to find out if the maximum color effects were due to hydrogen ion and not to the anion, iron salts of several acids were used with thiocyanate in a series of experiments similar to the ones described. The experiment with nitric acid showed that the tubes with acidities ranging from 0.005 to 0.01 *N* had the maximum color. When sulfuric acid or perchloric acid was used, the maximum color developed in the 0.01 *N* acid tube only. Calculations showed that the activity coefficient of the hydrogen ion in these solutions is of the order of 0.9. Apparently the hydrogen ion and not the anion is the effective agent in these low concentration ranges.

To determine the effect of the anion on the color produced, other experiments were made in which equivalent amounts of hydrochloric, nitric, sulfuric, and perchloric acids were used with ferric ion. In all tubes the CNS/Fe ratio was 60 and the iron and acid concentrations were 0.5 p. p. m. and 0.01 *N*, respectively. The solutions were mixed and compared immediately. The depth of color in the chloride, nitrate, and perchlorate tubes varied slightly and in the order $ClO_4^- > NO_3^- > Cl^-$, while the sulfate tube was practically colorless.

Effect of Salts

The initial amounts of reagents necessary to produce a color lasting at least 15 minutes were found to be

$FeCl_3$	0.0000179 *M* (0.1 p. p. m. Fe^{+++})
NaCNS	0.2 *N*
HCl	0.01 *N*
H_2O_2	0.0064 *N* (equivalent to 0.18 ml. of 3 per cent solution in 50 ml.)

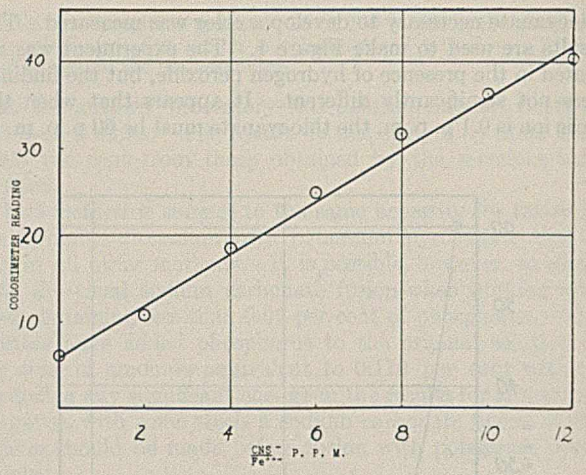

FIGURE 2. INCREASE OF COLOR WITH INCREASING THIOCYANATE

Acidity 0.01 *N*

Into a series of such solutions were put various salt solutions in the endeavor to find out the least amount of salt necessary to lower the intensity of the color. All solutions were compared with a fresh standard in Nessler tubes. The results are shown in Table III. In the case of all salts studied except the nitrate, the red color was decreased; with the nitrate the color was increased. The amounts of salts necessary to lower color intensity vary widely. Taken in order of decreasing efficiency they are pyrophosphate, monohydrogen phosphate, tertiary phosphate, dihydrogen phosphate, sulfate, chloride, and nitrate. Sodium chloride interfered least with the red ferric thiocyanate color. Table III also shows the salt/Fe and the salt/CNS ratios existing at the point where the salt first causes a lessening in the color intensity. These ratios show that at the point where salt interference began the molar concentration of sodium chloride was 260,000 times that of the iron, while the sodium pyrophosphate was only 0.84 times that of the iron. The values of the salt/iron ratios for the other salts which decreased the red color varied between these two limits.

TABLE III. MINIMUM AMOUNTS OF SALTS NECESSARY TO REDUCE RED FERRIC THIOCYANATE COLOR INTENSITY

Salt	Molarity of Salt	$\frac{Salt}{Fe}$	$\frac{Salt}{CNS}$	Color Greater or Less than Standard
		M/M	*M/M*	
$NaNO_3$	0.67	370,000	3.4	+
NaCl	0.46	260,000	2.3	−
Na_2SO_4	0.076	42,500	0.38	−
NaH_2PO_4	0.00065	360	0.0033	−
Na_3PO_4	0.00063	350	0.0032	−
Na_2HPO_4	0.00017	95	0.0009	−
$Na_4P_2O_7$	0.0000015	0.84	0.000008	−

Leeper (*8*) gave values of sodium monohydrogen phosphate and sodium pyrophosphate which interfere in 50 ml. of ferric thiocyanate solution as 100 to 120 mg. and 0.40 mg., respectively, calculated as phosphorus pentoxide. The authors' work shows the values for these same salts as 0.47 and 0.004 mg., respectively. Leeper's solutions were 0.4 *N* with sulfuric acid and 0.25 *N* with ammonium thiocyanate, while the authors' solutions were 0.01 *N* with hydrochloric acid, 0.2 *N* with sodium thiocyanate, and 0.0032 *M* with hydrogen peroxide. This seems to indicate that the increase of acid concentration increases the tolerance of the two phosphate salts mentioned.

Ether Extraction

To see whether the CNS/Fe ratio had any effect on the ether extraction of the red color, 5 ml. of ether were added to 50-ml. Nessler tubes containing varying amounts of thiocyanate and constant amounts of iron and acid were used. With lesser amounts of thiocyanate, color was observable which would not extract with ether, but as the amounts of thiocyanate increased the colored substance was extracted. The data are shown in Table IV, tubes 1 to 10. Other solutions, tubes 11 to 13, extracted with 7 ml. of ether, showed that color was first extracted at a CNS/Fe ratio of 464. To prove further that ether extracts the colored substance only at higher CNS/Fe ratios, a solution which gave an extractable red color was taken. Part of this solution was diluted to a point where color should not extract and iron and acid were added to match the original concentrations. No color was extractable. The nonextractable color was more brownish than the usual ferric thiocyanate color, but in a Nessler tube, by a human eye comparison, it would be read as iron.

Theory

Water molecules may be present in the ferric thiocyanate complex and may produce hydrogen ions leaving hydroxyl ion in the complex, as follows from the theory of olation (*15*), and also from the work of Bray and Hershey (*2*) and Lamb and Jacques (*6*) which requires that hydroxyl ion change to water below the hydrolysis point.

TABLE IV. EFFECT OF CNS/Fe RATIO ON ETHER EXTRACT OF FERRIC THIOCYANATE

(Fe, 1.0 p. p. m.; HCl, 0.01 *N*)

Tube No.	$\frac{CNS}{Fe}$	Aqueous Layer	Ether Layer
1	300	Colored	No color
2	1,200	Colored	No color
3	1,392	Colored	Pink
4	1,624	Colored	Pink
5	1,856	Colored	?
6	2,088	Colored	Pink
7	2,320	Orange	Pink
8	4,640	Orange	More pink than 7
9	9,280	Orange	More pink than 8
10	92,800	Orange	More pink than 9
11	232	Color	No color
12	325	Color	No color
13	464	Color	Slight color

The production of color by higher thiocyanate ion concentration at lower acidities apparently indicates a contest between the thiocyanate ion and water for a place in the complex. When the thiocyanate ion is high less water would be expected to enter and so less hydrogen ion would be necessary to prevent hydrolysis; consequently a more intense color is seen. This indicates that the pH at which iron precipitates is dependent upon the other ions in solution in addition to hydrogen.

The fact that the most intense color appears at an acid concentration of 0.01 *N* indicates that at lower acid concentrations the hydrogen ion splits off from the water molecules in the ferric-aquo complex. The less intense color at high concentrations of acid is to be expected from the salt effect. Further, the action of acid may show itself in reducing the ionization of thiocyanic acid. Latimer (*7*) gives the value of K for thiocyanic acid as 1×10^{-4}. Consequently, the increase of hydrochloric acid should be effective in reducing the thiocyanate ions available for complex formation and thus be part of a mechanism in which increased acidity produces less of the colored substance. However, the less intense color at higher concentrations of hydrochloric acid may be due also to the chloride ion getting a position in the complex in the place of thiocyanate ions; that such action is probable is inferred from the work quoted (*6*), which gives evidence of the existence of $FeCl^{++}$. At higher concentrations of thiocyanate ion the chloride ion would be expected to have greater difficulty in forcing its way into the complex and so it is possible to explain the fact that the lesser amount of colored substance, produced when the chloride-ion concentration is high, is increased when the concentration of thiocyanate ion is greater. The action of salt ions in lessening the color is similar; each forces its way into the complex according to its individual tendency in competition with the thiocyanate ions. The explanation of the descending order of effect on color of the series perchlorate, nitrate, chloride, sulfate, would lie in the fact, as stated by Bray and Hershey (*2*), that chlorates and nitrates do not form complexes with iron while chlorides may form $FeCl^{++}$. The formation of sulfate complexes is commonly assumed. The more iron is used up to form other complexes the less is left for union with thiocyanate.

The increase in color intensity from a given amount of iron, when the thiocyanate concentration is continually increased, indicates that there is no end to the increase in colored substance. The conclusion from this is that the ferric thiocyanate complex is highly dissociated. That the reaction is so sensitive to concentration changes may be due to the high color intensity of the complex. The practical application is to emphasize the need for the same concentration of thiocyanate in both sample and standard.

The failure to extract the brownish-red colored substance by ether at low thiocyanate concentrations points to a complex of lesser thiocyanate composition not soluble in ether. Evidence that there is more than one colored substance present in ferric thiocyanate solutions has been offered recently by Møller (*10*).

Summary

Acidity is a factor in color development of ferric thiocyanate. In general, the most favorable acidity is 0.01 *N*, larger and smaller amounts of acid giving less color.

Increasing the thiocyanate overcomes the effect of higher concentrations of hydrochloric acid to lessen color intensity; also at higher concentrations of thiocyanate less acid is needed to develop the same color intensity.

Increasing the thiocyanate progressively increases the colored substance with no indication of reaching a maximum.

A variation in amount of iron, over a limited range, does not change the amount of acid necessary for maximum color intensity.

The minimum amounts of several anions which reduce the color intensity of ferric thiocyanate, within the limits of the experiments here cited, are in the order pyrophosphate, primary phosphate, tertiary phosphate, secondary phosphate, sulfate, chloride, nitrate.

The extraction of the red color by ether depends upon the CNS/Fe ratio, and a high ratio is necessary for iron extraction.

Literature Cited

(1) Bongiovanni, C., *Gazz. chim. ital.*, 38, 5–9 (1908).
(2) Bray, W. C., and Hershey, A. V., *J. Am. Chem. Soc.*, 56, 1899 (1934).
(3) DuBois, R., *J. Chem. Education*, 14, 324 (1937).
(4) Elvehjem, C. A., and Hart, E. B., *J. Biol. Chem.*, 67, 43 (1926).
(5) Hedenström, A., and Kunau, E., *Z. anal. Chem.*, 91, 17–25 (1932).
(6) Lamb, A. B., and Jacques, A. G., *J. Am. Chem. Soc.*, 60, 1215 (1938).
(7) Latimer, W. M., "Oxidation Potentials", p. 128, New York, Prentice-Hall, 1938.
(8) Leeper, G. W., *Analyst*, 55, 370 (1930).
(9) Liberalli, C. H., *Rev. soc. brasil. chim.*, 2, 485 (1931).
(10) Møller, M., *Kem. Maanedsblad*, 18, 138 (1937).
(11) Peters, C. A., MacMasters, M. M., and French, C. L., IND. ENG. CHEM., ANAL. ED., 11, 502 (1939).
(12) Schlesinger, H. I., and VanValkenburgh, H. B., *J. Am. Chem. Soc.*, 53, 1212 (1931).
(13) Smith, H. J., and Cooke, J. H., *Analyst*, 51, 503 (1926).
(14) Szegoe, L., and Cassioni, B., *Giorn. chim. ind. applicata*, 15, 281 (1933).
(15) Thomas, A. W., and Whitehead, T. H., *J. Phys. Chem.*, 35, 27 (1931).
(16) Walker, W. B., *Analyst*, 50, 279 (1925).

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Analysis of Petroleum Oil–Soluble Sulfonic Acid Soaps

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The source and types of petroleum sulfonic acid soaps are discussed, and the analytical methods used by the authors for estimating oil-soluble soaps, or so-called "mahogany" soaps, are described.

PETROLEUM sulfonic acids are produced in the course of sulfuric acid treatments of petroleum distillates, particularly in the manufacture of medicinal white mineral oils, by drastically treating suitable raw stocks with fuming sulfuric acid. The ordinary acid treatment which is often employed in refining lubricating oil stocks does not produce sulfonic acids of good quality, since normally the acid is weaker in strength, and only sufficient acid is used to remove the undesirable components of an aromatic and asphaltic nature and perhaps certain of the sulfur, nitrogen, or similar compounds. In view of the fact that the original petroleum distillates consist of a large number of individual compounds of molecular weights varying over a wide range, the resulting sulfo acids will consist of similarly complex mixtures. Some of the acids remain dissolved in the oil layer; these are called "mahogany" acids. The others are found in the acid layer; these are called "green" acids. In actual practice the acids are not recovered as such, but in the form of their sodium soaps.

The oil-soluble sulfonate salts, or soaps, as they are sometimes called, have frequently been referred to as petroleum sludge soaps or sulfonate naphthenates, but it is believed that this has created confusion, and that the term "mahogany soap" or "petroleum oil-soluble sulfonate" is more correct and should be employed. The mahogany sulfonates have been more important commercially than the water-soluble green sulfonates, because they are effective emulsifiers and help to form unusually stable emulsions of oil and water. They permit the manufacture of mineral oil compositions which emulsify readily, even in hard water. Their emulsifying power depends a great deal upon their purity—i. e., freedom from contamination with inorganic salts—and the purer the soaps the better their emulsifying ability. Depending on the application and the specific properties desired, frequently small amounts of other products, such as glycols, fatty acid soaps, resinates, and fatty sulfonates, are used in conjunction with the petroleum sulfonates to enhance their emulsifying power. Generally, however, less than 10 per cent of a good grade of the purified soap is required to emulsify petroleum oil in water without the use of any accessory emulsifier.

The chemistry of the sulfonic acids is discussed in detail by Ellis (*8*) and Dunstan, Nash, Brooks, and Tizard (*7*). The mahogany or oil-soluble sulfonic acids generally consist of the compounds of higher molecular weight, and according to Schestakoff (*11*) they possess the empirical composition $C_nH_{2n}.6SO_4$ and $C_nH_{2n}.9SO_4$.

The process used at the Bayway Refinery of the Standard Oil Company of New Jersey for the manufacture and purification of the sulfonate soaps is briefly as follows:

> After separation of the sludge containing the water-soluble green acids, the "acid oil" layer, consisting of the treated oil, is neutralized with alkali, and the resulting oil-soluble sodium mahogany soap is extracted from the oil with aqueous isopropyl alcohol. The crude soap extract solution thus obtained contains, in addition to the complex mixture of sodium mahogany soaps, a certain amount of mineral oil, an excess of alkali, some of the impurities present in the original alkali, and some sodium sulfite and sulfate. The crude soap solution is then further purified by suitable processes whereby most of the salts are precipitated and a refined soap solution is obtained.

Commercially the oil-soluble sulfonates are available in at least three forms: (1) the so-called crude soap, (2) the refined soap in water, and (3) the refined soap in oil. They are usually not available in the pure soap form, since the dry soap without solvent is for most purposes too viscous to handle commercially. The crude soap, which is obtained by evaporating the crude alcoholic soap solution described above is generally a viscous product containing 1 to 25 per cent of water and from 1 to 10 per cent of inorganic salts. The actual oil-soluble soap content of this product is generally around 50 per cent. The remainder is oil, part of which may have been added to make the material more fluid and to aid in stripping off the solvent and water at temperatures (below 150° C.) which will not cause any decomposition.

The refined oil-soluble soap is fairly pure and generally contains only a trace of inorganic salts. A mixture of the refined soap with 20 to 35 per cent of water is possible when heated to 60° to 80° C., and it is this mixture which is marketed as the refined soap in water. The third form, the refined soap in oil, is the most common, and this consists of a blend of approximately equal parts of oil and the refined soap.

Many of the analytical methods published in the literature refer to the water-soluble sulfonic acids or so-called green acids. Thus, Burton and Robertshaw (*6*) refer to water-soluble sulfonic acids in admixture with naphthenic acids. Analytical methods for such splitting agents or mixtures of mahogany and green acids have been published by von Pilat and Sereda (*10*) who refer at length to the work of Schestakoff,

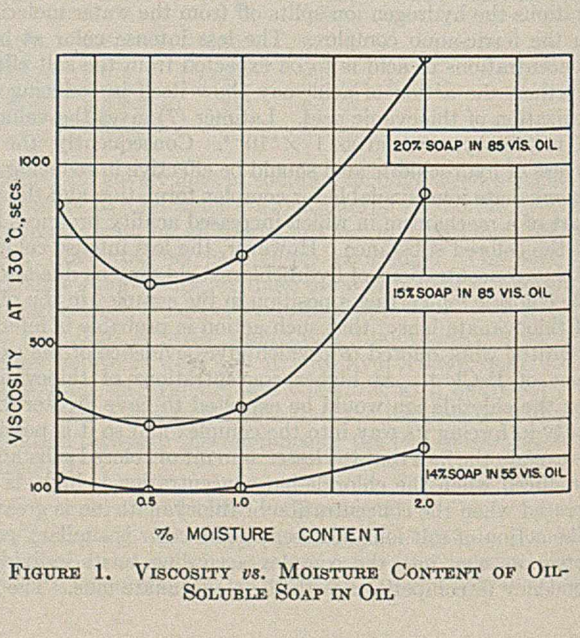

FIGURE 1. VISCOSITY *vs.* MOISTURE CONTENT OF OIL-SOLUBLE SOAP IN OIL

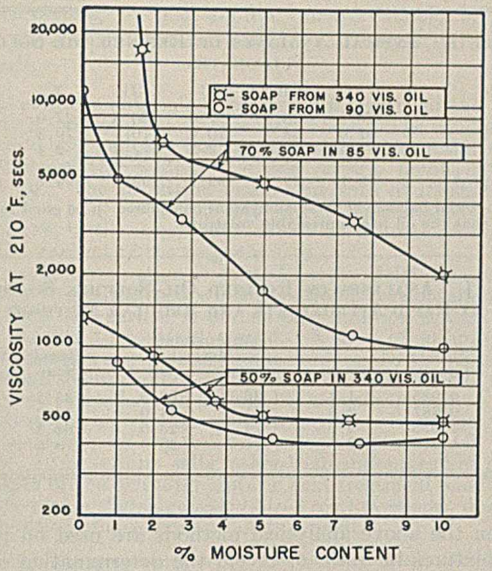

Figure 2. Viscosity *vs.* Moisture Content of Oil-Soluble Soap in Oil

Ilmenjew, and Dobrjanskiij. Such methods are of necessity very complicated, since the separation of both water-soluble and oil-soluble acids, naphthenic acids, and mineral oils is involved. Simpler procedures can be used for the analysis of oil-soluble soaps which are generally free from sulfonated acids of low molecular weight as well as naphthenic acids. The analytical methods described in this paper are limited to the estimation of the soaps of the oil-soluble sulfonic acids.

Methods

Evaluation of the oil-soluble soap is frequently desirable and includes specific gravity, color, viscosity, water content, salt content, oil content, alkalinity, and soap content.

Specific Gravity. The specific gravity is determined most conveniently by warming the sample and mixing it with a mineral oil of 50 to 100 Saybolt seconds at 36.67° C. (100° F.). This lowers the viscosity of the sulfonate, so that the specific gravity may be determined by means of a hydrometer spindle after cooling to room temperature. The gravity of the sample is calculated from the amount of oil added to it and the known specific gravity of this oil used. The specific gravity can also be determined by pouring a heated sample into a standard 100-cc. graduated cylinder, cooling to room temperature, and reading the volume occupied. The weight of the sample is determined by weighing the graduate before and after filling. Either method gives results accurate to 0.5 per cent.

Color. The color of crude oil-soluble sulfonate is difficult to determine in the presence of inorganic salts. It is therefore customary to dissolve 20 cc. of the sample in 80 cc. of naphtha, filter through paper, and determine the color of the filtrate with the Tag Robinson or Lovibond colorimeter.

Viscosity. The viscosity of oil-soluble sulfonate is of importance as a measure of the pumpability of the material. When it is measured at 99° C. (210° F.) by means of a Saybolt Universal viscometer it is necessary to avoid the evaporation of moisture from the sample, since the viscosity of oil-soluble sulfonate in oil is very sensitive to the moisture content. This is illustrated by the viscosity–moisture content curves of various soap-oil mixtures in Figures 1 and 2. As the soap is hygroscopic, there is also a chance of error where the sample is exposed to humid air at ordinary temperature.

Water Content. The water content of oil-soluble sulfonate is determined by distilling it with naphtha under a reflux condenser provided with a water trap (*3*). The size of the sample used is adjusted to the capacity of the trap, or for samples of very high water content a trap provided with a stopcock may be used for withdrawal of the water as separated. The latter type of apparatus is valuable where the sample is to be examined for volatile water-soluble materials such as alcohol, amines, or volatile acids. These are readily detected by determining the specific gravity of the water recovered or by titration, etc.

Salt Content. The inorganic salt content is of importance mainly on the crude sulfonate. For an accurate determination, it is necessary to filter out and weigh the salts from the dry naphtha solution of the sample from the moisture determination. Frequently, it is difficult to filter these salts because of their colloidal condition and it is preferable to decant the naphtha solution from the centrifuge and to wash the salts with two portions of petroleum ether, agitating, centrifuging, and decanting the clear supernatant layer at each wash. The salts residue is then washed into a small tared beaker with petroleum ether, evaporated, dried, and weighed.

A more rapid determination of inorganic salts in oil-soluble sulfonate is made by cooling the dry naphtha solution of the sample obtained as a residue from the moisture determination and by centrifuging it in a conical graduated tube. The apparatus and general technique described in A. S. T. M. method D91-35 (*2*) are convenient for this purpose. The reading at the bottom of the tube is converted to per cent by volume based on the weight of the sample used. The practice of reporting inorganic salts (sometimes called "gum") in this manner originates from the fact that crude oil-soluble soap is frequently compounded with petroleum oil to make a fluid product which is later settled to remove the insoluble material and the volume of the sediment represents an actual loss of the product included therein.

Oil Content. The oil content of oil-soluble sulfonate can be approximately determined by dissolving a weighed sample in 50 per cent aqueous isopropyl alcohol and measuring the volume of the supernatant layer of undissolved oil. This is conveniently carried out in a test bottle with a graduated neck and with the aid of a centrifuge to separate the oil layer speedily. The Babcock milk bottle may be used or the A. S. T. M. technique (*4*) is very effective. The rapid and complete separation of the oil is favored by acidifying the alcoholic solvent with sulfuric acid, and isopropyl alcohol has been found to be somewhat more satisfactory than ethyl alcohol because the former is more selective. A 10-cc. sample is used, measured with a standardized pipet which is washed into the bottle with the aqueous alcohol. The tip is broken from the pipet to aid in the filling and subsequent washing. The pipet should then be recalibrated for total content obtainable by washing. For the more viscous soap mixtures the pipet is warmed during use.

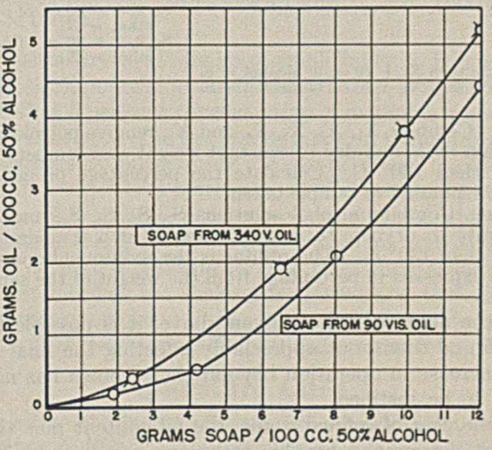

Figure 3. Solubility of Oil in Soap Solutions in Isopropyl Alcohol at 30° C.

The oil content determination described above is open to the objection that alcohol makes an incomplete separation between the oil-soluble sulfonate and the oil layer. The solubility of the oil in 50 per cent isopropyl alcohol is small but increases rapidly with increasing amounts of oil-soluble sulfonate in the dilute alcohol. This is shown in Figure 3.

The simultaneous direct determination of soap and oil content is accomplished by means of extraction with 50 per cent isopropyl alcohol coupled with counterextraction with petroleum ether. This effectively separates these two ingredients, so that they may be dried and weighed.

SOAP EXTRACTION METHOD. The sample is accurately weighed, taking about 2.0 grams, which are dissolved in 25 cc. of 50 per cent aqueous isopropyl alcohol. The solution is transferred to a 150-cc. stoppered separatory funnel and thoroughly shaken with 25 cc. of petroleum ether, the extraction being carried out at room temperature. The pressure in the funnel is occasionally released by turning the funnel upside down and gently opening the stopcock. (The petroleum ether method for the extraction of unsaponifiable matter in animal and vegetable fats and oils after saponification and solution of the soap in 50 per cent alcohol is official with the AMERICAN CHEMICAL SOCIETY, *1*, American Oil Chemists' Society, *1*, and the Association of Official Agricultural Chemists, *5*.) On standing, the liquid will separate almost immediately into two layers. The lower alcohol layer is drawn into another 150-cc. separatory funnel and extracted again with petroleum ether, while the upper petroleum ether layer is extracted with 50 per cent alcohol, a number of such extractions being carried out until most of the mineral oil is concentrated in the petroleum ether fractions and the soap in the 50 per cent alcohol fractions.

When this analysis is carried out as a routine method, its accuracy is increased by limiting the number of operating steps to the minimum required for consistent results. The following flow diagram gives a satisfactory procedure:

The equipment required is two 150-cc. separatory funnels set in rings one above the other on a single stand. The petroleum ether and 50 per cent isopropyl alcohol are measured out by means of a 25-cc. graduate, and two 150-cc. beakers are used to collect the intermediate washings as well as to hold the final fractions to be evaporated and weighed. The separatory funnels and stoppers are rinsed with 50 per cent alcohol at the close of the test and the washings are added to the alcoholic extract beaker. The portions of alcohol are marked S_1, S_2, etc., and the portions of ether X_1, X_2, etc.

Operation	50% Isopropyl Alcohol	Petroleum Ether
1	Sample + 25 cc. of alcohol = S_1	....
2	....	S_1 + 25 cc. of petroleum ether = X_1
3	....	S_1 + 25 cc. of petroleum ether = X_2
4	X_1 then X_2 + 20 cc. of alcohol = S_2	....
5	X_1 then X_2 + 20 cc. of alcohol = S_3	....
	S_1, S_2, and S_3 are combined	....
6	....	$S_{1, 2, 3}$ + 20 cc. of petroleum ether = X_3
7	....	$S_{1, 2, 3}$ + 20 cc. of petroleum ether = X_4
8	X_3 then X_4 + 20 cc. of alcohol = S_4	....
9	X_3 then X_4 + 20 cc. of alcohol = S_5	....

Oil. Combine X_1, X_2, X_3, X_4, and X_5, remove petroleum ether on steam bath, and dry to constant weight at a temperature not higher than 130° C. Calculate the percentage of mineral oil from the amount of sample taken.

Soap. Combine alcohol solutions S_1, S_2, S_3, S_4, and S_5, and evaporate to dryness to constant weight at a temperature not higher than 130° C. The residue is the sodium sulfonate which can be expressed in percentage from the weight of the sample.

Of the nine operations given above, it is possible to omit Nos. 5 and 9 without appreciably affecting the final results. Any increase in operation beyond the 9 shown has not been found to be justified.

In the case of refined soaps, the oil content plus the soap content determined by this technique can be added to the moisture content to give very close to 100 per cent, as shown in Table I. The salts present in crude sulfonate are included in the weight of the soap extracted according to this method. It is determined as mentioned above and is deducted from the soap found.

A comparison between the analyses of refined oil-soluble soap by the rapid approximate method and the regular analysis is given in Table II. The soap content by the regular method is about 94 per cent of that determined by the rapid approximate method.

ALKALINITY. The alkalinity of the oil-soluble sulfonate is conveniently determined by titrating the alcoholic solution from the oil determination test with a standard mineral acid, using phenolphthalein as an indicator.

TABLE I. TYPICAL ANALYSES OF REFINED OIL–SOLUBLE SULFONATES

Sample	A	B	C	D	E	F
Oil	36.1	28.8	27.0	26.8	27.0	27.2
Soap	61.6	68.4	70.4	70.7	70.3	70.7
Water	1.4	2.0	2.3	2.3	2.4	2.4
Accounted for	99.1	99.2	99.7	99.8	99.7	100.3

The material balance of these analyses is considered to be good in view of the fact that the oil has appreciable volatility.

TABLE II. ANALYSES OF REFINED OIL–SOLUBLE SOAP IN OIL BY RAPID APPROXIMATE AND REGULAR METHODS

Sample	Specific Gravity	Water	Approximate Method Soap	Approximate Method Oil	Regular Method Soap	Regular Method Oil
G	0.925	1.4	36.6	62.0	35.8	62.8
H	0.987	2.0	54.0	44.0	50.6	47.4
I	1.035	2.6	74.4	23.0	68.2	29.2
J	1.040	2.3	74.7	23.0	70.4	27.3

When the above analytical methods are used on purified soap mixtures in water or in oil, the determination of inorganic salts is generally omitted, since the sample is clear of suspended matter. A visual inspection of the naphtha residue from the moisture determination should, however, be noted.

The reproducibility of the above analytical tests on various types of soap products is shown in Table III, which gives results obtained from two independent laboratories using the same methods.

The analysis of crude oil-soluble sulfonate by the extraction procedure is sometimes made difficult by the presence of insoluble impurities. In this case the alcoholic solution should be filtered through paper before proceeding with the analysis.

Special Analytical Methods

The extraction procedure described above gives duplicate results generally agreeing within 0.2 per cent on the total sample. However, soaps of certain types of sulfonic acids are appreciably soluble in petroleum ether. It follows that, while the above extraction procedure will give reproducible results, the petroleum ether solution may still contain sulfonated soaps. It is therefore advisable to carry out an ash determination on the separated mineral oil after its final weighing, also on the recovered soap. According to Hart (*9*) ignition of a pure sodium sulfonate will leave sodium sulfate, and half of the organic combined sulfur trioxide will be volatilized, unless excess alkali in some form is present as an impurity which would retain some of the excess sulfur trioxide. It may be assumed that the ash content of the refined soap should be approximately the same as that of the soap dissolved in the petroleum ether washings. Accordingly, a correction for any soap present in the separated mineral oil may be calculated on the basis of the ash content of the mineral oil. Thus, if the purified soap has an ash content of x per cent and the separated mineral oil y per cent, the amount of soap remaining in the mineral oil will be equivalent to $\frac{100y}{x}$. The weight of soap and oil found in the sample is readily adjusted by this quantity to arrive at a more accurate soap and oil analysis. Table IV gives a typical analysis in which the soap and oil analyses of a sample have been corrected for the ash content of the oil.

In the case of sample A, the correction is so small that it could well be neglected. It occasionally happens, however, that as much as 30 per cent of soap may be left in the separated oil. In such cases the correction is necessary.

The purity of the separated soaps may be checked by carrying out total sulfur and ash determinations. If the soaps are pure sulfonates, the ash should consist entirely of sodium sulfate the sulfur in the ash being equal to exactly half of the total sulfur.

Total sulfur is determined by fusing 0.5 gram of the purified soaps with sodium peroxide in a Parr bomb. The residue is dissolved in water and any insoluble metallic oxides resulting from the action of the sodium peroxide on the bomb metal are filtered off. The filtrate is made acid with hydrochloric acid, brought to a boil, and the sulfate ions are precipitated with barium chloride in the usual way. Blank corrections are made for the sulfur content of the reagents used.

The ash determination is carried out by weighing accurately 2 grams of the purified soaps into a platinum crucible and igniting gently until the carbon is burned off. Ignition is then carried out to redness, to constant weight. A drop of sulfuric acid is added to convert any sodium sulfide produced by the reduction of some of the sodium sulfate by the carbon; the excess of sulfuric acid is gently expelled and the residue is finally heated to redness to constant weight, some ammonium carbonate being occasionally added to decompose any sodium hydrogen sulfate which may be present. If no sodium salts, other than sulfonates are present, the weight of the ash after sulfuric acid treatment should show not more than a slight increase (2 to 3 mg.) in weight, due to the decomposition of any sodium sulfide present.

Table III. Analytical Results on Soap Mixtures

(Alkalinity expressed as gas-free Na_2CO_3 per 100-cc. sample)

Laboratory	Specific Gravity	Soap and Salts	Oil	Moisture	Salts	Alkalinity	Color, *R*	Viscosity, 210° F.
					Vol. %			
				Crude Soap Analysis				
A	1.033	48.7[a]	42.2[a]	2.1	7.0[a]	0.45	4.25	671
B	1.034	48.3[a]	42.7[a]	2.0	7.0[a]	0.412	4.25	728
				Refined Soap in Water[b]				
		Soap		Water				
A	1.056	58.4	8.6	33.0	...	...	..	...
B	1.052	58.6	7.9	33.5	...	...	..	...
				Refined Soap in Oil[c]				
A	0.987	52.2	46.4	1.6	...	...	..	620
B	0.988	52.0	46.3	1.7	...	...	26	624

[a] Approximate methods.

[b] Oil present in this sample was that which is unavoidably associated with sulfonate during manufacture.

[c] Color given here is % of sample diluted in white oil which matches 9 Robinson color.

Table IV. Correction of Analysis of a Soap Mixture for Ash Content of Oil Recovered

	Sample A %		Sample B %
Oil content found	3.15		3.66
Ash on above separated oil	0.08		1.50
Ash on pure soap	14.00		14.00
Soap content in oil = $\frac{100 \times 0.08}{14}$ =	0.52	= $\frac{100 \times 1.5}{14}$ =	10.70
Soap content in mineral oil, calculated on original sample $\frac{3.15 \times 0.52}{100}$ =	0.52	= $\frac{3.66 \times 10.7}{100}$ =	0.39
Corrected mineral oil content (3.15 − 0.02)	3.13	(3.66 − 0.39)	3.27
Direct soap determination by extraction	46.15		46.04
Corrected soap content = (46.15 + 0.02)	46.17	(46.04 + 0.39)	46.43

The ash content of the pure oil–soluble sulfonate can be used for determining the combining weight of the sulfonic acids. The figure determined by this method agrees closely with that obtained by titration of the pure acid. The sulfonic acid can be prepared from sodium sulfonate by treating it with dry hydrochloric acid to precipitate the sodium as sodium chloride in a petroleum ether solution of the purified oil-free soap. The clear naphtha solution is then evaporated on a steam bath, and the residue is weighed, taken up in alcohol, and titrated. On one sample of soap the ash gave a combining weight of 487, as compared with 478 by titration of the pure acid.

The ultimate analysis of oil-soluble sulfonate varies with the viscosity of the oil from which it is made. The base stock from which the oil was obtained also affects the analysis (Table V).

Table V. Analysis of Oil-Soluble Soap

Source	C	H	S	Analysis of Ash	Combining Weight From S	Combining Weight From ash
Coastal 85 viscosity/100° F.	67.02	9.08	6.96	Ca 4.60	460	441
Coastal 340 viscosity/100° F.	65.26	9.09	6.26	Ca 3.82	511	492
Hydrogenated 85 viscosity/100° F.	66.55	8.77	7.76	Na 5.41	413	391

Emulsion Tests

Emulsion tests on oil-soluble sulfonate are used to evaluate it for making emulsible oils, as for metal cutting or textile purposes. The presence of impurities such as dissolved inorganic salts adversely affects the emulsibility of sulfonate soaps.

The emulsibility test consists in determining the border line concentration of sulfonate in a mixture with a standard oil which just gives an oil-in-water emulsion. Lubricating oils vary considerably in aromatic and unsaturate content, so that the amounts of soap to emulsify them vary accordingly. Oils having an appreciable neutralization number generally require more soap to emulsify them than neutral oils. Oil-soluble soaps having a high water content should be dried before testing for emulsibility in order to eliminate the effect of that variable.

White oil of about 90 viscosity at 100° F. Saybolt makes a good standard for testing soap emulsions. The soap is carefully measured and mixed with a known volume of oil, which is increased by stages until the border of emulsibility is attained. In testing for the emulsion, 45 cc. of distilled water are placed in a 50-cc. stoppered graduate, a 5-cc. portion of the mixture to be tested is added, and the graduate is shaken by hand with 20 vigorous strokes and allowed to stand 5 minutes. This is repeated twice and then the graduate is allowed to stand for 0.5 hour. At the borderline of emulsibility no free oil layer should separate and the volume of the upper layer of emulsion cream should not exceed 5 cc.; otherwise a higher concentration of soap should be tested.

It is customary to set limits of emulsibility to be met—for example, a commercial grade of refined soap should pass the above test at 5 per cent concentration of available soap in the white oil solution. The test can be modified to meet practical considerations by substituting a water of known hardness for the distilled water or a petroleum oil of a standard grade for the white oil. The shaking procedure outlined above was adopted since it aided in canceling out various operating variables. The partial emulsification of the sample when added to the water before the shaking is started and the adhering of this primary emulsion to the walls of the graduate tend to affect the final result unless the outlined procedure is followed.

Literature Cited

(1) American Oil Chemists' Society, Official and Tentative Methods, p. 30, 1933.
(2) Am. Soc. Testing Materials, Committee D-2, Report 1939, Method D91-35, p. 190.
(3) *Ibid.*, Method D95-30, p. 277.
(4) *Ibid.*, Method D483-38T, p. 239.
(5) Assoc. Official Agr. Chem., Official and Tentative Methods of Analysis, p. 420 (1935).
(6) Burton, D., and Robertshaw, G. F., "Sulfated Oils and Allied Products", Chap. VI, New York, Chemical Publishing Co., 1940.
(7) Dunstan, Nash, Brooks, and Tizard, "The Science of Petroleum", London, Oxford University Press, 1938.
(8) Ellis, C., "Chemistry of Petroleum Derivatives", New York, Chemical Catalog Co., 1934.
(9) Hart, R., *J. Am. Leather Chem. Assoc.*, **15**, 404 (1920); **16**, 159 (1921).
(10) Pilat, St. von, and Sereda, J., *Fettchem. Umschau*, **41**, 9, 171 (1934).
(11) Schestakoff, P. J., *Russ. Phys. Chem. Soc.*, **45**, 664 (1913).

Colorimetric Determination of Iron with Kojic Acid

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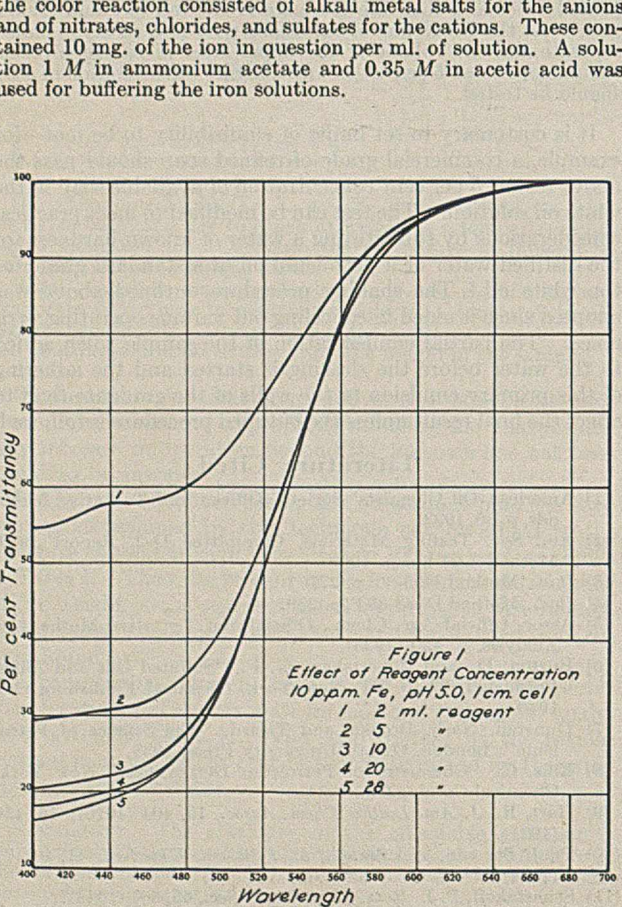
IN A recent paper (*1*) Barham mentioned that Corbellini and Gregorini (*2*) and Tamiya (*6*) had studied the course of certain fermentations producing kojic acid by means of colorimetric determinations of the acid with ferric chloride. It seemed probable, therefore, that this process might be reversed by using the organic compound as a reagent for iron. As tests confirmed this prediction, a spectrophotometric study of the reaction was undertaken in the hope that this new colorimetric method for determining iron would have advantages over existing procedures. Kojic acid (2-hydroxymethyl-5-hydroxy-γ-pyrone) is unique as a reagent for iron, in that no organic compound previously so used is a pyrone derivative.

Apparatus and Solutions

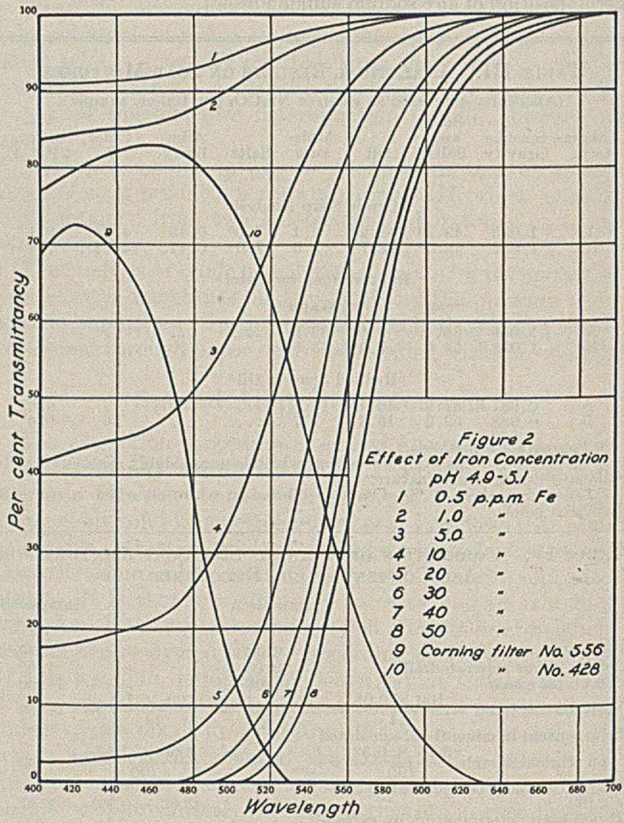
A standard solution containing 0.05 mg. of iron per ml. was prepared by dissolving iron wire of reagent quality in nitric acid and diluting with redistilled water. One milliliter of this solution is equivalent to 1 p. p. m. of iron when diluted to 50 ml.

An aqueous solution containing 0.1 per cent of kojic acid was used as the reagent. More concentrated solutions are susceptible to mold formation on continued standing, although this may be inhibited by using 20 per cent ethanol as solvent or by adding 1 p. p. m. of phenyl mercuric nitrate.

Standard solutions for the study of the effect of diverse ions on the color reaction consisted of alkali metal salts for the anions and of nitrates, chlorides, and sulfates for the cations. These contained 10 mg. of the ion in question per ml. of solution. A solution 1 M in ammonium acetate and 0.35 M in acetic acid was used for buffering the iron solutions.



In preparing solutions for transmittancy measurements the iron solution was measured and buffered with 10 ml. of the acetate solution. Ten milliliters of the reagent were then added and the solution was diluted to 50 ml. Addition of buffer preceded extraneous ions in determining the extent of interference from these sources. It is recognized that this sequence differs from the situation prevailing in an actual analysis, but it eliminates from the color measurements several undesirable effects, such as precipitation of the iron on addition of basic solutions.



Transmittancy measurements were made in 1.000-cm. cells with a General Electric recording spectrophotometer adjusted for a spectral band width of 10 mμ. A glass electrode assembly (*4*) was used for pH measurements.

Color Reaction

NATURE OF REACTION. Data obtained according to the method of Vosburgh and Cooper (*7*) indicate that the iron and kojic acid react in a molecular ratio of 1 to 3 at a pH of 5 to 6. It has been shown that the hydroxymethyl group is not concerned in the color reaction, but that the enolic hydroxy is essential (*9*). This suggests formation of a salt with possible implication of the carbonyl group in a five-membered ring. An inner complex salt in accordance with the above ratio would be consistent with the coordination tendencies of iron, although such nonelectrolytes, as a rule, are insoluble (*3*). Other colored constituents may be present, especially in solutions of lower pH.

Effect of Reagent Concentration. With kojic acid, as with ferron, the intensity of the color developed with iron depends upon the concentration of the color-forming reagent. This effect, shown in Figure 1, necessitates a relatively careful measurement of the quantity of reagent. Ten milliliters of 0.1 per cent solution are sufficient to produce a deep color with 10 to 20 p. p. m. of iron in 50 ml. and little is gained by using excessive amounts.

Effect of Iron Concentration. Transmittancy curves for solutions containing from 0.5 to 50 p. p. m. of iron and 10 ml. of 0.5 per cent reagent in 50 ml. of solution are shown in Figure 2. A linear relationship between iron concentration and log transmittancy prevails, in accordance with Beer's law, for concentrations up to about 40 p. p. m. A permanent calibration curve may thus be established by determining the transmittancy for a given iron concentration and drawing a straight line through the determined point to 100 per cent at zero concentration, on semilogarithmic paper. Conformity to Beer's law should not be a critical consideration in evaluating a method, but it is an advantage in fulfilling the requirements for use of a variable-depth comparator of the Duboscq type. This law is not valid for solutions containing equal amounts of iron but different quantities of reagent.

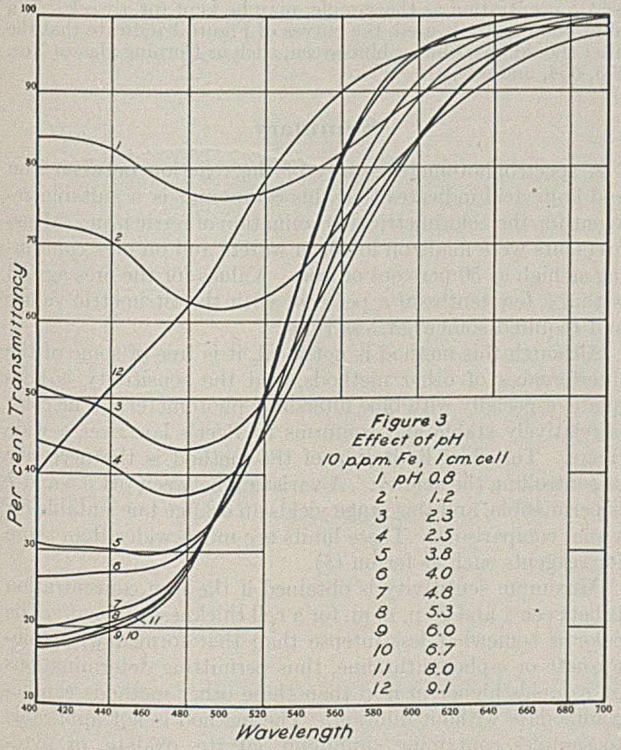


Figure 3
Effect of pH
10 p.p.m. Fe, 1 cm. cell

The concentration range over which the method is applicable depends upon the cell thickness and the means of comparison. One can distinguish 0.05 p. p. m. of iron from a blank in 30-cm. Nessler tubes. Comparison of amounts greater than 5 p. p. m. is difficult. Photoelectric instruments can detect 0.1 p. p. m. in a 1-cm. cell and the upper limit is about 20 p. p. m. The sensitivity is improved by acetone, but the effect is much less than in the thiocyanate method (*8*).

The change of transmittancy with concentration is more pronounced than that of the trichromatic or monochromatic values, as is usually the case in such systems. The red and green values are practically equal.

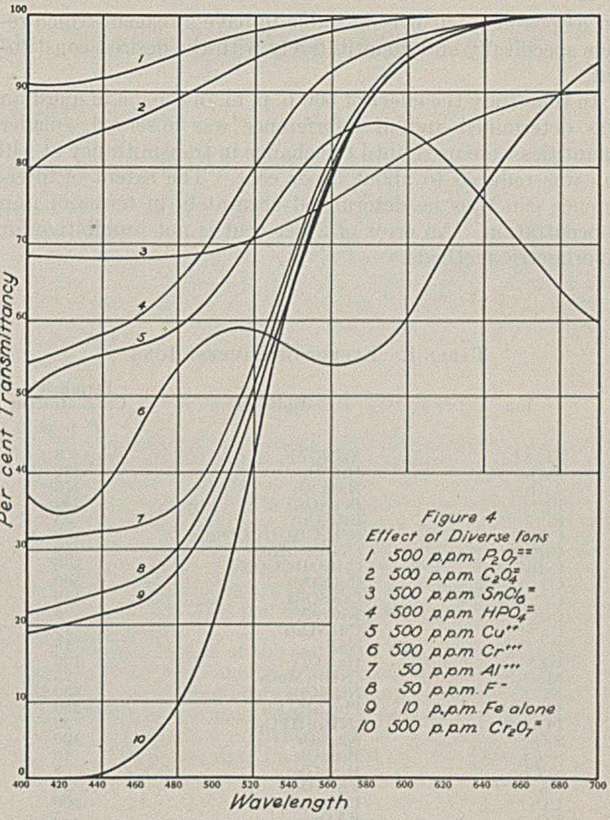


Figure 4
Effect of Diverse Ions

Effect of Acid Concentration. As acid concentration exerts considerable influence on the intensity and hue, it should be controlled within rather narrow limits. Strong acids or bases destroy the color, the change in basic solution being irreversible. Figure 3 represents solutions containing 10 p. p. m. of iron and 10 ml. of reagent in 50 ml. of solution at pH values from 1 to 9. The orange hue at pH 5 was stable for more than 5 weeks. A low pH is desirable in order to avoid precipitation of iron, although the tendency to fade increases with the acid concentration.

It is desirable to maintain the pH between 5.5 and 7 during the color measurements, since this range is best for achieving optimum color stability, small variation of transmittancy with pH change, and high absorption in the blue region. Ammonia may be added for adjustment of pH only after development of the color. Otherwise, precipitation of some iron is likely to occur. Ammonium acetate is a convenient buffering agent.

Effect of Diverse Ions (Figure 4). An outstanding disadvantage of colorimetric methods for ferric iron is the fact that certain ions react with the iron to form stable complexes which decrease the ferric-ion concentration. This is encountered especially with phosphates, fluoride, and several organic ions. Other types of interference include formation of colorless complexes by the reagent with various metals, precipitation of insoluble products, presence of colored constituents, and development of a color by the reagent with some ion other than iron. Reduction of part of the iron by certain ions may lead to low results for total iron, although this effect has no relation to the color reaction itself. No reagent free from all these kinds of interference has been reported for ferric iron. Ordinarily, the treatment of the sample is designed to circumvent interference by other substances as far as possible, but it is desirable to have a reagent which reacts specifically and quantitatively with the desired constituent.

In this study the effect of 500 p. p. m. of the ion in question was determined and, if interference was observed, smaller quantities were used until the change in transmittancy at 440 mμ was reduced to about 5 per cent. The extent of interference can thus be determined accurately in terms of iron concentration. An error of 2 per cent is not prohibitive for colorimetric methods.

TABLE I. EFFECT OF DIVERSE IONS

Ion	Added as	Permissible Concentration P. p. m.
Al^{+++}	$Al(NO_3)_2$	3
AsO_4^{---}	H_3AsO_4	30
AsO_3^{---}	Na_3AsO_3	170
Be^{++}	$Be(NO_3)_2$	250
Bi^{+++}	$Bi(NO_3)_3$	25
$C_3H_5O_2^{--}$	$(CH_3CHOHCOO)_2Ca$	130
$C_4H_4O_6^{--}$	$(NH_4)_2C_4H_4O_6$	50
$C_7H_5O_3^{-}$	$C_6H_4OHCOONa$	500
Co^{++}	$Co(NO_3)_2$	500
Cr^{+++}	$Cr_2(SO_4)_3$	10
$Cr_2O_7^{--}$	$K_2Cr_2O_7$	5
Cu^{++}	$Cu(NO_3)_2$	19
F^{-}	NaF	15
Hg^{+}	$HgNO_3$	100
MoO_4^{--}	$(NH_4)_2MoO_4$	25
Ni^{++}	$Ni(NO_3)_2$	330
Pb^{++}	$Pb(C_2H_3O_2)_2$	250
PO_4^{---}	$(NH_4)_2HPO_4$	20
SiO_3^{--}	Na_2SiO_3	100
$SnCl_4^{--}$	H_2SnCl_4	10
$SnCl_6^{--}$	H_2SnCl_6	5
Th^{++++}	$Th(NO_3)_4$	25
UO_2^{++}	$UO_2(C_2H_3O_2)_2$	200
VO_3^{-}	KVO_3	5
WO_4^{--}	Na_2WO_4	30
Zn^{++}	$Zn(NO_3)_2$	140
ZrO^{++}	$ZrO(NO_3)_2$	5

No effect on the color was observed in solutions containing 500 p. p. m. of each of the following ions: acetate, silver, barium, borate, benzoate, bromide, calcium, cadmium, chloride, chlorate, perchlorate, carbonate, formate, mercuric, potassium, lithium, magnesium, manganese, sodium, ammonium, nitrate, thiocyanate, sulfate, and strontium. Table I shows the maximum permissible quantities of various ions not already mentioned which may be present without causing an error greater than 2 per cent.

Reducing ions, such as cyanide, iodide, nitrite, and sulfite, did not interfere if added to the iron solution after addition of the acetate buffering solution. If the ion was added before buffering the solution at pH 5, however, low results were obtained. Such ions would be oxidized in the normal treatment of the sample and thus present no difficulty.

Low results are caused by certain ions, including phosphates, fluoride, and a few organic acids. Citrate, oxalate, and pyrophosphate must be entirely absent.

The extent of fluoride influence may be applied for determining this element, although the sensitivity is probably too low for the method to be practical in visual work. The relation between fluoride concentration and transmittancy of a solution containing 1 p. p. m. of iron and kojic acid is close to linear up to 100 p. p. m. of fluoride. A change in transmittancy of only 1 per cent corresponds to 6 p. p. m. of fluoride, however, which would necessitate very accurate measurement of the color.

Aluminum, zinc, and a few other metals form colorless complexes with the reagent, thus lowering its effective concentration and leading to low results. This source of interference cannot be eliminated satisfactorily merely by adding more reagent, since the color reaction is not stoichiometric.

All highly colored compounds should be absent unless their absorption bands can be eliminated by proper setting of the monochromator.

Recommended Procedure

Procure a representative portion of the material to be analyzed and subject it to the necessary preparative treatment.

Weigh or measure by volume a quantity of sample containing 1 mg. of iron or less.

TREATMENT OF SAMPLE. Ores may be dissolved in hot hydrochloric acid. Chlorostannous acid should not be added to hasten dissolution unless the solution is to be diluted to 1 liter or more. Organic matter combined with the iron necessitates the use of ashing procedures.

After dissolution of the sample, oxidize the iron by boiling with a little concentrated nitric acid. Other oxidants, such as persulfate or hydrogen peroxide, may be used.

Dilute the oxidized solution with iron-free water and add 1 gram of ammonium acetate. Filter if the solution is not clear. Transfer the solution to a 100-ml. volumetric flask, add 10 ml. of 0.1 per cent kojic acid solution, dilute to the mark, and mix well.

MEASUREMENT OF DESIRED CONSTITUENT. The color, which is developed immediately, may be measured by the usual methods. Standards for visual comparison, prepared with the same acid concentration as the sample, may be kept for a week. If a filter photometer is used, the curves of Figure 1 indicate that the filter should be a blue or blue-green, such as Corning glasses Nos. 533, 554, and 429.

Summary

A spectrophotometric study of the reaction between iron and kojic acid indicates that this compound is a suitable reagent for the colorimetric determination of ferric iron. Measurements were made on low-iron waters and on ores containing as high as 50 per cent of iron. Values for the ores agreed within a few tenths of a per cent with the titrimetric values and required somewhat less time.

Although this method is not ideal, it is free of some of the interferences of other methods, and the sensitivity is adequate, especially with blue filters in a photometer. The color is relatively stable and conforms to Beer's law over a wide range. The chief limitation of the method is the necessity of controlling the acidity. A variation between pH 5.5 and 7 is permissible, and this range yields an orange hue suitable for visual comparisons. These limits are much wider than those for reagents such as ferron (*5*).

Maximum sensitivity is obtained if the iron concentration is between 1 and 20 p. p. m. for a cell thickness of 1 cm. The color is somewhat less intense than that formed with thiocyanate or *o*-phenanthroline, thus permitting determinations on samples higher in iron than these other methods can accommodate without dilution. The method is not applicable to samples containing aluminum, citrate, oxalate, or pyrophosphate.

Acknowledgment

H. N. Barham of Kansas State College very kindly furnished the kojic acid.

Literature Cited

(1) Barham, IND. ENG. CHEM., ANAL. ED., 11, 31 (1939).
(2) Corbellini and Gregorini, *Gazz. chim. ital.*, 60, 244 (1930).
(3) Diehl, *Chem. Revs.*, 21, 39 (1937).
(4) Mellon, "Methods of Quantitative Chemical Analysis", p. 413, New York, Macmillan Co., 1937.
(5) Swank and Mellon, IND. ENG. CHEM., ANAL. ED., 9, 406 (1937).
(6) Tamiya, *Acta Pnytochim.* (Japan), 3, 51 (1927).
(7) Vosburgh and Cooper, *J. Am. Chem. Soc.*, 63, 437 (1941).
(8) Woods with Mellon, IND. ENG. CHEM., ANAL. ED., 13, 551 (1941).
(9) Yabuta, *J. Chem. Soc.*, 125, 575 (1924).

ABSTRACTED from a thesis presented by M. L. Moss to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of master of science, June, 1940.

The Chemistry of Menhaden Oil

Component Fatty Acids

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OILS of domestic origin are becoming more important by reason of the increasing inability to import foreign oils. Marine oils in particular are available in large quantities and should be given serious consideration as replacements for foreign materials. Because much is still unknown of the chemistry of marine oils, the present investigation has been undertaken. Menhaden oil was chosen for the start of this research, since it is the most abundant marine oil produced on the Atlantic coast.

Table I records some of the published results.

Twitchell (*8*) in 1917 investigated the composition of menhaden oil by the lowering of the melting point of the mixtures of fatty acids which he isolated. Saturated and unsaturated acids were studied separately, the latter after hydrogenation. His results revealed no unsaturated acids with fewer than 18 carbon atoms. Brown and Beal (*2*) fractionated the methyl esters, finding acids of 14, 16, 18, 20, and 22 carbon atoms. Armstrong and Allan (*1*) reported, in addition to those previously found, small amounts of saturated acids with 20 and 22 carbon atoms. Richardson, Knuth and Milligan (*5*) have published ester distillation data and more recently Stingley (*7*) has reported the component fatty acids of menhaden oil (Table I).

TABLE I. COMPONENT FATTY ACIDS OF MENHADEN OIL

Carbon Atoms	Twitchell (*8*)	Armstrong and Allan (*1*)	Stingley (*7*)	This Research
	%	%	%	%
		Saturated Acids		
14	9.2	5.9	7.0	8.3
16	22.7	16.3	16.0	14.9
18	1.8	0.6	1.0	4.7
20	..	0.6	..	..
22	..	0.8	..	..
		Unsaturated Acids		
12	..	..	..	Trace
14	..	..	Trace	5.8
16	..	15.5	17.0	23.4
18	24.9	29.6	27.0	31.1
20	22.2	19.0	20.0	8.4
22	20.2	11.7	12.0	3.4

Commercial menhaden oil from the Atlantic coast was examined by the ester fractionation procedure. Among the saturated acids (Table I) were found myristic, 8.3 per cent; palmitic, 14.9 per cent; and stearic, 4.7 per cent. Myristic and palmitic acids were isolated from the corresponding esters. Attempts to isolate an acid of higher molecular weight than palmitic have ended with mixtures. Fraction 6 yielded a mixture with a melting point of 57.5–58.5° C. and a neutral equivalent of 264.8 which lies between that calculated for palmitic and stearic acids. The neutral equivalent and the freezing point of 55.8° C., according to the data of Shriner, Fulton, and Burks (*6*), indicate a mixture of 0.85 mole of palmitic acid and 0.15 mole of stearic acid. This mixture has a neutral equivalent calculated to be 260.4.

The fractional distillation of the methyl esters of the unsaturated acids and the saponification equivalents of the fractions were used to calculate the composition. As a check upon this method, the acid from fraction 4 was hydrogenated catalytically to palmitic acid.

Analytical Methods

The methyl esters were fractionated through an electrically heated column packed with small helices. On top of the column was fitted a head designed for total reflux with partial take-off. Saponification equivalents were determined by the method of Chargoff (*3*). The Hanus method was used for the determination of iodine numbers. Neutral equivalents were determined in warm alcohol by direct titration with alkali to a phenolphthalein end point.

Experimental Procedure

Six hundred grams of commercial oil produced by centrifugation were saponified with alcoholic potassium hydroxide and the unsaponifiable matter was removed with ether. The residual soaps were acidified. The fatty acids were taken up in ether, washed with distilled water, and dried with anhydrous sodium sulfate, and the ether was removed. The recovered acids weighed 552 grams, a yield of 92 per cent of the original oil. Double precipitation of the lead soaps in alcohol and liberation by the usual methods yielded 27.9 per cent saturated and 72.1 per cent unsaturated acids.

The methyl esters of the saturated acids were prepared by dissolving in dry methanol and saturating with dry hydrogen chloride gas. After standing at room temperature for 12 hours they were treated in the usual manner. The methyl esters so obtained had a saponification equivalent of 267.4 and an iodine number of 4.0. The esters were fractionated and the data are tabulated in Table II.

Fraction 1 was saponified with alcoholic potassium hydroxide and acidified and the precipitate was crystallized from 95 per cent alcohol. The observed melting point was 53° C., while Francis and Piper (*4*) reported 54.4° C. for synthetic myristic acid. From fraction 3 an acid was separated and crystallized from acetone. The observed melting point was 63° C.; reported for palmitic acid, 62.9° C. (*4*).

The acid isolated from fraction 6 was crystallized from acetone and recrystallized from methanol and had a melting point of 57.5–58.5° C. The observed neutral equivalent was 264.8; that calculated for palmitic acid is 256.3 and for stearic acid is 284.3. The freezing point of this mixture as calculated from cooling curves was found to be 55.8° C. Shriner, Fulton, and Burks (*6*) have studied the cooling curves of many mixtures of palmitic and stearic acids and of the two mixtures reported freezing at 55.8° C.; that consisting of 0.85 mole of palmitic acid and 0.15 mole of stearic acid has a calculated neutral equivalent of 260.5 which comes closer to the observed.

TABLE II. FRACTIONATION OF METHYL ESTERS OF SATURATED FATTY ACIDS

Fraction	Weight	Boiling Range (5 Mm.)	Saponification Equivalent
	Grams	° *C.*	
1	11.1	147–154	244.1
2	9.9	154–160	254.5
3	7.3	160–165	258.2
4	18.7	165–169	279.2
5	12.5	161–163[a]	277.1
6	4.4	170–178	284.9
Residue[b]	5.4	...	...

[a] Difficulty was experienced in maintaining pressure at 5 mm. A new pump and other improvements helped in later experiments.
[b] Dark brown in color.

The methyl esters of the unsaturated acids prepared by the methanolic hydrochloric acid method had a saponification equivalent of 293.7 and an iodine number of 187.4. The data for the fractions obtained from the electrically heated packed column are summarized in Table III.

Table III. Fractionation of Methyl Esters of Unsaturated Fatty Acids

Fraction	Weight	Boiling Range (5 Mm.)	Saponification Equivalent	Iodine No.
	Grams	° C.		
1	2.2	120–123	248.5	24.8
2	1.8	123–135	260.0	83.6
3	3.6	135–140	254.7	103.7
4	10.7	140–147	272.0	123.1
5	3.2	147–155	280.0	125.4
6	6.9	155–160	291.0	127.3
7	6.6	160–165	292.0	153.1
8	7.2	165–170	298.0	166.5
9	4.5	170–175	308.0	183.2
10	6.2	175–180	310.0	212.2
11	3.7	180–185	325.0	226.2
12	5.5	185–190	311.5	208.1
13	4.4	190–195	352.0	232.7
Residue[a]	9.3	.....	...	...

[a] Dark brown in color.

To confirm the composition as calculated from the saponification equivalents, the saponification product from fraction 4 was acidified, extracted with ether, and dried, and the ether was removed. Hydrogenation in acetic acid with palladium-barium sulfate catalyst produced an acid with a melting point of 61° C.; that recorded for palmitic acid is 62.9° C. (*4*). The neutral equivalent found was 258.3, while that calculated for palmitic acid is 256.3.

Literature Cited

(1) Armstrong, E. F., and Allan, J., *J. Soc. Chem. Ind.*, 43, 207T (1924).

(2) Brown, J. B., and Beal, G. D., *J. Am. Chem. Soc.*, 45, 1289 (1923).

(3) Chargoff, E., *Z. physiol. Chem.*, 199, 221 (1931).

(4) Francis, F., and Piper, S. H., *J. Am. Chem. Soc.*, 61, 577 (1939).

(5) Richardson, A. S., Knuth, C. A., and Milligan, C. H., Ind. Eng. Chem., 17, 80 (1925).

(6) Shriner, R. L., Fulton, J. M., and Burks, D. J., *J. Am. Chem. Soc.*, 55, 1494 (1933).

(7) Stingley, D. V., Ind. Eng. Chem., 32, 1217 (1940).

(8) Twitchell, E., *Ibid.*, 9, 581 (1917).

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Reducing Power of Starches and Dextrins

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A rapid ferricyanide method for determining the reducing power of starches and dextrins is presented in which the reduced iron is measured directly by a ceric sulfate titration. For starches hydrolyzed by hot or cold acid or oxidized by alkaline hypochlorite, and for raw starches and dextrins, the reducing power values by this method parallel those determined by the longer procedure of Richardson, Higginbotham, and Farrow. Many other modified starches such as the "chlorinated" and "thin-boiling" types have been measured.

THE copper number has been used extensively for reporting the reducing power of cellulosic materials and recently by Richardson, Higginbotham, and Farrow (*7*) for starch. This paper describes a much simpler method for determining the reducing power or copper number of starches and dextrins, which shortens the time required to less than 25 minutes.

While measuring the reducing power of a series of starches by the Gore and Steele (*2*) modification of the Hagedorn and Jensen (*3*) method, the authors noticed that the apparent maltose equivalent of the more soluble products when converted to milligrams of copper gave values equal to the copper numbers determined by the Richardson, Higginbotham, and Farrow method. For raw starch and very slightly solubilized starch, high values were obtained by the Gore and Steele method. These high values were attributed to the visible entrapment in the starch of iodine which was very difficultly released for measurement in the thiosulfate titration.

In the determination of the maltose equivalent of starch-maltose mixtures Martin and Newton (*6*) avoided the difficulty due to iodine entrapment by using Hassid's (*4*) ceric sulfate titration. It seemed probable that the same ceric sulfate titration could be used to advantage here to measure the reducing power, not of a starch-maltose mixture, but of starch or dextrin alone. This proved to be true. Consideration of the above statements reveals that any reducing value obtained for maltose in the presence of dextrins and modified starches is only an apparent maltose value.

Table I. Reducing Power of Starches and Dextrins

Sample	R_{Cu}, Mg./Gram
Pearl starch (control)	6.8–7.9
Other commercial cornstarches	7.7, 9.4, 10.1, 11.2, 11.6
Waxy maize starch	9.0
Thin-boiling starch, 40-fluidity	6.5
Thin-boiling starch, 90-fluidity	27.2
Chlorinated starch, 2.5% chlorine	14.9
Chlorinated starch, 5% chlorine	32.9
Electrolytically oxidized starch	6.8, 3.0, 6.3, 4.5, 7.5
Alkali dextrin, A	10.5
Alkali dextrin, B	33.0
Alkali dextrin, C	71.0
Acid dextrin, A	12.0
Acid dextrin, B	25.5
Acid dextrin, C	39.0
Gore (*1*) starch, 5-hour conversion	19.6
Gore (*1*) starch, 42-hour conversion	61.6
Gore (*1*) starch, 96-hour conversion	120.0
Maltose	1900
Glucose	2800

The potentiometric measurement used by Martin and Newton was eliminated because the color change of the solution from green to yellow just before the large voltage change was a satisfactory indication of the end point. However, starch products with very little reducing power produced only a slight green color and made accurate determination of the end point difficult. The addition of a measured amount of glucose solution to each starch sample obviated this difficulty. A correction for the reducing power of this added glucose was made by a blank determination.

When, in the hydrolysis of starch by acid, the R_{Cu} values (milligrams of copper per gram of starch) were plotted against the time, there resulted a straight line for R_{Cu} values up to

1000. This is shown in Figure 1 where the simplified R_{Cu} determination is compared with the longer method of Richardson, Higginbotham, and Farrow. It is evident that the two methods give the same results in the starch and dextrin range but not in the range of the sugars. Figure 2 presents the change of rotatory power, of alkali number (*8*), and of iodine titration (*5*) as the same sample of starch was hydrolyzed. The alkali number became constant before the starch was one third converted to glucose.

This shorter method for copper numbers uses iron salts instead of copper salts, and the results, therefore, might be reported as R_{Fe} units. It seems better not to introduce another such unit, but to report the results as R_{Cu} units to allow comparisons with copper numbers. When the maltose, glucose, or iron equivalent is desired the following conversion factors are used:

$$\text{Per cent maltose equivalent} = \frac{R_{Cu} \times 100}{1900}$$

$$\text{Per cent glucose equivalent} = \frac{R_{Cu} \times 100}{2800}$$

$$R_{Fe} \text{ (mg. of Fe per gram of starch)} = R_{Cu} \times \frac{55.84}{63.57}$$

The utility of the method in the relative characterization of starches and dextrins is shown by Table I. The reducing power increases with increasing conversion of starch products except for the electrolytically oxidized starches, which, because of the method of oxidation and washing, have values equal to or lower than those of raw starches. This simplified determination of reducing power has been used to follow the acid and alkaline conversion of starch—e. g., on the "thin-boiling" starches, on the Gore starches (*1*), and on the dextrins formed by acid or alkaline catalyst (Table I).

Reagents

Alkaline Ferricyanide: 32.9 grams of potassium ferricyanide and 50 grams of anhydrous sodium carbonate dissolved in water and diluted to 1 liter. The solution is approximately 0.1 *N* with respect to potassium ferricyanide.

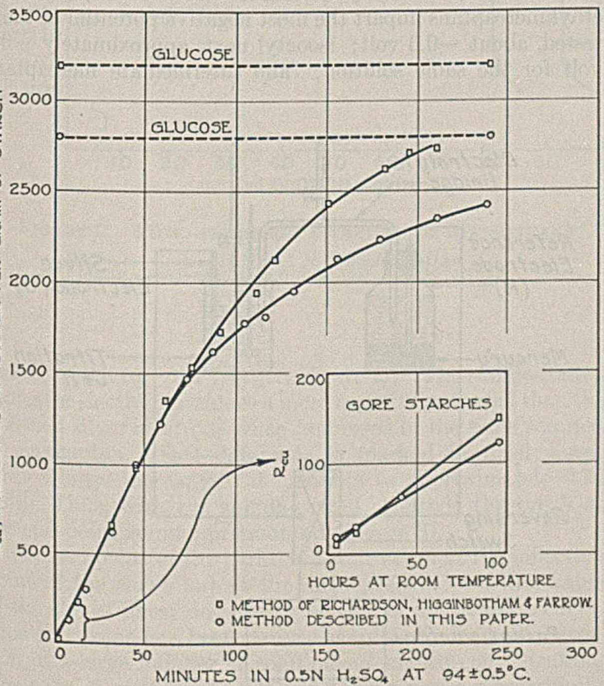

Figure 1. Comparative Determinations of Reducing Power during Hydrolysis of Starch

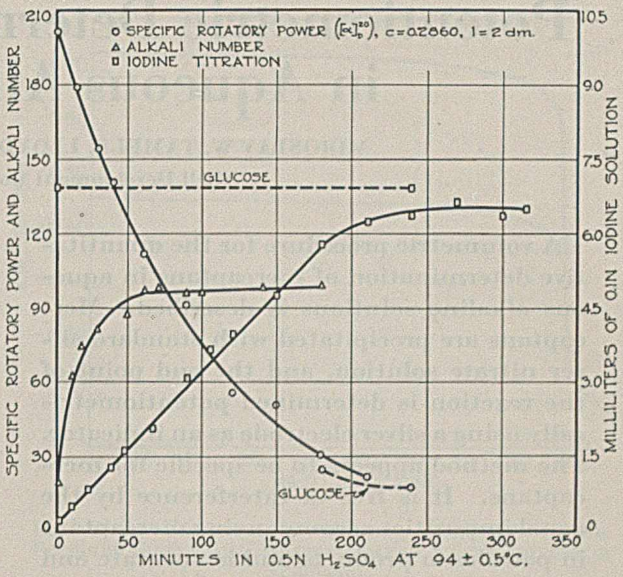

Figure 2. Change of Specific Rotation, Alkali Number, and Iodine Titration during Hydrolysis of Starch

Glucose Solution: a 0.2 per cent glucose solution containing a small amount of phenol.

Sulfuric Acid Solution (5 *N*): 139 ml. of concentrated sulfuric acid made up to 1 liter of solution.

Ceric Sulfate, 0.05 *N:* 26.5 grams of reagent ceric sulfate (G. Frederick Smith Chemical Co.) added to about 900 ml. of a solution containing 100 ml. of concentrated sulfuric acid. The mixture is digested until the solid has dissolved, cooled, and made up to 1 liter. The ceric sulfate solution is standardized against a standard ferrous ammonium sulfate solution potentiometrically or in the presence of *o*-phenanthroline indicator.

Procedure

Five hundred milligrams of the starch sample are weighed into a 300-ml. Erlenmeyer flask, and 25 ml. of alkaline ferricyanide reagent and 5 ml. of 0.2 per cent glucose solution are added. The flask is placed in a boiling water bath for exactly 15 minutes and is rotated while the starch is gelatinizing in order to give a uniform mixture. At the end of 15 minutes the flask is cooled under the tap to room temperature, 25 ml. of sulfuric acid solution are added, and the resulting green solution is titrated dropwise with standard ceric sulfate. The color change is from green to yellow. A blank determination is run on 5 ml. of the glucose solution. The equivalents of ceric sulfate are converted directly to milligrams of copper and reported as R_{Cu} units (mg. of copper per gram of starch).

$$\frac{\text{Ml. of ceric sulfate} \times \text{normality of ceric sulfate} \times 63.57}{\text{grams in sample}} = R_{Cu}$$

For starch products which have an R_{Cu} greater than 100 a smaller sample should be used.

Literature Cited

(1) Gore, Ind. Eng. Chem., 20, 865 (1928).
(2) Gore and Steele, Ind. Eng. Chem., Anal. Ed., 7, 324 (1935).
(3) Hagedorn and Jensen, *Biochem. Z.*, 135, 46 (1923).
(4) Hassid, Ind. Eng. Chem., Anal. Ed., 8, 138 (1936); 9, 228 (1937); 12, 142 (1940).
(5) Kline and Acree, *Ibid.*, 2, 413 (1930).
(6) Martin and Newton, *Cereal Chem.*, 15, 456 (1938).
(7) Richardson, Higginbotham, and Farrow, *J. Textile Inst.*, 27, T131 (1936).
(8) Schoch and Jensen, Ind. Eng. Chem., Anal. Ed., 12, 531 (1940).

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Potentiometric Determination of Mercaptans in Aqueous Alkaline Solutions

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A volumetric procedure for the quantitative determination of mercaptans in aqueous alkaline solutions is described. Mercaptans are precipitated with standard silver nitrate solution, and the end point of the reaction is determined potentiometrically using a silver electrode as an indicator. The method appears to be specific for mercaptans. It is free of interference by the usual impurities accompanying mercaptans in petroleum products and is accurate and sensitive.

THE large variety of sulfur compounds present in petroleum and the necessity of meeting widely different requirements of purity of petroleum products call for specific methods of treatment as well as for specific and sensitive methods of analysis. With increasing use of aqueous caustic solutions for the removal of acidic sulfur impurities (*1*, *4*, *5*, *7*), methods of analysis for sulfur compounds in such solutions have become necessary. A number of analytical methods for the determination of mercaptans in oils have been described. The method of Tamele and Ryland (*2*, *6*) combines the advantages of several older methods with the selectivity and sensitivity afforded by the potentiometric determination of the end point of the reaction. The present article describes a similar procedure suitable for determination of mercaptans in aqueous alkaline solutions.

Outline of Proposed Method

The procedure is based on the potentiometric titration of mercaptans with the silver–silver nitrate indicator system. The titration is performed in aqueous alkaline solutions to which ammonium hydroxide has been added to prevent the coprecipitation of small amounts of silver oxide with the insoluble silver mercaptides. The indicator electrode is a silver rod, either polished or coated electrolytically with a thin layer of silver sulfide; the sulfide-coated electrode is more generally applicable and gives a greater potential drop at the end point, but the polished silver electrode is satisfactory and was used, unless otherwise stated, for the titration of pure mercaptan solutions. Only a few substances are likely to interfere with the determination because of the relatively high potential values at which silver mercaptides are precipitated. Hydrogen sulfide, which is often present with the lower mercaptans in refinery scrubbing solutions, is precipitated as black silver sulfide at a considerably more negative potential than the light-colored mercaptides, and thus it cannot be readily confused with mercaptans.

Apparatus and Reagents

A suitable arrangement of apparatus is shown in Figure 1. The indicator electrode, *S*, is a silver rod, either polished or coated with silver sulfide. Any standard reference electrode may be used; a layer of mercury covered with a 0.1 *N* solution of sodium acetate, either aqueous or alcoholic, was used with satisfactory results. The electrolyte bridge was filled with the same solution of sodium acetate as used in the reference electrode. Any potentiometer with a range of 1.0 volt and moderate accuracy is adequate. Where a large number of determinations must be carried out, a continuous-reading instrument is preferable.

All reagents used were C. P. grade or better. The standard 0.1 *N* solutions of silver nitrate were prepared by exact weighing of the dry salt (Merck's reagent) and were standardized by potentiometric titration of potassium iodide (*3*). The 0.01 *N* and 0.001 *N* solutions were made from this solution as required by exact dilution. The investigation was limited to the aliphatic mercaptans including methyl, ethyl, *n*-butyl, *tert*-butyl, *n*-amyl, *n*-heptyl, and isooctyl mercaptan. The mercaptans were purchased from the Eastman Kodak Company. To obviate the difficulty of preparing standard, aqueous, caustic solutions of mercaptans which are easily oxidized by air, approximately 0.1, 0.01, and 0.001 *N* solutions were made in ethyl alcohol and the exact concentration of the solutions was determined by potentiometric titration in alcoholic sodium acetate immediately before use (*6*); samples for titration were prepared from these standard solutions by further dilution with aqueous sodium hydroxide.

Procedure

The sample of aqueous mercaptan solution is adjusted to suitable alkalinity by addition of sodium hydroxide or by dilution with water; the alkalinity should be approximately 1 *N*. Increasing the concentration above 2 to 3 *N* may actually have an adverse effect because of the "salting out" action of the stronger caustic solutions which may overshadow the slightly more favorable distribution between free mercaptan and mercaptide ions caused by the increase in alkalinity (*7*). The solution is then made approximately 0.05 *N* with respect to ammonia by the addition of strong ammonium hydroxide solution. This amount was found sufficient to prevent precipitation of dark brown silver oxide. The final volume should be about 50 to 100 ml. The silver electrode is immersed in the solution, silver nitrate (0.1, 0.01, or 0.001 *N*) is introduced while the solution is gently stirred, and potential measurements are recorded.

The polished electrode assumes a negative potential which varies with the nature of the mercaptan and the composition of the solution. For a solution 1 *N* in sodium hydroxide and 0.05 *N* in ammonium hydroxide, and using alcoholic 0.1 *N* sodium acetate–mercury reference electrode, methyl and ethyl mercaptans impart the most negative potential of those tested, about −0.6 volt; isooctyl next, approximately −0.5 volt for the same solution; and intermediate mercaptans

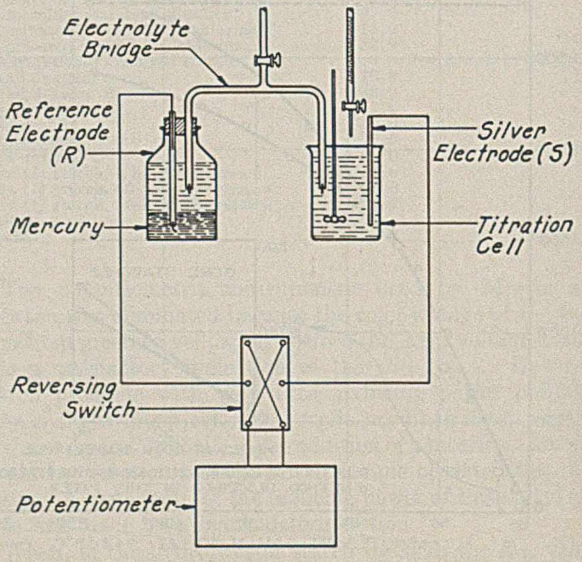

FIGURE 1. APPARATUS FOR POTENTIOMETRIC TITRATION OF MERCAPTANS

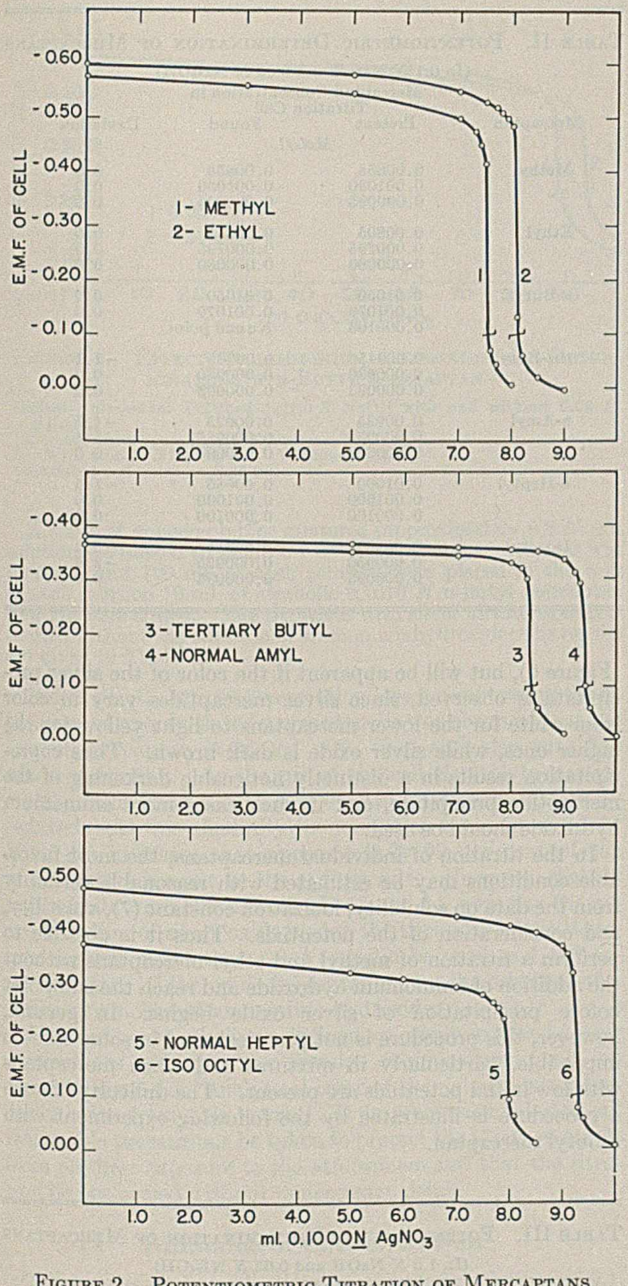

Figure 2. Potentiometric Titration of Mercaptans

Reference electrode: Hg|0.1 N alcoholic NaOAc
Indicator electrode: Ag|1.0 N NaOH, 0.05 N NH_4OH

around −0.3 to −0.4 volt (cf. Figure 2). The sulfide-coated indicator electrode assumes a more negative potential than the polished silver electrode when immersed in the same solution of mercaptan. This difference is marked in most cases; with *n*-butyl mercaptan, it amounts to approximately 0.28 volt. Thus, with the sulfide-coated electrode the break at the end point is more pronounced (Figure 3).

The end point of the titration is not taken at the inflection point of the curve but at the most positive potential value of the almost linear descending portion of the titration curve. This end point has been derived empirically from the titration of a large number of solutions of known concentration. The e. m. f. of the cell at the end point varies substantially with the composition of the solution (Figure 4). Increasing the concentration of caustic causes the initial potential of either indicator electrode to be somewhat more negative, but this advantage is more than offset by a shift to more negative values of the final potential which the electrodes assume when the mercaptan has been completely precipitated. The total change in potential is therefore less as the concentration of caustic is increased.

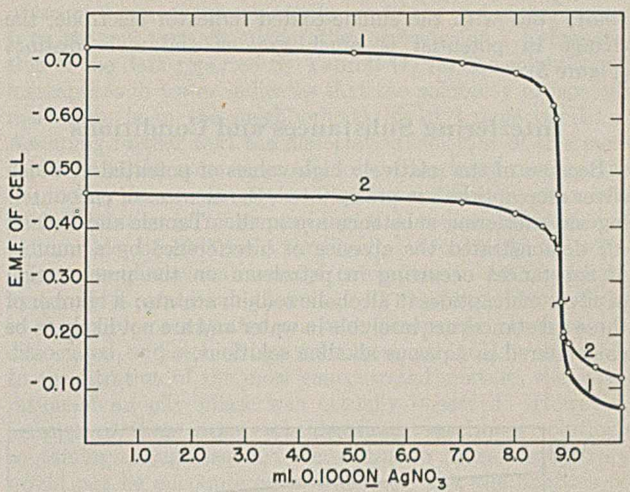

Figure 3. Titration of *n*-Butyl Mercaptan with Polished Silver and Sulfide-Coated Silver Indicator Electrode

Reference electrode: Hg|0.1 N aqueous NaOAc
Indicator electrode: Ag or Ag, Ag_2S|1.0 N NaOH, 0.05 N NH_4OH
1. Sulfide-coated electrode. 2. Polished silver electrode

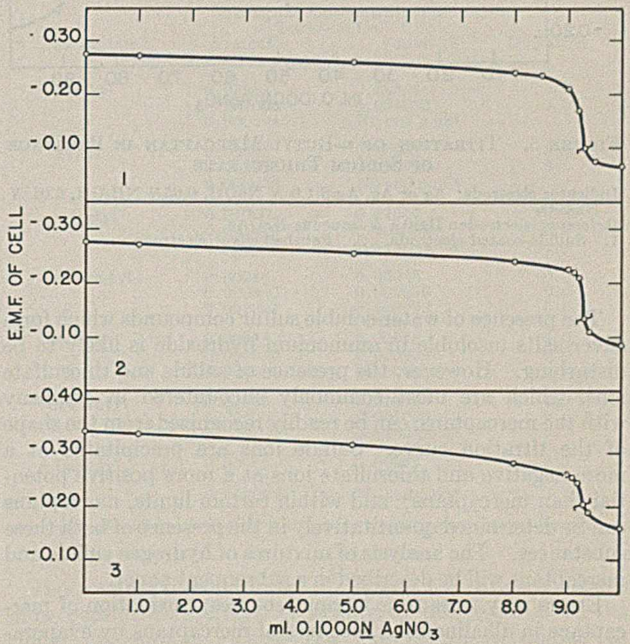

Figure 4. Effect of Concentration of Sodium Hydroxide on Titration of *tert*-Butyl Mercaptan

Indicator electrode: Polished Ag|(x) N NaOH, 0.05 N NH_4OH
Reference electrode: Hg|0.1 N alcoholic NaOAc
1. 0.1 N NaOH. 2. 1.0 N NaOH. 3. 10.0 N NaOH

The more negative potential of the sulfide-coated electrode in mercaptan solutions is of distinct advantage in the presence of ions which form insoluble silver salts. Thus, the titration of mercaptans in the presence of thiosulfate with the polished silver electrode gives a barely detectable inflection point; but with the sulfide-coated indicator electrode, the change in potential is much greater and more distinct (Figure 5).

Interfering Substances and Conditions

Because of the relatively high values of potential at which silver mercaptides are precipitated, the chances of encountering an interfering substance are small. Tamele and Ryland (*6*) demonstrated the absence of interference by a number of substances occurring in petroleum on the precipitation of silver mercaptides in alcoholic sodium acetate; a number of these substances are insoluble in water and are not likely to be encountered in aqueous alkaline solutions.

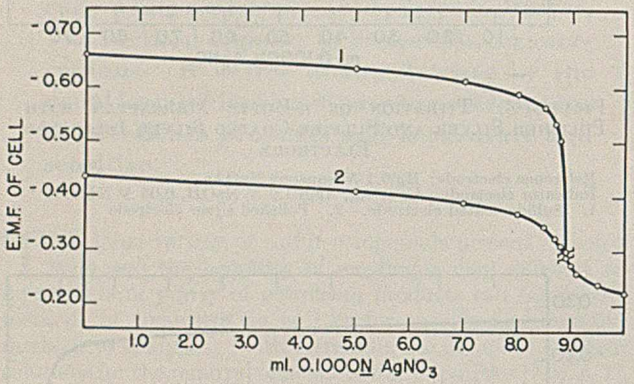

FIGURE 5. TITRATION OF *n*-BUTYL MERCAPTAN IN PRESENCE OF SODIUM THIOSULFATE

Indicator electrode: Ag or Ag, Ag_2S|1.0 *N* NaOH, 0.05*N* NH_4OH, 0.01 *N* $Na_2S_2O_3$
Reference electrode: Hg|0.1 *N* aqueous NaOAc
1. Sulfide-coated electrode. 2. Polished silver electrode

The presence of water-soluble sulfur compounds which form silver salts insoluble in ammonium hydroxide is likely to be disturbing. However, the presence of sulfide and thiosulfate ions, which are most commonly encountered in company with the mercaptans, can be readily recognized from the shape of the titration curve. Sulfide ions are precipitated at a more negative and thiosulfate ions at a more positive potential than mercaptans; and within certain limits, mercaptans can be determined quantitatively in the presence of both these substances. The analysis of mixtures of hydrogen sulfide and mercaptans will be described in a subsequent paper.

Errors may arise from various sources: oxidation of mercaptans in alkaline solutions, loss of mercaptans by evaporation, and coprecipitation of silver oxide due to lack of sufficient amount of ammonium hydroxide in the solution.

The coprecipitation of silver oxide with silver mercaptide cannot be detected from the shape of the titration curve (Figure 6), but will be apparent if the color of the silver precipitate is observed, since silver mercaptides vary in color from white for the lower mercaptans to light yellow for the higher ones, while silver oxide is dark brown. Thus coprecipitation results in a distinctly noticeable darkening of the mercaptide precipitate, and in such cases more ammonium hydroxide should be used.

TABLE I. POTENTIOMETRIC TITRATION OF 0.00918 *M* *n*-BUTYL MERCAPTAN SOLUTION

Concentration of Mercaptan in Titration Cell, Found	Deviation	Electrolyte	pH
Mole/l.	%		
0.00795	−13.4	Aqueous buffer mixture	7.0
0.00786	−14.4	Aqueous buffer mixture	8.0
0.00795	−13.4	Aqueous buffer mixture	9.0
0.00768	−16.2	Aqueous buffer mixture	10.0
0.00814	−11.3	Aqueous buffer mixture	11.0
0.00860	− 6.4	Aqueous buffer mixture	12.0
0.00924	+ 0.7	0.1 *N* NaOH	13.0
0.00924	+ 0.7	1.0 *N* NaOH	14.0

TABLE II. POTENTIOMETRIC DETERMINATION OF MERCAPTANS

(In 0.1 *N* NaOH and 0.05 *N* NH_4OH)

Mercaptan	Mercaptan Concentration in Titration Cell		Deviation
	Present	Found	
	Mole/l.		%
Methyl	0.00855	0.00855	0.0
	0.001050	0.001050	0.0
	0.000095	0.000095	0.0
Ethyl	0.00805	0.00805	0.0
	0.000795	0.000795	0.0
	0.000080	0.000080	0.0
n-Butyl	0.01050	0.01050	0.0
	0.001070	0.001070	0.0
	0.000103	No end point	...
tert-Butyl	0.00945	0.00935	−1.1
	0.000930	0.000930	0.0
	0.000093	0.000093	0.0
n-Amyl	0.00935	0.00925	−1.1
	0.000935	0.000925	−1.1
	0.000094	0.000094	0.0
n-Heptyl	0.01000	0.00985	−1.5
	0.001000	0.001000	0.0
	0.000100	0.000100	0.0
Isooctyl	0.00965	0.00915	−5.2
	0.000950	0.000925	−2.6
	0.000095	0.000095	0.0

In the titration of individual mercaptans, the most favorable conditions may be estimated with reasonable certainty from the data on solubility, ionization constant (*7*), volatility, and consideration of the potentials. Thus it is possible to perform a titration of methyl and ethyl mercaptans without the addition of ammonium hydroxide and reach the end point before precipitation of silver oxide begins. In general, however, this procedure is not practical, and in some cases is impossible, particularly in mixtures and when mercaptans with low initial potentials are present. The difficulty of such a procedure is illustrated by the following experiment with *n*-butyl mercaptan.

TABLE III. POTENTIOMETRIC DETERMINATION OF MERCAPTANS

(In 1.0 *N* NaOH and 0.05 *N* NH_4OH)

Mercaptan	Mercaptan Concentration in Titration Cell		Deviation
	Present	Found	
	Mole/l.		%
Methyl	0.00855	0.00855	0.0
	0.00105	0.00105	0.0
	0.000095	0.000095	0.0
Ethyl	0.00805	0.00805	0.0
	0.000795	0.000795	0.0
	0.000080	0.000080	0.0
n-Butyl	0.01050	0.01050	0.0
	0.00107	0.00107	0.0
	0.00010	No end point	...
tert-Butyl	0.00945	0.00935	−1.1
	0.000930	0.000930	0.0
	0.000093	0.000093	0.0
n-Amyl	0.00935	0.00935	0.0
	0.000935	0.000935	0.0
	0.000094	0.000094	0.0
n-Heptyl	0.01000	0.01000	0.0
	0.001000	0.001000	0.0
	0.000100	0.000100	0.0
Isooctyl	0.00965	0.00925	−4.1
	0.000950	0.000925	−2.6
	0.000095	0.000095	0.0

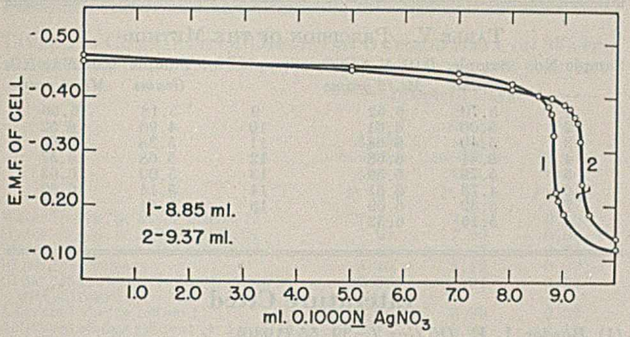

FIGURE 6. EFFECT OF AMMONIUM HYDROXIDE ON DETERMINATION OF *n*-BUTYL MERCAPTAN

Indicator electrode: Polished Ag|1.0 *N* NaOH with and without 0.05 *N* NH_4OH
Reference electrode: Hg|0.1 *N* aqueous NaOAc
1. With 0.05 *N* NH_4OH. 2. Without NH_4OH
Calculated end point = 8.85 ml.

A series of aqueous buffer mixtures (approximately 0.2 *N* salt solutions) adjusted to definite pH values in unit increments was prepared and 100 ml. of each solution were placed in the cell; to each solution 10 ml. of alcoholic 0.1010 *N* *n*-butyl mercaptan solution were added. The titrations with silver nitrate were performed without the addition of ammonium hydroxide; the results are given in Table I.

Below pH 13, serious evaporation losses occur owing to the presence of undissociated mercaptan; it was observed that the loss of mercaptan increased with time and also with the speed of stirring. As the pH of the cell electrolyte was increased from 10 to 13, the evaporation losses were materially reduced. At this alkalinity the ionization constant of 2.2×10^{-11} (*7*) indicates that approximately 99 per cent of the mercaptan is present as the sodium salt. However, slightly high results were obtained at pH 13 and 14, owing to the coprecipitation of silver oxide during the titration. It is therefore recommended that 1.0 *N* caustic be used and the coprecipitation of the oxide be prevented by the addition of a sufficient amount of ammonium hydroxide.

Mercaptans in alkaline solutions are easily oxidized by air to disulfides and other compounds. Serious errors far in excess of the inherent analytical error of the determination can easily arise from this source. It is recommended that all reasonable precautions be taken to protect the alkaline sample from needless exposure to the atmosphere and that the titration be performed without unnecessary delay.

Influence of Concentration

Three series of determinations were made in solutions of 0.1, 1.0, and 10.0 *N* sodium hydroxide. The concentration of mercaptans in the cell solution was varied from approximately 0.01 to 0.0001 *N*. The titrations were performed as follows: Mercaptan solutions in ethyl alcohol, approximately 0.1, 0.01, or 0.001 *N*, were standardized immediately before use. Ten milliliters of the solution of the desired strength were placed in the titration cell, the volume was brought to 95 ml. with the solution of sodium hydroxide, and 5 ml. of approximately 1.0 *N* ammonium hydroxide were added. (Thus the determinations were actually carried out in an aqueous 10 per cent solution of alcohol.) The results are assembled in Tables II, III, and IV.

The best results were obtained in solutions of 1.0 *N* sodium hydroxide. The small error reported in the titration of the most concentrated solution of tertiary butyl mercaptan cannot well be ascribed to the loss of mercaptan from the cell by evaporation; the solubility (0.0107 mole per liter) and the dissociation constant (0.89×10^{-11}) indicate that in solutions containing 0.01 mole per liter all of the mercaptan should be retained by 1.0 *N* sodium hydroxide (*7*). This error appears thus to be merely accidental. However, the errors observed in the titration of the more concentrated solutions of isooctyl mercaptan are attributed to the loss of mercaptan from the cell through evaporation or occlusion. Extrapolation of the data reported by Yabroff (*7*) for the solubility of mercaptans in water indicates that the solubility of isooctyl mercaptan is in the neighborhood of 10^{-5} mole per liter. Assuming further that the dissociation constant of this mercaptan is of the same order as those of the lower mercaptans (C_2 to C_7), the concentration of undissociated mercaptan in a 0.01 *N* solution of mercaptan in 1.0 *N* sodium hydroxide is of the order of 10^{-5} mole per liter. Undoubtedly the solubility of undissociated isooctyl mercaptan in 1.0 *N* sodium hydroxide is considerably less than 10^{-5} mole per liter. Thus in the more concentrated mixtures a separate phase of undissociated, undissolved isooctyl mercaptan could be expected. In the titration of the most concentrated mixture, the separation of an oily phase was actually observed. However, because of these same considerations, scrubbing solutions containing enough isooctyl mercaptan to cause these errors would not be encountered in practice. For the analysis of nonaqueous solutions containing mercaptans, it is recommended that the titrations be performed in alcoholic medium (*6*).

TABLE IV. POTENTIOMETRIC DETERMINATION OF MERCAPTANS

(In 10.0 *N* NaOH and 0.05 *N* NH_4OH)

Mercaptan	Mercaptan Concentration in Titration Cell Present	Mercaptan Concentration in Titration Cell Found	Deviation
	Mole/l.		%
Methyl	0.00855	0.00855	0.0
	0.001050	0.001050	0.0
	0.0000945	No end point	...
Ethyl	0.00805	0.00805	0.0
	0.000795	0.000795	0.0
	0.000078	No end point	...
n-Butyl	0.01050	0.01050	0.0
	0.001070	0.001080	+0.9
	0.000103	No end point	...
tert-Butyl	0.00945	0.00945	0.0
	0.000930	0.000930	0.0
	0.000093	0.000093	0.0
n-Amyl	0.00935	0.00935	0.0
	0.000935	0.000935	0.0
	0.000094	No end point	...
n-Heptyl	0.01000	0.01000	0.0
	0.001000	0.001000	0.0
	0.000100	No end point	...
Isooctyl	0.00965	0.00945	−2.1
	0.000945	0.000930	−1.6
	0.000095	No end point	...

The results obtained in 0.1 *N* sodium hydroxide solutions show considerable errors, especially in the titration of the higher mercaptans. These can likewise be attributed to evaporation and occlusion losses. Increasing the concentration of sodium hydroxide to 10 *N* reduces the sensitivity of the method at least tenfold and does not increase the accuracy of the method over that obtained in 1.0 *N* sodium hydroxide. Apparently the beneficial effect which could be expected with a shift in the equilibrium favoring the presence of a greater proportion of the isooctyl mercaptan as isooctyl mercaptide ion is offset by the salting-out effect of the stronger caustic solution.

Accuracy

The accuracy attainable by the method appears to be influenced by a number of factors, including the nature and concentration of the mercaptan, its solubility and volatility, and the oxidizability of its alkaline solution. With due precautions and under the specified conditions the accuracy appears to be about equal to the accuracy of the standardization of the alcoholic solutions by the potentiometric method of Tamele and Ryland (*6*). Alkaline solutions of mercaptans are very readily oxidized by air. Errors greater than those inherent in the method may arise from undue exposure of samples to atmospheric oxygen. By careful manipulation as described, the errors can be kept within reasonable limits without resorting to air exclusions.

Precision

The precision of the results is difficult to estimate accurately, owing to the above-mentioned instability of dilute mercaptan solutions. Without taking any special precautions it was found that the standard deviation (root mean square deviation) as determined from fifteen titrations of a sample of *n*-butyl mercaptan with 0.01 *N* aqueous silver nitrate in 1.0 *N* sodium hydroxide and 0.05 *N* ammonium hydroxide was within 0.05 ml. It is believed that this figure is affected somewhat by oxidation of the standard mercaptan solution, as the results (Table V) show a slight trend to lower values as successive samples were withdrawn.

TABLE V. PRECISION OF THE METHOD

Sample No.	Sample *Grams*	0.01 *N* $AgNO_3$ *Ml./5 grams*	Sample No.	Sample *Grams*	0.01 *N* $AgNO_3$ *Ml./5 grams*
1	5.70	6.62	9	5.18	6.56
2	5.00	6.61	10	4.96	6.52
3	5.40	6.68	11	5.38	6.65
4	5.41	6.68	12	5.68	6.57
5	5.79	6.59	13	5.00	6.63
6	4.73	6.61	14	5.14	6.63
7	5.32	6.69	15	5.54	6.57
8	5.16	6.52			

Literature Cited

(1) Border, L. E., *Oil Gas J.*, 39, 55 (1940).

(2) Ellis, C., "Chemistry of Petroleum Derivatives", p. 1157, New York, Reinhold Publishing Corp., 1937.

(3) Kolthoff, I. M., and Lingane, J. J., *J. Am. Chem. Soc.*, 58, 1528 (1936).

(4) LaCroix, H. N., and Coulthurst, L. J., *Refiner Natural Gasoline Mfr.*, 18, 90 (1939).

(5) Robinson, P. M., *Natl. Petroleum News*, 32, No. 34, R-298 (1940).

(6) Tamele, M. W., and Ryland, L. B., IND. ENG. CHEM., ANAL. ED., 8, 16 (1936).

(7) Yabroff, D. L., IND. ENG. CHEM., 32, 257 (1940).

Sulfamic Acid Modification of the Winkler Method for Dissolved Oxygen

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ACCORDING to Gordon and Cupery (*3, 4*) the recent development of a practical process for commercial scale manufacture of sulfamic acid (NH_2HSO_3) has aroused much interest in this chemical. It has long been known that nitrites react rapidly with sulfamic acid to yield nitrogen and sulfuric acid. A novel industrial application of this reaction is the removal of excess nitrite following diazotization—for example, in dye and lake manufacture. Sulfamic acid is two to six times more effective on a weight basis than urea, which is commonly used for such purposes. This ability to react with and destroy nitrites led to the authors' belief that sulfamic acid might be substituted for sodium azide as a preliminary treatment for removal of nitrites in the Winkler method for dissolved oxygen.

Properties of Sulfamic Acid

Dry sulfamic acid is a stable, nonhygroscopic, odorless, colorless, crystalline product. It is moderately soluble in water, its solubility varying from 14.68 grams at 0° to 47.08 grams at 80° C. per 100 grams of water. Its solubility in water is decreased by presence of sulfuric acid or sodium sulfate and becomes negligible in 70 to 100 per cent sulfuric acid. Sulfamic acid is highly ionized in aqueous solution. The strength of the acid is indicated by its reaction with basic oxides, hydroxides, and carbonates to form sulfamates. These salts are practically all soluble in water.

Sulfamic acid is essentially stable in water solution at ordinary temperature. At elevated temperatures the acid is slowly hydrolyzed to ammonium acid sulfate (*3*). Salts of sulfamic acid are stable in neutral or alkaline solution, and such solutions may be evaporated to dryness on the steam bath without hydrolysis of the amide group.

In cold solution, chlorine, bromine, and chlorates oxidize sulfamic acid to sulfuric acid. Potassium permanganate, chromic acid, and ferric chloride exert no oxidizing action. Nitric acid yields nitrous oxide and sulfuric acid. Nitrites react rapidly with sulfamic acid, liberating nitrogen and forming sulfuric acid. This reaction may be utilized for the analytical determination of nitrites or of sulfamic acid (*2, 5*).

The properties indicate that sulfamic acid might prove a desirable agent for the destruction of nitrites in the determination of dissolved oxygen and biochemical oxygen demand. It has recently been shown that sodium azide is very satisfactory for this purpose in stream-pollution and sewage studies (*1, 6, 7*). Sulfamic acid is theoretically only two thirds as effective as sodium azide on a weight basis, as the following equations show:

$$NH_2SO_2OH\ (97) + HNO_2 \rightarrow H_2SO_4 + N_2 + H_2O$$

$$NaN_3\ (65) + H_2SO_4 + HNO_2 \rightarrow N_2 + H_2O + N_2O + NaHSO_4$$

However, sulfamic acid possesses the advantages of cheapness, availability, nonpoisonous nature, stability in sulfuric acid, and the formation of soluble sulfamates. Consequently, a comparative study of sulfamic acid and sodium azide for nitrite destruction in the dissolved oxygen determination was undertaken.

Experimental

A comparative study of the reaction times of 2 per cent sodium azide and 4 per cent sulfamic acid solutions showed that the reaction between sodium azide and nitrites in acid solution proceeded more rapidly than the corresponding reaction with sulfamic acid. However, the latter reaction was sufficiently rapid to justify further experimental work on the use of sulfamic acid as a nitrite-destroying reagent.

TABLE I. COMPARATIVE DISSOLVED OXYGEN DATA ON WATER, DILUTE SEWAGE, AND TREATMENT PLANT EFFLUENT SAMPLES

	Dissolved Oxygen[a]		
	Azide modification	Sulfamic acid modification	Deviation
	P. p. m.	*P. p. m.*	*P. p. m.*
Water + 2 p. p. m. of nitrite N	7.74	7.84	0.10
Water + 4 p. p. m. of nitrite N	7.92	7.92	0.00
Water + 6 p. p. m. of nitrite N	7.85	7.89	0.04
10 per cent sewage	8.10	8.17	0.07
10 per cent sewage + 5 p. p. m. of nitrite nitrogen	7.96	8.04	0.08
Activated sludge effluent	8.96	8.98	0.02
Activated sludge effluent + 5 p. p. m. of nitrite nitrogen	8.78	8.88	0.10
Trickling filter effluent	7.96	8.03	0.07
Trickling filter effluent + 5 p. p. m. of nitrite nitrogen	7.84	7.86	0.02

[a] Each value is mean of three determinations.

Tables of solubility of sulfamic acid (*3*) in varying concentrations of sulfuric acid show that a 20 per cent sulfuric acid solution will dissolve approximately 5 grams of sulfamic acid per 100 ml. of solution at 30° C. This being true, it should be possible to add the sulfamic acid as a solution in dilute sulfuric acid in the preliminary treatment for nitrites. Accordingly, the sulfamic solutions used in all of the following experiments, unless otherwise stated, were prepared as follows:

> Four grams of sulfamic acid are dissolved in 50 ml. of distilled water and 50 ml. of cold 40 per cent sulfuric acid are added. In this manner very little heat is evolved, thus eliminating the possibility of hydrolysis of the amino group. The solution thus prepared is slightly turbid, but this is of no consequence. One milliliter of this solution was used as preliminary treatment for destruction of nitrites in a 300-ml. dissolved-oxygen sample bottle. As applied, this quantity of sulfamic acid will destroy 19.3 p. p. m. of nitrite nitrogen and is ample for all samples likely to be encountered in water and sewage work. After addition of the reagent the bottle is stoppered and shaken and then allowed to stand for 10 minutes. From this point on, the procedure is identical with that of the azide modification.
>
> Solutions of varying concentrations of nitrites in distilled water were prepared containing from 2 to 6 p. p. m. of nitrite nitrogen. Dissolved oxygen was then determined on this water by the azide and sulfamic acid modifications. A similar comparison was run on sewage dilutions, trickling filter effluent, and activated sludge effluent both alone and with addition of nitrites.

Enough nitrogen was liberated in the destruction of the higher concentrations of nitrites to cause the manganese hydroxide floc to rise to the top of the bottle. However, upon reshaking the bottles in the course of dissolved-oxygen determinations, the bubbles were disengaged from the precipitate, which then settled well. The results are given in Table I. The deviations in the results obtained with these modifications vary between 0.02 and 0.10 p. p. m. and are of the same order of magnitude whether or not nitrite was added to the samples. These data demonstrate the efficacy of the use of sulfamic acid in the dissolved-oxygen procedure.

A series of experiments was carried out toward the development of a shorter, simpler procedure employing sulfamic acid. It was found that the addition of sulfamic acid along with the alkaline iodide reagent (like the azide in the original Alsterberg procedure) was valueless, because the sodium sulfamate formed in alkaline solution does not remove nitrite and the sulfamic acid produced after the final acidification did not remove it in the presence of free iodine. It is possible to apply the sulfamic acid with the manganous sulfate solution and allow time for the nitrite removal reaction before the alkaline iodide reagent is added. This was tried, employing 2 ml. of a manganous sulfate solution (480 grams of manganous sulfate tetrahydrate and 40 grams of sulfamic acid per liter) in a 300-ml. sample.

The data obtained in the determination of dissolved oxygen by several procedures in the presence of nitrites and copper and nitrites and organic matter are given in Table II. They indicate that all modifications tried were satisfactory in the presence of 100 p. p. m. of copper and 14.4 p. p. m. of nitrite nitrogen. In the presence of large amounts of organic matter the nitrites were removed effectively by all modifications tried except C, employing the manganous sulfate-containing sulfamic acid. This procedure definitely fails to remove nitrites satisfactorily in the presence of peptone or glucose. Although the so-called short Winkler technique was employed on these samples, the effect of oxidation of peptone and glucose during alkalinization with the subsequent reduction in the dissolved oxygen by 0.30 to 0.41 p. p. m. from the initial values in the distilled water is indicated by all satisfactory nitrite-removing modifications.

Azide and Sulfamic Acid as Preservatives for Dissolved Oxygen Samples

In field studies of sewage-treatment plants or polluted streams, it is sometimes desirable or necessary to delay the determination of dissolved oxygen for several hours after the samples have been collected. To do this it is necessary to inhibit biochemical oxidation, besides taking precautions to prevent gain or loss of oxygen due to temperature changes. It has been shown (*6*) that the sulfuric acid–sodium azide treatment is more effective for preserving the initial dissolved oxygen values than either sulfuric acid treatment alone or the application of the complete Winkler procedure followed by the iodine titration after the interval of storage. The efficacy of the sulfamic acid treatment for dissolved-oxygen sample pres-

TABLE II. COMPARATIVE DISSOLVED OXYGEN RESULTS

(Obtained under adverse conditions with several azide and sulfamic acid modifications)

Concentration of Interfering Substances Added to Distilled Water	Initial D. O. in Distilled Water	D. O. Results Obtained with Each Modification A	B	C	D	E
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
100 p. p. m. of Cu^{++} + 1.7 p. p. m. of nitrite N	7.76	7.77	7.75	7.79	7.74	7.72
100 p. p. m. of Cu^{++} + 8.4 p. p. m. of nitrite N	7.76	7.75	7.75	7.88	7.76	7.80
100 p. p. m. of Cu^{++} + 14.4 p. p. m. of nitrite N	7.15	7.14	7.12	7.25	7.24	7.15
1000 p. p. m. of glucose + 1.7 p. p. m. of nitrite N	7.79	7.52	7.32	7.80	7.51	7.44
1000 p. p. m. of glucose + 8.4 p. p. m. of nitrite N	7.79	7.61	7.42	10.65	7.52	7.41
500 p. p. m. of peptone, no nitrite	7.65	7.35	7.30	...	7.28	7.25
500 p. p. m. of peptone + 4.8 p. p. m. of nitrite N	7.65	7.33	7.27	...	7.30	7.31
500 p. p. m. of peptone + 9.6 p. p. m. of nitrite N	7.65	7.29	7.24	...	7.28	7.24
500 p. p. m. of peptone + 14.4 p. p. m. of nitrite N	7.65	7.30	7.25	...	7.35	7.28

A = Sulfuric acid–sodium azide preliminary treatment.
B = Sulfamic acid preliminary treatment.
C = Manganous sulfate–sulfamic acid preliminary treatment.
D = Alsterberg azide treatment.
E = C and D combined.

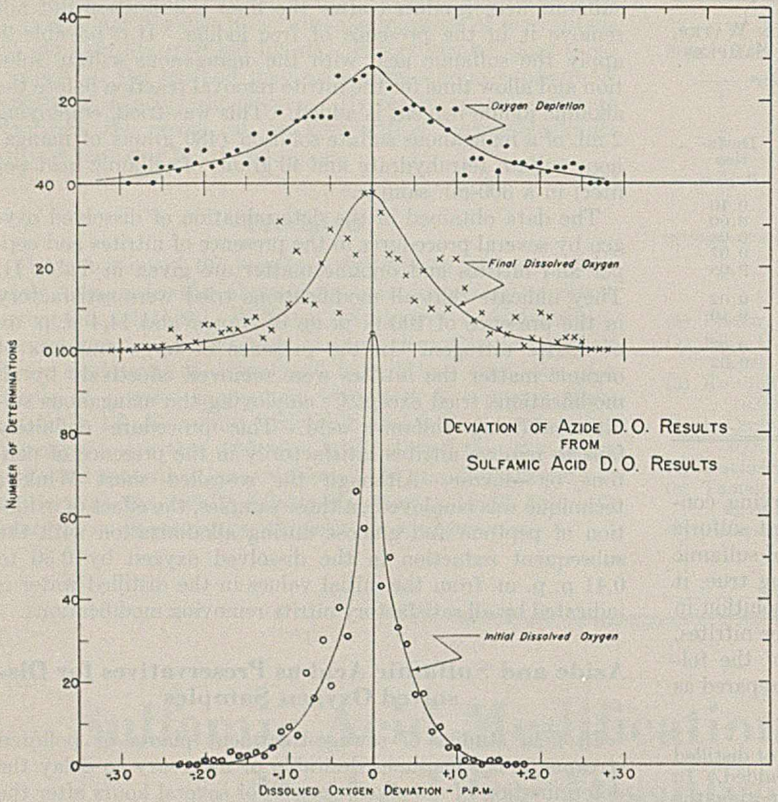

Figure 1. Dissolved Oxygen

Table III. Dissolved Oxygen Results on Preservation Tests

	25% Sewage		10% Sewage		Activated Sludge Effluent (100%)		Trickling Filter Effluent (100%)	
	Azide	Sulfamic acid	Azide	Sulfamic acid	Azide	Sulfamic acid	Azide	Sulfamic acid
Initial	8.51	8.56	8.27	8.24	7.57	7.60	7.67	7.80
2-hour interval	8.41	8.46	8.15	8.19	7.44	7.48	7.62	7.79
4-hour interval	8.10	8.25	8.02	8.15	7.33	7.32	7.38	7.56
24-hour interval	7.92	7.91	7.07	7.03	7.12	7.11	7.09	7.17
			Loss of Dissolved Oxygen					
After 2 hours	0.10	0.10	0.12	0.05	0.13	0.12	0.05	0.01
After 4 hours	0.41	0.31	0.25	0.09	0.24	0.28	0.29	0.24
After 24 hours	0.59	0.65	1.20	1.21	0.45	0.49	0.58	0.63

ervation was, therefore, compared to the sulfuric acid–sodium azide treatment. The material selected for this test was a 25 per cent mixture of sewage with dilution water. This constitutes a more stringent test than is necessary for stream-pollution work.

Twenty-four bottles were put up, twelve of which were dosed with the azide reagents and twelve with the sulfamic acid reagent. Of these, six were used for initial dissolved oxygen, three with the sulfamic acid and three with the azide treatment. The remainder were allowed to stand at room temperatures and dissolved-oxygen determinations were made on these after intervals of 2, 4, and 24 hours. Similar tests were also made on trickling filter and activated sludge effluents. These results are shown in Table III, all titration figures being the average of three determinations.

Comparative B. O. D. Determinations by Azide and Sulfamic Acid Methods

In an extensive, practical, comparative study, samples from four different sources were used: the Ohio River and tributary streams in the Cincinnati area, settled sewage, an experimental trickling filter effluent, and activated sludge effluent. In all, a total of 652 duplicate samples was analyzed by the two procedures and the mean results obtained are shown in Table IV.

The individual differences between the initial dissolved-oxygen results obtained by these two modifications upon all the samples were tabulated and a frequency curve for these data is plotted in Figure 1. Positive differences signify that the azide value is greater, and negative differences that the sulfamic acid result is greater. Similar plots showing the frequency distribution of the differences in the final dissolved-oxygen results and the oxygen-depletion results are shown on higher levels in the same figure. All these curves indicate practically normal probability distribution. There may be a slight tendency for a larger frequency of negative differences in the initial dissolved-oxygen data, indicating slightly higher results for the sulfamic acid modification. This tendency is not apparent in the final dissolved-oxygen data.

The standard deviations obtained in each of the above sample groups and for all of the samples combined are given in Table V and are in general in very close agreement. There is, however, a slightly greater variation between the initial and final dissolved-oxygen deviations and between the initial dissolved-oxygen and oxygen-depletion deviations than between the final dissolved-oxygen and oxygen-depletion deviations. This is probably due to the added factor of bacterial action in oxygen consumption during the 5-day incubation period.

The sulfamic acid method is not recommended when the sample contains interfering substances such as suspensions of river mud, quantities of ferrous and ferric iron (50 p. p. m. or less of ferric iron do not interfere), sulfite wastes, or other oxidizing and reducing agents.

Summary

A modified Winkler procedure, employing a solution of 4 per cent sulfamic acid in 20 per cent sulfuric acid as a pre-

Table IV. Mean Comparative Dissolved Oxygen and Oxygen Depletion Data

(Obtained with azide and sulfamic acid modifications of Winkler method)

Samples	No. of Samples Compared	Dissolved Oxygen: Initial, Azide modification	Dissolved Oxygen: Initial, Sulfamic acid modification	Dissolved Oxygen: Final, Azide modification	Dissolved Oxygen: Final, Sulfamic acid modification	Oxygen Depletion in 5 Days[a]: Azide modification	Oxygen Depletion in 5 Days[a]: Sulfamic acid modification
		P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
Ohio River and tributaries	322	8.80	8.80	6.53	6.54	2.25	2.26
Raw sewage dilutions	119	8.36	8.37	5.52	5.51	2.84	2.87
Activated sludge effluent dilutions	90	8.11	8.11	6.41	6.41	1.71	1.72
Trickling filter effluent dilutions	121	8.27	8.28	5.50	5.45	2.78	2.81

[a] Values for each method are multiplied by a dilution factor to obtain 5-day B. O. D.

Table V. Comparison of Standard Deviations of Results Obtained by Azide and Sulfamic Acid Modifications of Winkler Method

Samples	No. of Samples in Series	Standard Deviation Initial dissolved oxygen	Standard Deviation Final dissolved oxygen	Standard Deviation Oxygen depletion
		P. p. m.	*P. p. m.*	*P. p. m.*
Ohio River and tributaries	322	0.070	0.12	0.14
Raw sewage dilutions	119	0.073	0.18	0.19
Trickling filter effluent dilutions	121	0.052	0.15	0.16
Activated sludge effluent dilutions	90	0.047	0.15	0.16
Combined	652	0.065	0.14	0.16

liminary treatment for the removal of nitrites in the dissolved oxygen determination is as satisfactory as the azide modification for the determination of dissolved oxygen and biochemical oxygen demand in sewage-treatment and river-pollution studies.

The two modifications, azide and sulfamic acid, appear to have equal value in the prevention of biochemical oxidation when it is necessary to store a dissolved-oxygen sample for a short time.

Acknowledgment

The authors wish to acknowledge the assistance of Oliver R. Placak in the analytical work and R. S. Smith in preparation of Figure 1.

Literature Cited

(1) Barnett, G. R., and Hurwitz, E., *Sewage Works J.*, **11**, 781 (1939).
(2) Baumgarten and Marggraff, *Ber.*, **63**, 1019 (1930).
(3) Cupery, M. E., Ind. Eng. Chem., 30, 628 (1938).
(4) Gordon, W. E., and Cupery, M. E., *Ibid.*, **31**, 1237 (1939).
(5) Hahn and Baumgarten, *Ber.*, **63**, 3028 (1930).
(6) Placak, O. R., and Ruchhoft, C. C., Ind. Eng. Chem., Anal. Ed., **13**, 12 (1941).
(7) Ruchhoft, C. C., Moore, W. A., and Placak, O. R., *Ibid.*, **10**, 701 (1938).

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Polarographic Determination of Ascorbic Acid

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SINCE polarographic analysis is essentially based on current voltage curves and ascorbic acid is a reducible electrolyte, this method seems suitable for vitamin C determinations. The determination is not hindered by the presence of pigments, it is specific, and it is sensitive to small amounts of electrolyte. Very complete discussions have been published by Kolthoff and Lingane (*4*) and Muller (*5*).

Preliminary vitamin C determinations were made with a Fisher Elecdropode (*2*) or polarograph. To run a determination, the beaker containing the solution to be analyzed is placed under the dropping mercury electrode. About 5 mm. of pure mercury are placed in the bottom of the beaker to act as the quiet mercury electrode and the platinum anode contact is immersed. Nitrogen is then passed through the solution as a steady stream of bubbles. This is continued for 15 minutes in order to eliminate any dissolved atmospheric oxygen, which might interfere with the curve, since it is easily reduced at the dropping electrode. Just before starting the determination, the nitrogen is started flowing across the surface of the solution instead of through it. If the gas is not thus cut off, fluctuations occur in the curve. During the determination the rate of dropping of the mercury should be kept at one drop every 3 to 6 seconds, if accurate results are to be expected. Too slow dropping causes slow oscillations in the polarogram and instability in the record. Too fast dropping produces undesirable agitation and mixing effects in the surrounding electrolyte. The dropping rate can be adjusted by changing the height of the mercury reservoir attached to the electrode.

Kodicek and Wenig (*3*) suggested the use of a 0.067 N phosphate buffer and used the dropping mercury electrode polarized as an anode in the determination of vitamin C on the polarograph. Since 2 per cent metaphosphoric acid has been found very satisfactory as an extractant, work was started using it as the base solution in the determination and very satisfactory curves were obtained (Figure 1). One to 3 cc. of an ascorbic acid solution, which was approximately 0.001 N, were added to about 50 cc. of the base solution. Curves were drawn using the dropping mercury electrode both as the anode and as the cathode. No very sharp rise was noted when the electrode was polarized as the anode; however, on one set of curves there did seem to be a very definite rise at about +0.33 volt, which was in the vicinity of that noted by Kodicek and Wenig. The difference in height caused by varying concentrations was slight even on this curve. A much sharper drop occurred at −1.77 volts. This reading was constant, varying not more than ±0.05 volt for all the curves run.

Since 0.067 N phosphate buffer at pH 7 had been suggested, this, an acetate buffer of pH 2.2, and a potassium acid phthalate–hydrochloric acid buffer of pH 2.2 were also tried, but none gave very consistent results. The phosphate buffer gave a rise which was not typical; the acetate buffer caused too rapid dropping of the mercury as the voltage rose and the half-wave potential came at decreasing voltages with increasing ascorbic acid concentration; the potassium acid phthalate–hydrochloric acid buffer resulted in pronounced maxima and the rise caused by the buffer occurred at the same voltage as that caused by vitamin C. As this was the only base solution causing maxima, no precautions were taken for their prevention. A 5 per cent sulfuric acid solu-

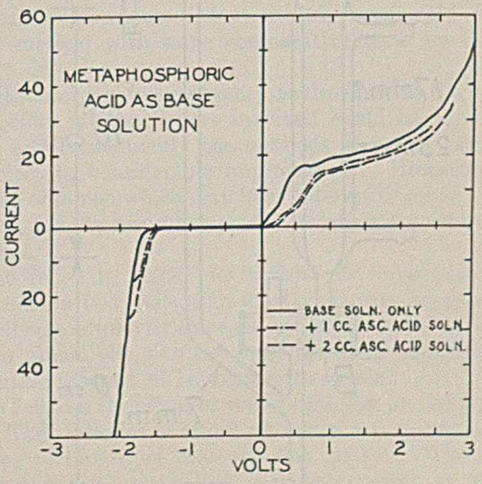

Figure 1. Polarographic Curve

tion was tried as base solution, but increased the rate of flow of the mercury drops to such an extent that no readings could be made.

Since each compound results in a characteristic rise at a specific voltage with the use of the proper base solution, the interference of such substances as cystine and glutathione would be eliminated. The acid base solution used for this ascorbic acid determination inhibits the production of current rises by these compounds. They are determined polarographically in ammoniacal solutions of cobaltous chloride in ammonium chloride (*1*).

Since this work was only preliminary, no quantitative determinations of ascorbic acid were run. However, results obtained indicated that this method could be adapted for accurate quantitative analysis by comparing the curves obtained when an unknown solution was used with calibration curves.

Acknowledgment

The author is indebted to C. G. King of the University of Pittsburgh for assistance and guidance during the investigation and to the Buhl Foundation for a research grant which made the investigation possible.

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Literature Cited

(1) Brdicka, R., *Coll. Czech. Chem. Commun.*, **5**, 112–28, 148–63 (1933).
(2) Fisher Scientific Co., *Laboratory*, **10** (5), 97 (1939).
(3) Kodicek, E., and Wenig, K., *Nature*, **142**, 35 (1938).
(4) Kolthoff, I. M., and Lingane, J. J., *Chem. Rev.*, **24** (1), 1 (1939).
(5) Muller, O. H., *Ibid.*, **24** (1), 95 (1939).

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A Simplified, Water-Jacketed, Fraction Receiver

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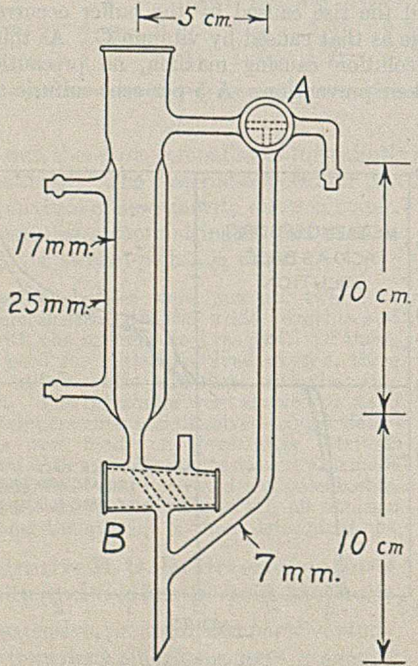
WITH the development of precision fractionating columns for use under reduced pressure has come a need for a receiver which will permit an indefinite number of fractions to be obtained without disturbing the pressure within the still. The older types of vacuum receivers, such as the Bruhl receiver, and the many varieties of multiple rotating receivers (*2*) are inadequate since the number of fractions which may be obtained with them is strictly limited.

Several variations of the Thorne (*4*) distillation triangle are described in Morton (*2*), some of them very satisfactory. Cloke (*1*) has recently proposed a water-jacketed modification, and Noonan (*3*) has designed a vacuum receiver in which the usual four two-way stopcocks have been replaced by a single multiple-way stopcock. The greatest disadvantage of these receivers is that they are expensive, owing to the large number or special nature of the stopcocks required, or that they require considerable glass-blowing skill to make.



The accompanying figure shows a fraction receiver which the authors developed in the organic preparations laboratory at the University of Notre Dame.

It combines the advantages of the earlier types with greater simplicity of manufacture and operation, and reduced cost. It can be easily made by an amateur glass-blower. Only two standard 2-mm. bore stopcocks are required: a three-way T stopcock (Corning No. 7420) and a three-way parallel stopcock (Corning No. 7380). The cost is considerably less than that of four two-way stopcocks. The dimensions given are those which have been found most satisfactory with the ordinary laboratory stills, but a larger or smaller reservoir may be made for special work.

The operation of the apparatus is simple. The sample is transferred from the reservoir of the fraction receiver to the receiver through stopcock *B*. *B* is closed and *A* is given a half turn, so that the receiver is disconnected from the pump but the still remains under vacuum. Air is admitted to the receiver through *B*. After the receiver containing the fraction has been removed and a fresh receiver attached, *B* is closed and *A* is turned clockwise a quarter turn, so that the still is temporarily disconnected from the pump while the new receiver is being evacuated. When the correct pressure has been established in the receiver, *A* is turned clockwise again a quarter turn, so that the still and the receiver are both connected to the vacuum line as shown.

Ground-glass joints may be used to connect the fraction receiver to the column and to the receiver, but this raises the cost without materially adding to the usefulness of the apparatus. A double tube may be used to connect the fraction receiver to the receiver to avoid any difficulty with viscous liquids rising in the equalizing arm, but for the most part this refinement has not been found necessary.

Acknowledgment

The authors wish to thank Kenneth N. Campbell for his suggestions during the course of this work.

Literature Cited

(1) Cloke, J. B., Ind. Eng. Chem., Anal. Ed., **12**, 329 (1940).
(2) Morton, A. A., "Laboratory Technique in Organic Chemistry", p. 110, New York, McGraw-Hill Book Co., 1938.
(3) Noonan, E., Ind. Eng. Chem., Anal. Ed., **10**, 34 (1938).
(4) Thorne, L. T., *Ber.*, **16**, 1327 (1883).

Determination of Peroxide Values for Rancidity in Fish Oils

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Customary peroxide methods for determining rancidity of fish oils are entirely empirical, only a portion of the peroxide reacting with the iodide to liberate iodine. The extent of the reaction depends upon the experimental conditions of the procedure used, such as peroxide concentration present, reaction time, etc. Moreover, with highly unsaturated oils, much of the liberated iodine may be absorbed by the oil.

Some of the factors controlling the reaction have been studied, and it is shown how the empirical nature of this determination can be decreased, and the reaction made more nearly quantitative and less dependent upon experimental conditions by increasing the acidity of the reaction mixture through the addition of strong mineral acids. Several other modifications in the conventional procedures are also suggested to improve precision.

PEROXIDE numbers have been widely used as an index of rancidity of oils. A number of different procedures are available for making such determinations, but results by the different methods do not always show good agreement, and in using a given method, results are often not reliable. At least with fish oils, precision is often poor, end points are vague, and correlation between peroxide number and organoleptic rancidity is uncertain.

Since fish oils are among the most unsaturated of edible oils, rancidity is of considerable importance, and the Fish and Wildlife Service has been concerned with the problem of determining it. A considerable amount of data has been obtained as to the limitations of this method for fish oils and the purpose of this report is to discuss these data.

The peroxide test suffers certain fundamental limitations which cannot be improved upon. The peroxide compounds, being intermediate and not in themselves responsible for the rancid flavors or odors, can be proportional to rancidity only so long as they are formed from the fresh oil at a greater rate than they are decomposed to the rancid products.

Thus, in the reaction: fresh oil $\xrightarrow{A}$ peroxide $\xrightarrow{B}$ rancid oil, so long as the rate of reaction A exceeds that of reaction B, the peroxide value will increase with increasing rancidity and a certain measure of its development will be obtained. If, however, the rate of reaction B should exceed that of reaction A, then the peroxide value will decrease with increasing rancidity of the oil. Accordingly, factors which affect these two rates are of importance in determining the value of the peroxide test as a measure of rancidity. One such factor is the temperature of storage of the oil. The temperature coefficient of reaction B can be considered to be much greater than that of reaction A, so that with increasing storage temperatures, peroxide numbers become less and less a reliable measure of rancidity.

Another case of the failure of peroxide values to correlate with rancidity is illustrated by the result obtained for the oil in salt fish (*4*). Such fish are normally stored at room temperature and the oil after several months' storage becomes extremely rancid. The peroxide values, however, do not give any measure of such rancidity. They show a slight rise followed by a drop to zero.

In using the peroxide test under a new set of conditions it is always first necessary to be sure a correlation is obtained with organoleptic rancidity, and unreliable results are often obtained if peroxide values obtained for an oil stored under one set of conditions are compared with those for the oil stored under some other conditions.

Errors of another type include those caused by faulty procedure. Evidence of the existence of such errors has been available for some time.

Thus, Lowen, Anderson, and Harrison (*5*) show that the peroxide value obtained depends upon the size of the oil sample used. Other errors include vague end points in some cases, poor checks on duplicate samples, and different peroxide values when different procedures are used.

Taffel and Revis (*6*) heat the oil with glacial acetic acid in the presence of nitrogen gas and solid barium or potassium iodide. They state that the greater the degree of rancidity, the more difficult it becomes to make all the peroxide react with the iodide. For very rancid oils, they recommend a longer heating period and the use of more iodide.

Wheeler (*7*) points out that in the Taffel and Revis method the oil and acetic acid form two phases, making considerable shaking necessary. He advocates the use of chloroform to form a homogeneous mixture when the iodide is added as a saturated aqueous solution. Under these conditions, he believes it unnecessary to heat the reaction mixture or to use an inert atmosphere.

Lea (*3*) proposes a method midway between that of Taffel and Revis and that of Wheeler. He uses chloroform in order to keep the oil in solution but adds the iodide as solid potassium iodide and heats the reaction mixture in the presence of nitrogen. French, Olcott, and Mattill (*1*) describe an essentially identical method.

In an effort to determine the most suitable procedure for fish oils, some of the factors involved have been studied rather comprehensively. Most attention has been paid to the Wheeler method with some comparative tests by the Lea method.

Unfortunately, it was necessary to discontinue the investigation before all the factors involved could be thoroughly studied, and consequently the methods described below are still subject to considerable improvement. However, data have been obtained which may be of interest to other workers and some definite improvements in existing procedure have been made.

In the following experiments fish oils have been used, largely salmon body oils. In most instances, an extremely rancid oil was employed since, according to Taffel and Revis (*6*), such rancid oils give the most difficulty in obtaining a quantitative reaction of peroxide with iodide.

Table I shows the effect of the sample size on the peroxide value. The Wheeler method shows a somewhat greater effect due to this cause than the Lea method. The former method gives peroxide values varying as much as 300 per cent when the sample size increases from 0.1 to 5.0 grams.

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TABLE I. EFFECT OF SAMPLE SIZE ON PEROXIDE VALUE

Oil Sample	Peroxide Value[a] Lea Method Oil 1	Peroxide Value[a] Wheeler Method Oil 1	Peroxide Value[a] Wheeler Method Oil 2
Grams			
5.0	..	6.4	6.7
2.5	7.9	6.9	7.6
1.0	8.7	8.7	9.7
0.50	8.8	9.0	11.0
0.25	9.6	9.6	13.1
0.10	12.0	13.3	21.8
0.050	[b]	[b]	23.3

[a] Milliequivalents of peroxide per kg. of oil.

[b] End point extremely vague.

Effect of Acidity

In the determination of hydrogen peroxide a fairly high acidity is recommended (*2*). In the ordinary peroxide number determination in an oil, acetic acid, a fairly weak acid, is used. Moreover, since a nonaqueous medium is used the acidity may be much less than in aqueous medium.

Table II gives the results obtained when various strong acids are present in the solvent: 1 *N* sulfuric acid gives the highest peroxide number and also the nearest to identical results with 1- and 0.1-gram samples of oil, but it gives a very high blank; 0.1 *N* hydrochloric acid gives results next to those with 1 *N* sulfuric acid in regard to good checks with varying sample size, and fairly high peroxide numbers, and a low blank is obtained; moreover, a sharper end point is attained. Accordingly, considerable attention was given to the use of hydrochloric acid in the solvent.

Peroxide numbers were run with hydrochloric acid in the solvent in varying concentrations and using 1- and 0.1-gram samples of oil, as follows:

Concentration of Hydrochloric Acid in Acetic Acid, *N*	Peroxide Value with 1 Gram of Oil / Peroxide Value with 0.1 Gram of Oil
0	0.60
0.5	0.73
0.1	0.89
0.05	0.98
0.02	1.05

Results indicate that closest checks are obtained for the two sizes of sample when a normality of about 0.05 *N* is used. It is believed that higher concentrations cannot advantageously be used on account of the necessity of adding considerable water to the solvent. $HCl = 37\%$ gas + 63% water.

The effect of the presence of water in the solvent on the peroxide value when 1- and 0.1-gram samples of oil were used is shown by the following:

Water Added, Ml.	Peroxide Value 1 gram oil	Peroxide Value 0.1 gram oil	Peroxide Value with 1 Gram of Oil / Peroxide Value with 0.1 Gram of Oil
0	53.2	53.5	0.995
0.5	52.8	60.5	0.875
1.5	48.4	...	...
4.0	30.1	52.0	0.58

50 ml. of solvent used in each case

A number of experiments were run with hydrochloric acid solvent under different conditions. The results indicate that one of the most important factors is the oxidation of the oil by air. Not only must the air in the space above the reaction mixture be removed, but that dissolved in the solvent as well. This is best accomplished by saturation of the reagent with carbon dioxide or other inert gas. The oxidation of the oil by air occurs in the regular Wheeler method as well as in the modified procedure. Sometimes this effect is masked by a compensation of errors, the tendency toward high results through oxidation being balanced by incomplete reaction between the peroxide and iodide. When hydrochloric acid is present, not only is the reaction between peroxide and iodide accelerated but also that between any oxygen present and the oil and iodide. Hence, in the presence of strong acid, exclusion of air is of special importance.

Other conclusions drawn from these experiments include:

1. Upon standing exposed to air the peroxide value for both the Wheeler and hydrochloric acid methods increases indefinitely; if air is excluded the values tend to approach a maximum value, but only after prolonged standing.
2. In the presence of air, light accelerates the reaction.
3. Decreasing the ratio of chloroform to acetic acid gives increasing peroxide values but at the expense of precision and of accuracy with different sample sizes.
4. Standing of the oil with the solvent before adding the iodide tends to give low peroxide values, and this effect is more pronounced when using an inferior grade of acetic acid.

TABLE II. EFFECT OF ACIDITY OF SOLVENT ON PEROXIDE VALUE

Added Acid and Its Concentration in Acetic Acid	Size of Blank, Ml. 0.005 *N* Thiosulfate	Peroxide Value with 1 Gram of Oil[a]	Peroxide Value 1 Gram of Oil / Peroxide Value 0.1 Gram of Oi
1 *N* sulfuric acid[b]	7.0	102	1.01
0.1 *N* hydrochloric acid	0.95	84	0.91
1 *N* phosphoric acid	1.3	80.5	0.87
1 *N* hydrochloric acid	1.3	90.5	0.80
0.1 *N* sulfuric acid	1.6	79	0.75
0.1 *N* trichloroacetic acid	0.6	70	0.72
None	0.7	60.5	0.70
0.1 *N* phosphoric acid	0.6	70	0.60

[a] Milliequivalents of peroxide per kg. of oil.

[b] Very poor end point obtained.

Hydrochloric Acid Procedure

The oil is dissolved in 20 ml. of chloroform or carbon tetrachloride in a 500-ml. Erlenmeyer flask. A vigorous stream of carbon dioxide is passed through and then 30 ml. of a good grade of acetic acid containing 4 ml. of concentrated hydrochloric acid per liter are added. After about 1 minute the stream of carbon dioxide is diminished to about one bubble per second and 1 ml. of saturated potassium iodide is added. After exactly 5 minutes, 100 ml. of water (250 ml. if a dark-colored oil has been used) are added to the flask, and the iodine is titrated with dilute thiosulfate solution, adding starch and shaking vigorously near the end point.

Sulfuric Acid Method

Two disadvantages are presented by the use of sulfuric acid. A marked purple color develops which obscures the end point. The exact nature of the reaction is uncertain but it is related to the vitamin A content of the oil. An old, crude test for vitamin A was to treat the oil in chloroform and acetic acid with sulfuric acid, the color developed being proportional to the vitamin A content of the oil. A second disadvantage involves the high blanks obtained. It was found that both these disadvantages could be minimized by cooling the reagents in an ice bath before adding the iodide and keeping the flask so submerged during the reaction. Under these conditions little or no color developed to interfere with the end point and the size of the blank was greatly reduced.

Table III gives results obtained by the 1 *N* sulfuric acid method using an ice bath. For comparative purposes, the results obtained by the Wheeler method but using an ice bath and a carbon dioxide atmosphere are given. Assuming the value obtained by the sulfuric acid method after 3 hours to be correct (reaction 100 per cent complete), then the reaction in the regular Wheeler method is only 65 per cent complete and by the Lea method, only 72 per cent complete.

A more detailed study of the effect of sulfuric acid concentration on peroxide values and size of blanks is shown in Figure 1. The optimum concentration of sulfuric acid in

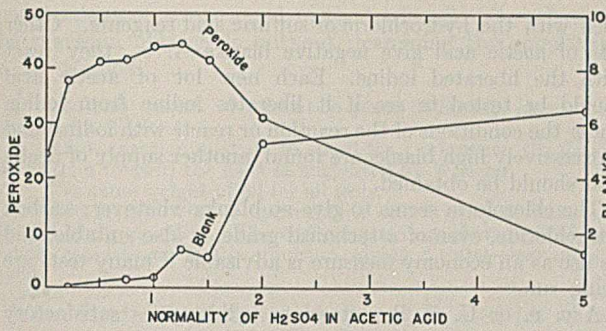

FIGURE 1

acetic acid appears to be about 1.25 *N*. Higher or lower concentrations give lower peroxide values. The size of the blank increases with sulfuric acid concentration, a marked rise occurring above about 0.6 *N*. Accordingly, a sulfuric acid concentration of 0.6 *N* in the acetic acid is suggested as most suitable, since in spite of somewhat higher results with 1.25 *N* acid, the lower blank at 0.6 *N* makes this concentration more suitable. Several other factors in connection with the use of 0.6 *N* sulfuric acid were considered and the following conclusions were drawn from the experiments made:

1. Light has no influence on the reaction in absence of air.
2. Oil must not be allowed to stand with reagents before adding iodide or low results will be obtained.
3. 1.0 ml. of saturated potassium iodide per 50 ml. of solvent gives best results.

TABLE III. PEROXIDE VALUES

(Obtained by Wheeler and sulfuric acid methods with varying reaction times)

Reaction Time	Peroxide Value[a] Wheeler method[b]	Peroxide Value[a] Sulfuric acid method
Min.		
1	32.2	89
5	50	101
30	63	104
Hours		
3	78	106
15	93	[c]
49	104	[c]
Regular Wheeler method	69	
Lea method	77	

[a] Milliequivalents of peroxide per kg. of oil.
[b] Modified by use of carbon dioxide atmosphere and ice bath.
[c] Blanks were higher than determination.

Sulfuric Acid Procedure

REAGENTS. Solvent. Five parts by volume of concentrated sulfuric acid are added slowly with shaking to an ice-cold mixture of 300 parts by volume of glacial acetic acid (Baker's C. P. analyzed) and 200 parts by volume of carbon tetrachloride (technical grade). The solvent is kept in a refrigerator at 0° C. until ready for use and should be prepared fresh daily.

Saturated aqueous potassium iodide (U. S. P. XI), containing 0.3 per cent sodium carbonate.

Sodium thiosulfate 0.1 *N* containing 0.01 per cent sodium carbonate.

Potassium dichromate 0.1000 *N* for standardizing sodium thiosulfate.

Before using, the sodium thiosulfate solution is diluted 20 times, and 0.01 per cent sodium carbonate is added. This dilute solution is stable for not more than 1 week.

Carbon dioxide or nitrogen in cylinder with needle valve.

Starch, 0.2 per cent, in water containing 0.001 per cent mercuric iodide.

PROCEDURE. Dissolve the oil in carbon tetrachloride which has been saturated with carbon dioxide by bubbling through a vigorous stream of the gas for 1 minute. The concentration of oil in the carbon tetrachloride should be about 5 grams made to 25 ml. in a volumetric flask.

Place 50 ml. of the cold solvent in a 500-ml. Erlenmeyer and immerse in an ice bath until the temperature is 1° C. or less. Saturate the potassium iodide solution, some distilled water, the solvent, and the starch solution with the inert gas.

Add 1 ml. of saturated potassium iodide to the flask and immediately add exactly 2 ml. of the oil in carbon tetrachloride. Allow a very slow stream of carbon dioxide to pass through the flask which still remains in the ice bath. After exactly 5 minutes add 250 ml. of water saturated with the gas, and titrate at once with 0.005 *N* thiosulfate, adding the starch near the end point. By using all reagents saturated with inert gas, no trouble is encountered with a reappearing blue starch color as is otherwise the case. The end point remains colorless for at least several hours. Run a blank in which 2 ml. of carbon tetrachloride are added in place of the oil solution.

In using this procedure great attention to detail is required in order to obtain satisfactory results. High or irregular blanks are sometimes obtained, due to a number of causes such as failure to cool the reaction mixture completely, failure to remove air completely, or use of acetic acid of inferior grade. Even when following the procedure carefully, unusually high blanks are sometimes obtained. The method is unquestionably cumbersome and for most purposes it is doubtful whether the advantages outweigh the disadvantages.

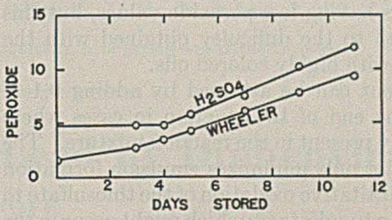

FIGURE 2

Figure 2 shows peroxide values for an oil during rancidity development determined by the sulfuric acid method and by the Wheeler method. The former method gives a sharper break in the curve at the end of the induction period. For the Wheeler method, in the early stages, very little air oxidation occurs, so that the lack of completion of the reaction tends to give low results. As the end of the induction period is reached, air oxidation counterbalances lack of completion of the reaction, so that higher results are obtained. This gives a greater slope to the curve during the induction period and makes an estimation of the end of the induction period difficult.

Other Procedures

Some experiments were run whereby the ordinary methods were drastically altered. These include substitution of other oxidation reduction systems for iodide-iodine, and use of other solvents. As shown in Table IV, most of these attempts were unsuccessful. The use of acetone in place of chloroform–acetic acid as a solvent for the oil gave some promise. The iodide was introduced as calcium iodide or as potassium iodide in methyl alcohol. As long as no water was present, the acetone did not react with the iodine, and the latter could be estimated colorimetrically by carrying out the reaction in Nessler tubes and comparing with suitable standards. The method was not worked out in detail, but might prove successful.

End Points and Precision

In titrating the iodine after the addition of water, an emulsion of some of the oil in the water layer usually is formed which is very slow to break. When a colored oil such as salmon is used, the color of the water emulsion is often of a gray-blue hue which makes the starch end point very difficult to distinguish, and either long periods of waiting for the emulsion to break are required between additions of the thiosulfate near the end point, or one must be satisfied with very poor precision. This difficulty can be minimized by the use of a large ratio of water added to solvent originally present. Using 50 ml. of solvent, about 250 ml. of water should be added if emulsion formation is to be held at a

TABLE IV. RESULTS OBTAINED BY VARIOUS PROCEDURES

Method	Remarks
Substitution of $SnCl_2$ for KI	Reaction of Sn^{++} and peroxide too slow
Substitution of Fe^{++} for KI	Blanks too high owing to presence of traces of Fe^{+++}; water of crystallization present in some pure ferrous salts interferes
Use of excess of thiosulfate in reaction mixture to remove iodine as fast as it is liberated and prevent its absorption by oil	Thiosulfate does not titrate quantitatively to tetrathionate when present in excess in acid media; hence poor precision obtained
Use of molybdates or tungstates to catalyze peroxide iodide reaction (*2*)	Tungstate has little or no effect. Molybdate accelerates reaction but gives poor precision. Solubility of each extremely low in reaction mixture
Substitution of acetone for chloroform–acetic acid solvent. Addition of iodide in methyl alcohol or as calcium iodide in acetone	Acetone reacts slowly with iodine when water added during titration
Acetone method as above, but iodine concentration determined colorimetrically without adding water	Method gives some promise. Blanks are hard to correct for; colored oils interfere

minimum. Addition of such a large amount of water causes sufficient dilution to make the starch iodine end point less sharp, especially for oils having low peroxide values, but this effect is small compared to the difficulty obtained with the dark emulsions formed with highly colored oils.

A further improvement can be attained by adding 0.1 *N* hydrochloric acid at the end of the reaction in cases where strong acid is not already present in the reaction mixture. The presence of strong acid not only minimizes emulsion formation but also ensures the quantitative oxidation of the thiosulfate to tetrathionate rather than to sulfate (*2*) which might occur in the weak acid solution of extremely dilute iodine present (as low as 0.00001 *N* iodine). By using these simple precautions much better precision is obtained.

If difficulty is still encountered, as with some intensely colored oils, the end point can be determined electrometrically by immersing a platinum wire in the solution and connecting through a calomel half-cell to a potentiometer. The following readings were obtained with a saturated calomel half-cell, using an oil which was not highly colored in order to be able to compare the starch end point directly with the electrometric method:

0.005 *N* Thiosulfate Added *Ml.*	Starch Color	E. M. F. *Volt*
0.00	Deep blue	0.230
13.5	Medium blue	0.230
13.85	Light blue	0.230
13.91	Very light blue	0.229
13.96	Practically colorless	0.201
14.03	Colorless	0.200
14.90	Colorless	0.190

A small but decided decrease in e. m. f. is observed at the end point. In the titration of a highly colored oil, enough thiosulfate is first added until the starch color begins to fade and then readings are taken after the addition of each drop. Equilibrium is rapidly obtained and the titration can usually be completed within 5 minutes. Ordinarily, however, it is not necessary to resort to the electrometric method.

Reagents

It is of special importance to use a good grade of acetic acid. Some acetic acid, even though meeting A. C. S. specifications, gives high and irregular blanks, especially when used with the hydrochloric or sulfuric acid reagents. Other lots of acetic acid give negative blanks—i. e., they react with the liberated iodine. Each new lot of acetic acid should be tested to see if it liberates iodine from iodide under the conditions of the reaction or reacts with iodine, and if excessively high blanks are found, another supply of acetic acid should be obtained.

The chloroform seems to give no blanks whatever; carbon tetrachloride, even of a technical grade, is also suitable, and its use as an economy measure is advisable if many tests are being run.

A C. P. or U. S. P. potassium iodide gives satisfactory results.

Stability of Reagents

The potassium iodide solution, especially in the presence of light, is oxidized rapidly to iodine. Addition of a few tenths per cent of sodium carbonate prevents such oxidation and allows the solution to be kept indefinitely.

Blank tests were made on the acetic acid–chloroform solvent with and without hydrochloric and sulfuric acid after varying storage periods. The blanks for the sulfuric acid reagent showed a rapid increase on standing, so that this reagent should be prepared daily. The other reagents showed no increase in the blank after one month, and hence can be kept for at least this long.

Some tests were made as to the stability of the dilute thiosulfate (0.005 *N*) used for the titration. The concentration changed about +1.5 per cent in 2 weeks if 0.01 per cent sodium carbonate were added and about −4 per cent without carbonate. Use of boiled distilled water and of storage in the dark did not materially increase the stability.

Recommended Procedures

The following general precautions are recommended in running peroxide tests regardless of the exact procedure; in addition, other precautions are recommended in case of special procedures.

1. Do not allow oil to stand with solvent before adding potassium iodide.
2. A technical grade of carbon tetrachloride can be used in place of chloroform as an economy measure.
3. Use the best grade of acetic acid obtainable.
4. Run both "positive" and negative blanks, the latter with standard iodine solution.

For many routine tests the Wheeler method will give results of sufficient accuracy for the purpose. Several

TABLE V. RELATIVE ADVANTAGES OF METHODS

Methods	Advantages	Disadvantages	Application
Wheeler (*7*)	Extreme simplicity	Lack of accuracy. Poor results when sample size varied	For routine tests where speed is more important than accuracy. Use modifications recommended
Lea (*3*) or French, Olcott, and Mattill (*1*)	Moderate accuracy and precision	Inconvenience and danger of heating reaction mixture. Results still not good when sample size is varied. Use of inert atmosphere required	Hydrochloric acid method below more convenient and at least as accurate
Hydrochloric acid method	Moderate accuracy and precision	Results only fairly good when using varying sample size. Inert atmosphere required	Use for most work where accuracy is important or where sample size must be varied
Sulfuric acid method	Great accuracy and precision if details of procedure are carefully followed. Good results with large sample size variation. Sharper break in induction curve	Procedure rather involved, great attention to detail required to avoid errors	Not recommended for ordinary tests

modifications of the original method will add somewhat to the precision obtainable without decreasing the simplicity of the method.

1. Use only 10 ml. of solvent in place of 50 ml., as recommended by Wheeler.
2. Allow reaction mixture to stand for 1 minute in the dark, rather than to swirl the flask as suggested by Wheeler.
3. Use same weight of oil for all tests.
4. Add 50 ml. of 0.1 *N* hydrochloric acid in place of water at the end of the reaction. The end point is then characterized by a more rapid break in the emulsion, giving a water-clear upper layer.

When identical sample weights cannot be used (as when using aliquot portions of a tissue extract) the Wheeler method may give highly erratic results. In such cases or where greater accuracy is required, another method should be used. While the Lea method (*3*) will often suffice, the hydrochloric acid method as described above is simpler and at least as accurate. Such a procedure eliminates the necessity of heating the reaction mixture, a dangerous process at best. The acetic acid–chloroform reagent is corrosive to the skin in the cold; when heated, especially in test tubes as recommended by Lea, there is considerable danger of foaming over and serious burns may result. The hydrochloric acid method not only eliminates this danger, but gives somewhat greater accuracy when using samples of differing weights.

When the greatest accuracy attainable is desired, the sulfuric acid method can be used, but because of the close attention to detail, occasional erratic results, and numerous cumbersome precautions, this method is not recommended for general use. It is to be hoped that further work may simplify this procedure and make it more generally applicable.

Table V summarizes the advantages and disadvantages of the various methods.

Literature Cited

(1) French, R. B., Olcott, H. S., and Mattill, H. A., Ind. Eng. Chem., **27**, 724 (1935).
(2) Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis", New York, Macmillan Co., 1936.
(3) Lea, C. H., *Proc. Roy. Soc.* (London), **B108**, 175 (1931).
(4) Lemon, J. M., Stansby, M. E., and Swift, C., *Food Industries*, **9**, 576 (1937).
(5) Lowen, L., Anderson, L., and Harrison, R. W., Ind. Eng. Chem., **29**, 151 (1937).
(6) Taffel, A., and Revis, C., *J. Soc. Chem. Ind.*, **50**, 87T (1931).
(7) Wheeler, D. H., *Oil & Soap*, **9**, 89 (1932).

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Colorimetric Determination of Lead by Diphenylcarbazide

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ADDITIONAL experience with determination of lead by the method described by Letonoff and Reinhold (*1*) has revealed several points in the procedure where difficulties may be encountered and where certain modifications, although minor, may permit more accurate results to be obtained.

The following precautions are important in connection with the reagents: (1) Ammonium acetate, 40 per cent solution, is unstable at room temperature and should be kept in a refrigerator; (2) a 15 per cent solution of acetic acid is substituted for the 25 per cent solution used originally, to avoid the possible addition of an excess; (3) lead acetate crystals used in preparation of standards should be kept well stoppered to protect against loss of water and uptake of carbon dioxide (lead nitrate is more stable and can be substituted); (4) lead chromate and acetate solutions should be stored in bottles that have been thoroughly cleaned.

The use of sodium oxalate as an anticoagulant has been abandoned. While causing no difficulty when the quantity originally specified is employed, amounts greatly exceeding the recommended concentrations have led to unreliable results, possibly because of difficulty in maintaining the calcium and lead oxalate precipitate in uniform suspension during sampling. It has been found more satisfactory to use clotted blood. Samples of blood, 5 to 8 cc. in amount, are measured into 13 × 100 mm. Pyrex tubes and allowed to clot. The tube with blood and stopper is weighed on an analytical balance to the nearest 0.1 gram, the blood is transferred to a silica dish for ashing, and the empty tube and stopper are reweighed.

Table I shows that approximately 5-gram samples of blood can be analyzed with satisfactory accuracy. Results were low for some specimens when samples much in excess of 10 grams were employed, probably because of interfering effects of salts. Samples of between 5 and 10 grams are recommended.

The method has been applied successfully to analysis of red blood cells. Samples of optimal size are obtained by allowing 5 to 10 cc. of blood to clot. After centrifugation, serum is removed and the resulting 2- to 4-gram sample of red blood cells and fibrin is used for analysis; 5 cc. of lead-free water are added to the sample and the determination is completed as described for whole blood.

Table I. Comparison of Lead Analyses on Samples of Blood

No.	Weight of Sample *Grams*	Lead Found *Mg./100 g.*	Weight of Sample *Grams*	Lead Found *Mg./100 g.*
1	5.1	0.321	9.1	0.311
2	5.9	0.033	10.0	0.032
3	6.3	0.531	13.1	0.526
4	4.6	0.055	9.7	0.054
5	5.0	0.060	9.6	0.058
6	6.0	0.056	10.0	0.054
7	5.2	0.022	10.1	0.021
8	6.0	0.050	10.3	0.051
9	5.0	0.044	10.3	0.043
10	5.8	0.043	11.4	0.044
Av.	5.5	0.122	10.4	0.119

A slight alteration in the technique of the determination has been introduced at the stage of pH adjustment just prior to precipitation of lead and immediately following the point at which the directions read "wash dish and paper four times with 1 cc. of 0.1 *N* ammonium hydroxide". At this point the control tube is employed as a standard for adjusting the pH of the unknown solutions. The control tube is prepared as described originally but instead of 1 drop of 25 per cent acetic acid 15 per cent acetic acid solution is added dropwise to each unknown until the red-orange color of the indicator in the control tube is matched. A yellow background is helpful. In this way possible addition of an excessive amount of acetic acid is excluded. The remainder of the procedure is carried out as described in the original publication.

Literature Cited

(1) Letonoff, T. V., and Reinhold, J. G., Ind. Eng. Chem., Anal. Ed., **12**, 280 (1940).

The Tackmeter, an Instrument for Analyzing and Measuring Tack

Application to Printing Inks

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WHILE the study and measurement of tack are of considerable interest to many industries, they are of prime importance to the manufacturer and consumer of printing inks. Proper control and adjustment of tack must be secured if "picking" is to be avoided and satisfactory "trapping" obtained. Picking occurs when the ink is too tacky, causing the surface of the paper stock to be damaged by tearing. "Trapping" is a printer's term designating the retention of one ink by another—for instance, if a red ink is to be printed on a yellow ink, the yellow, which is printed first, must retain the red ink and pull it from the printing plate as the plate leaves the paper. When this has happened it is said that the red "is trapped by the yellow". This result is satisfactory only when the order of tackiness is correct.

Comparatively little has appeared in the literature on the subject of tack, although Bekk (*1*) has published a number of papers on printing in which tack is discussed. He defines viscosity as the resistance of an ink to compression, and tack as resistance to an oppositely directed force—i. e., against the splitting of an ink layer. Bekk states that a relationship exists between tack and viscosity, but makes no attempt at an analysis which would show the mathematical relationship. He states that as far as printing is concerned, yield value will be of no consequence, but does not explain how he arrives at that conclusion.

Reed (*2*) has developed an instrument called the "Inkometer", composed of a series of rotating cylinders that are inked and in mutual contact. The ink causes a resistance to rotation. This resistance is recorded as torque which is defined as "tack".

Neither Bekk nor Reed seems to have considered the possibility of making a critical analysis of tack to discover the exact relationship between tack and the flow-resisting properties of a material, or to ascertain whether the somewhat arbitrarily arrived at definitions of tack are correct. To make such an analysis and so discover the factors upon which tack depends was the primary object in constructing the Tackmeter. Obviously, it was not known at the start, with any degree of certainty, just what phenomena produce tack. Investigators had instinctive ideas about tack but no serious attempt was made to establish their correctness experimentally. Before constructing a device for measuring tack, a preliminary analysis had to be made to indicate what qualifications such an instrument must have, but first it was necessary to select some simple test that would not only demonstrate tack but be practically synonymous with it in the mind of the practical inkman.

Both the manufacturer and the consumer of printing inks have used for many years a simple means for estimating the tack of printing inks. This is the so-called finger tap-out test, which is executed as follows:

> The ink is first rubbed out into a sufficiently thin layer with the finger tip, either on a nonporous material like glass or on coated paper. The finger tip is next firmly pressed into the film and then drawn away suddenly. When this motion is repeated a number of times in rapid succession, the sensation of stickiness arises, caused by the pull-resistance of the ink exerted on the finger tip. The amount of this pull-resistance is adjudged to be the tack.

An examination of this test shows that the ink film has divided, one part adhering to the finger and the other part remaining on the paper or plate. In order to predict what physical properties of the ink could create pull-resistance it is necessary to know how film splitting occurs. This might happen in three ways: by tearing, by abrupt rupture, or by the process of "necking down". The first of these possibilities hardly applies to liquids or to soft plastics like printing inks. Abrupt rupture would involve the tensile strength or cohesion of the liquid to such an extent that it would require thousands of pounds of force to break the film. The ink, however, being free to follow the path of least resistance will, instead, neck down to minute cross-sectional areas where rupture takes place with relative ease. Necking down is obviously, then, the most likely method by which film division occurs.

Causes of Pull-Resistance

Knowing how the splitting of printing ink films probably takes place, the next step is to understand the underlying causes of pull-resistance. Lining up the various possibilities gives the following list: (1) adhesion, (2) cohesion, (3) surface tension, (4) viscosity, and (5) yield value.

Throughout this paper the term "viscosity" is intentionally applied to plastics as well as to true liquids. The term when used in this manner must be understood to be in reference only to the cotangent of the curve—i. e., to the force in excess of the intercept divided by the rate of flow. The reciprocal of this type of viscosity is the "mobility", a term preferred by rheologists but one that would be awkward and difficult to

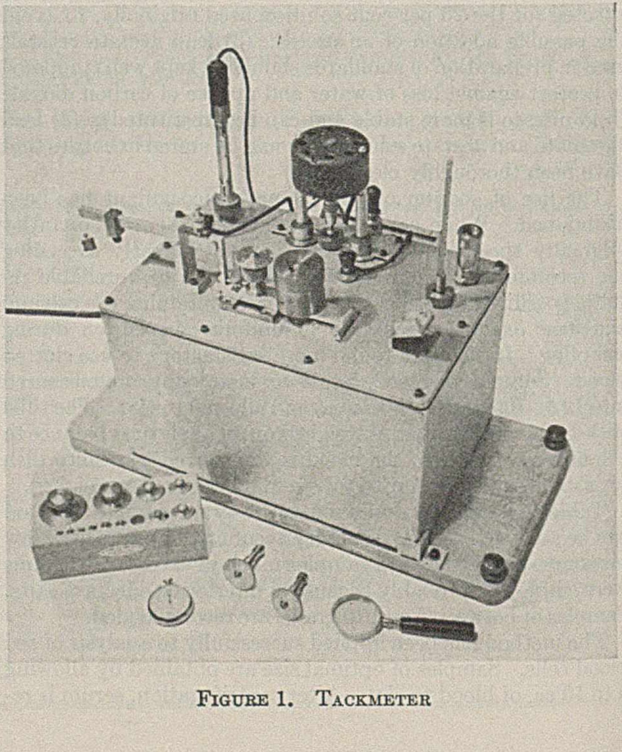

FIGURE 1. TACKMETER

introduce into the ink industry. Unfortunately there is no entirely satisfactory term analogous to viscosity that can be applied to plastics of the Bingham type.

It is difficult to imagine any other than the above five properties as being a possible cause of pull-resistance or tack. If this is so, an analysis of these properties in their relationships to the process of necking down should indicate which are the ones that a tack-measuring instrument must in some manner record.

Adhesion. This property enables the ink to adhere to the surfaces that are being separated, thus making it possible for the ink to neck down. In this connection one must be careful not to visualize the two surfaces as adhering to each other (the printing plate and the paper, or the finger tip and the paper). The ink film between the surfaces, though thin, is nevertheless of finite thickness and the two surfaces are never actually in mutual contact. The force of adhesion cannot act through the film but only at the interface between the ink and the surface involved.

Obviously, without adhesion necking down could not take place, but the magnitude of the force of adhesion, provided it is sufficient to produce complete adherence, cannot influence the magnitude of the pull-resistance. As no portion of the separating surfaces is stripped free from ink, no work is done against the force of adhesion.

Cohesion. The amount of work done against the force of cohesion at the moment of rupture must be relatively small, for the neck thins down to hairlike dimensions before breaking. It seems safe to conclude, therefore, that cohesion does not play a measurable part in creating pull-resistance. Bekk claims, however, that very thin layers of ink will rupture rather than neck down. This point will be discussed at the conclusion of the paper.

Surface Tension. When the ink film becomes divided on account of necking down, two new surfaces come into existence. Surface tension, therefore, must influence the magnitude of pull-resistance to a certain extent. Without actual Tackmeter measurements, however, the importance of this property could not be predicted. A subsequent analysis of tack measurements as shown below indicates that surface tension is of minor or negligible importance in the case of printing inks and their vehicles.

Viscosity and Yield Value. By a process of elimination it becomes apparent that pull-resistance must be accounted for mainly by the flow-resisting properties of the ink—i. e., viscosity and yield value—influenced, perhaps, to a certain extent by surface tension. The relative importance of these three properties can be determined only by experiment.

With the above in mind the Tackmeter was constructed to produce a division of the film and at the same time record the effects, if any, of surface tension, yield value, and viscosity. It was necessary that the area of contact, the film thickness, and the rate of pull (surface separation) could be varied, each one at a time, the other two remaining constant. Such an arrangement made it possible to study the effect of instrumental dimensions on the measurements.

The Tackmeter

The Tackmeter (patent applied for) is in effect a mechanical finger, paralleling in execution the finger tap-out test in its evaluation of pull-resistance, but capable of placing a numerical value on its measurements.

The instrument is shown in Figure 1 and depicted diagrammatically in Figure 2. It consists of two levers, *G* and *J*, connected by a loose-joint bar, *I*, the entire system being mounted on case-hardened pivots at *C*, *D*, and *E*. Into a threaded hole in bar *G* is inserted a bronze screw, *A*, the lower end of which functions as a finger tip. This tip is pressed into the ink at *B*, by placing a 500-gram weight on the bar at *G*. This causes the bar to rest firmly on the supports, *K*, *K'*, making it possible to maintain a suitable film thickness between the lower end of *A* and plate *L*. When the 500-gram weight is removed from *G*, the small weight, *w*, at the end of lever *J*, exerts a pulling action on lever *G*, causing finger *A* to be pulled upward, thereby necking the ink down at *B*. The upward motion is stopped as soon as the right-hand side of *J* meets the set screw at *H*.

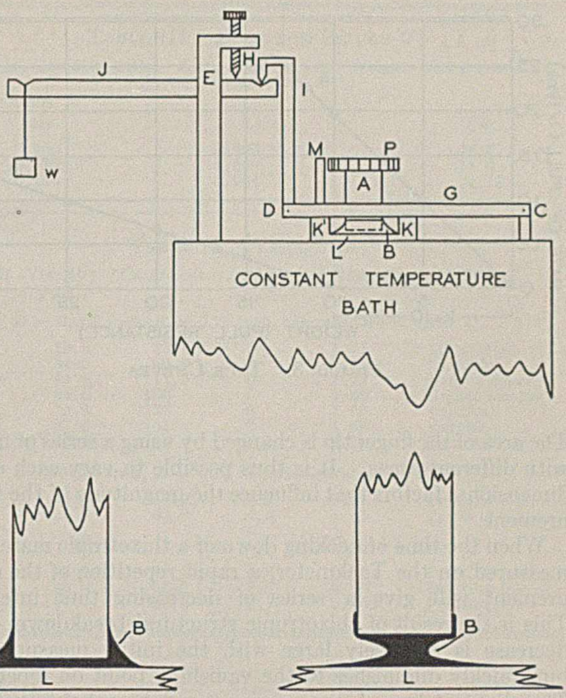

Figure 2. Diagram of Tackmeter

It is not at all necessary to use a carefully measured volume of ink. All that is required is a sufficient excess to form a reservoir of ink around the circumference of the finger tip. Because the resistance to necking down takes place under the finger tip and not around it, the exact size of the reservoir is not of serious importance. The amount of excess ink should not be so great that it touches lever arm *G*, nor so little that the reservoir is completely used up at the very start of the necking-down process. When the ink volume is properly adjusted variations in volume of as much as 100 per cent will not affect the tack readings.

The weight, *w*, will, at times, be referred to as the pull-resistance. In addition to knowing the magnitude of *w* it is also necessary to have the corresponding rate of break. This is obtained by taking the reciprocal of the time of break, which is measured with a stop watch, from the instant the 500-gram weight is removed until the instant the lever strikes *H*. It is not necessary that the necking down be carried out exactly to the point of rupture, because practically all the resistance is offered at the start and only a nonmeasurable amount exists toward the end of the operation. The entire apparatus is kept at constant temperature through an automatically controlled water bath filled so as to contact the top plate.

A measurement made like the one described gives the rate of necking down of the ink under the arbitrarily selected conditions of the experiment—i. e., with predetermined film thickness, finger-tip area, and pulling weight *w*. The pull-resistance is always given by the weight, *w*, which can be easily varied. The initial film thickness is controlled by the micrometer screw, *A*, by means of the graduated head, *P*.

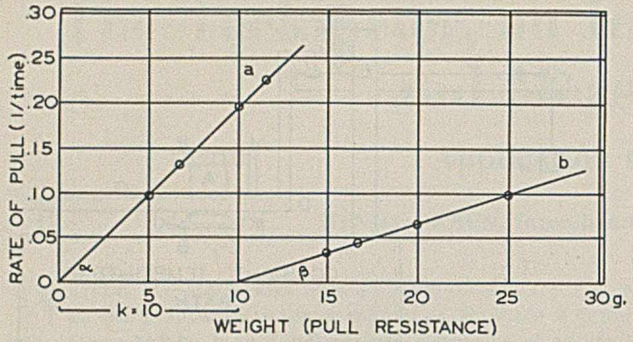

Figure 3. Tack Curves

The area of the finger tip is changed by using a series of fingers with different areas. It is thus possible to vary each of the dimensional factors that influence the magnitude of the measurement.

When the time of necking down of a thixotropic material is measured on the Tackmeter, a rapid repetition of the measurement will give a series of decreasing time intervals. This is the result of thixotropic structural breakdown. The decrease is relatively large with the initial measurements but quickly diminishes to the vanishing point on repetition. The slightest loss of time encountered here before making the next time measurement will allow thixotropic build-up to increase to some former level, for at the lowest level thixotropic build-up occurs as rapidly as breakdown. As long as the material is kept in motion there is very little chance for thixotropic build-up.

Table I. Data for Tack Curves of Figure 3

(Radius of finger tip, 0.788 cm. Film thickness, 0.01 cm., 0.004 inch)

Curve *a*		Curve *b*	
1/Time	Weight	1/Time	Weight
$\frac{1}{\text{Seconds}}$	*Grams*	$\frac{1}{\text{Seconds}}$	*Grams*
0.22	12.0	0.100	25.0
0.19	10.1	0.067	20.0
0.13	7.2	0.047	17.0
0.09	5.1	0.033	15.0
Viscosity, 20.56 poises, determined by National Bureau of Standards		Viscosity, 57.1 poises (k = 10 grams), determined with rotational viscometer	

The Law of Tack

When a given material, like an ink or a varnish, is tested on the Tackmeter with a series of different weights and these weights are plotted against their corresponding rates of break—i. e., the reciprocal of the time of break—a tack curve is produced.

From this type of curve (Figure 3 and Table I) a law can be empirically derived.

The Law. For Newtonian liquids the pull-resistance (tack) is directly proportional to the rate of break, $1/t$—the area of contact, πR^2, and the initial film thickness, D, remaining constant. For plastics (Bingham-bodies, using the Reiner nomenclature) the pull-resistance in excess of the intercept, k, is directly proportional to the rate of break, the other factors, as before, remaining constant.

The law states for Newtonian liquids that

$$1/t = \text{constant} \times w \ (R \text{ and } D \text{ remaining constant})$$

and for plastics,

$$1/t = \text{constant} \times (w - k) \ (R \text{ and } D \text{ remaining constant})$$

The constant in these equations depends on the flow-resisting factors of the material and on the instrumental dimensions, R and D. These equations can be written thus: For liquids,

$$1/t = K' K'' K''' w \quad (R \text{ and } D \text{ constant}) \tag{1}$$

For plastics,

$$1/t = K' K'' K''' (w - k) \quad (R \text{ and } D \text{ constant}) \tag{2}$$

where K' is a function of the flow-resisting property of the material and K'' and K''' depend on the dimensions of the instrument.

Film Thickness

The relationship of rate of break to film thickness is given for Newtonian liquids in Figure 4. If the square of the film thickness is plotted against the rate of break, w and R remaining constant, a curve will result which will not be quite linear. If to each D be added a small value, d, of such magnitude that the curve becomes rectified and passes through the origin, it will be found that d is constant for a given finger. The value for d was found to be 0.00096 cm. (0.00038 inch) for the finger used in obtaining the data for Table II. Actually the curve (Figure 4) will not reach the origin if d is constant, but end at $D = 0$. The film thickness at this point will be d, and $1/t$ will be small but finite. It is not known at present just what d represents, but it is evident that d could arise from the fact that the surfaces of the finger and the plate are not absolutely flat perfect surfaces and therefore a small space could exist between them, even at zero setting. This small space, d, plus the setting, D, on the micrometer head would be, then, the total film thickness.

The curve in Figure 4 can be written as follows: For liquids,

$$1/t = K'K''(D + d)^2 w \quad (w \text{ and } R \text{ constant}) \tag{3}$$

where K' is a function of the flow-resisting property of the liquid and K'' is an instrumental constant.

Comparing Equation 1 with 3 shows that K''' is $(D + d)^2$. Since K''' is independent of the nature of the material being tested, its value, $(D + d)^2$, can be substituted in Equation 2. Then if $w - k$ is maintained constant and D varies, we have for plastics

$$1/t = K'K''(D + d)^2(w - k) \quad [(w - k) \text{ and } R \text{ constant}] \tag{4}$$

Area of Finger Tip

The remaining dimensional factor that can be varied is the area of the finger tip. This is changed by using a series of fingers with different tip areas. By plotting time of break

Table II. Data for Figure 4

(Radius of finger tip, 0.625 cm., 0.250 inch. d, 0.00096 cm., 0.00038 inch. w, 10.1 grams. Viscosity of oil, 20.3 poises, determined by National Bureau of Standards)

D	$(D + d)^2$	1/Time	K (Exptl.)[a]	K (Calcd.)[b]
Inch	*Inches*	*Sec.*		
0.0002	0.336×10^{-6}	0.0076	0.015	0.019
0.0004	0.608	0.0151	0.032	0.034
0.0005	0.774	0.0198	0.039	0.044
0.0006	0.960	0.0241	0.048	0.054
0.001	1.90	0.052	0.106	0.108
0.002	5.66	0.164	0.331	0.321
0.003	11.4	0.323	0.652	0.647
0.004	19.2	0.560	1.10	1.09
0.005	28.9	0.830	1.68	1.64
0.006	40.7	1.15	2.35	2.31
0.007	54.5	1.53	3.15	3.09
0.008	70.2	1.98	4.08	3.98

[a] Experimental $K = \mu/wt$.
[b] Theoretically calculated $K = 4.6 \times 980\,(D + d)^2/\pi R^4$ (for c. g. s. units).

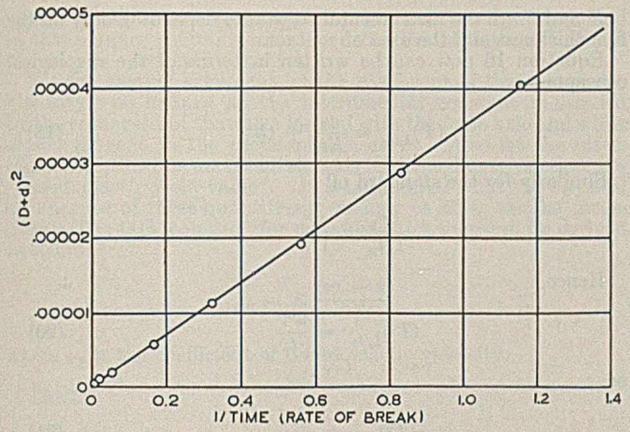

FIGURE 4. RELATIONSHIP OF RATE OF BREAK OF FILM THICKNESS

against various powers of the radii, it was found that a linear relationship results when the fourth power is used. Experimental results are shown in Figure 5. See Table III.

The curve in Figure 5 can be expressed as follows for liquids:

$$1/t = K'\left(\frac{1}{R^4}\right) K'''w \quad (D \text{ and } w \text{ constant}) \qquad (5)$$

where K' is a function of the flow-resisting property of the material, and K''' is $(D + d)^2$ as shown above.

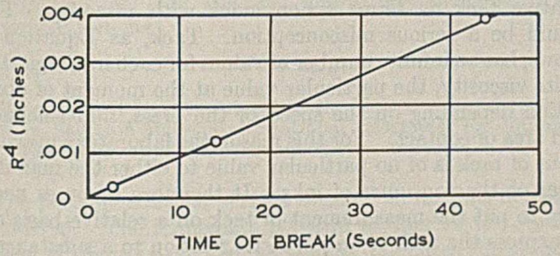

FIGURE 5. EFFECT OF AREA OF FINGER TIP

In comparing Equations 1 and 5, it will be seen in this case that K'' is $1/R^4$. Making the substitution as before gives for plastics

$$1/t = K'\left(\frac{1}{R^4}\right) K'''(w - k) \quad [D \text{ and } (w - k) \text{ constant}] \qquad (6)$$

Since the Tackmeter measures rate of flow and the force that causes it, the instrument is actually a viscometer. Therefore the curves shown in Figure 3 are rheological consistency curves. The cotangents of the angles α and β are functions of the instrumental dimensions, contact area and film thickness, and of the viscosity. The viscosity is directly proportional to the cotangent (Table IV). Yield value, therefore, must manifest itself in the intercept, k. The viscosities in Table IV were determined with a rotational viscometer.

The reason that curve b, Figure 3, is entirely linear may be that the Tackmeter uses a film thickness so thin that complete laminar flow ensues as far down as measurements can be made.

Since the cotangent is proportional to the viscosity, Equations 1 and 2 may be rewritten:
For liquids,

$$\mu = Kwt \qquad (7)$$

TABLE III. DATA FOR FIGURE 5

(Viscosity 560 poises. Heavy mineral oil. Weight, 20.1 grams. D, 0.0076 cm., 0.003 inch)

Radius, R Inch	R^4 Inches	t Sec.
0.250	3.906×10^{-3}	44.0
0.188	1.249	14.0
0.125	0.244	2.75

TABLE IV. VISCOSITIES

Sample	Viscosity Poises	Cotangent	k Grams	Cot/Viscosity	Material
D = 0.003 inch, R = 0.25 inch, temperature = 29.8° C.					
1	19.8	33.8	0	1.71	Mineral oil
2	34.0	59.3	0	1.74	Varnish
3	41.5	71.5	0	1.72	Bodied linseed
4	64.0	106	0	1.66	Bodied linseed
5	73.5	122	0	1.66	Varnish
6	97.0	161	0	1.66	Varnish
7	60.0	104	4.3	1.74	Printing ink
D = 0.004 inch, R = 0.25 inch, temperature = 29.8° C.					
8	58.0	56.0	2.8	0.97	Printing ink
9	65.0	65.8	4.8	1.01	Printing ink
D = 0.006 inch, R = 0.25 inch, temperature = 29.8° C.					
10	70.0	38.7	4.6	0.555	Printing ink
11	86.0	48.0	7.0	0.560	Printing ink
12	114	62.0	0.7	0.550	Printing ink

For plastics,

$$\mu = K(w - k)t \qquad (8)$$

where μ is the coefficient of viscosity and K is the proportionality constant, depending only on D and R.

Combining Equations 3 and 5 gives for liquids

$$1/t = K'\frac{(D + d)^2}{R^4}(w) \qquad (8a)$$

and similarly combining 4 and 6 gives for plastics

$$1/t = K'\frac{(D + d)^2}{R^4}(w - k) \qquad (8b)$$

where K' is again some function of the flow-resisting property of the material. Equations 7 and 8 can be put into a similar form:
For liquids,

$$1/t = \left(\frac{1}{\mu}\right) Kw \qquad (9)$$

For plastics,

$$1/t = \left(\frac{1}{\mu}\right) K\,(w - k) \qquad (9a)$$

Since K is purely an instrumental constant, a comparison of these last four equations would indicate that $K' = 1/\mu$. When K' was given this value, however, it produced unsatisfactory results unless π was simultaneously introduced into the denominator. Such a procedure gives the final equations:

For liquids,

$$\mu = \frac{(D + d)^2\, w(4.6 \times 980)t}{\pi R^4} \qquad (10)$$

and for plastics,

$$\mu = \frac{(D + d)^2\,(w - k)\,(4.6 \times 980)t}{\pi R^4} \qquad (11)$$

where 4.6 is the lever factor and 980 is the acceleration. The actuating force, F, equals $w \times 4.6 \times 980$.

Viscosities of Newtonian liquids and plastics can be determined with the Tackmeter readily enough by means other than Equations 10 and 11, if a liquid of known viscosity is

Table V. Viscosity Measurements

Sample	Material	Tackmeter $\mu = \mu^0\left(\frac{wt}{w^0t^0}\right)$	Tackmeter $\mu = \frac{(D + d)^2Ft}{\pi R^4}$	Rotational Viscometer, μ (Poises)
D = 0.003 inch, d = 0.00038 inch, temperature = 29.8° C., R = 0.25 inch				
1	Mineral oil	20.5	20.5	(B. S. 20.56)[a]
2	Varnish	33.9	33.8	34.0
3	Bodied linseed oil	42.4	42.5	41.5
4	Bodied linseed oil	64.5	64.4	64.0
5	Varnish	74.0	73.9	73.5
6	Varnish	98.0	97.8	97.0
7	Printing ink	64.1	63.7	60.0
D = 0.004 inch, d = 0.00038 inch, R = 0.25 inch, temperature = 29.8° C.				
8	Printing ink	59.5	58.2	58.0
9	Printing ink	68.0	67.0	65.0

[a] National Bureau of Standards measurement.

used for comparison. The comparison must be made with the same film thickness and contact area for both the known and unknown materials. Then for liquids,

$$\mu = \mu^0 \frac{wt}{w^0t^0} \qquad (12)$$

and for plastics,

$$\mu = \mu^0 \left[\frac{(w - k)t}{w^0t^0}\right] \qquad (13)$$

where μ^0, w^0, and t^0 are the viscosity, weight, and corresponding time of break for the standard or liquid of known viscosity. Table V gives some measurements made by both methods for liquids and plastics.

Tack and Relative Tack

Tack is defined as the pull-resistance exerted by an ink film adhering between two surfaces that are separating at a definite rate and with a known area of contact and known initial film thickness. This means that tack is as much a function of the instrument that measures it as it is of the ink itself. In order to present a completely definite measurement of tack it would be necessary to give it in the form of three curves such as those in Figures 3, 4, and 5. It is very much easier and more practical to put tack on a relative basis. When tack is computed in this way the instrumental constants are practically eliminated. Relative tack is the tack of the ink divided by the tack of a standard substance such as a stable mineral oil.

Figure 6 shows two tack curves: that of the standard oil, and that of an ink.

Case I. The Tack Curve Is Linear. Let $(w_p, 1/t_p)$ be any point on the tack curve of the ink, not necessarily within the range of the instrument. This point can be the tack and rate of pull existing at the speed of the printing press. It follows from Figure 6 that

$$\frac{(w_p - k)}{1/t_p} = \frac{(w - k)}{1/t} \qquad (14)$$

Then

$$w_p = \frac{(w - k)}{t_p} + k \qquad (15)$$

Since w_p is the tack at speed $1/t_p$, Equation 15 can be rewritten as follows, T symbolizing tack:

$$(T)_{1/t_p} = \frac{(w - k)t}{t_p} + k \qquad (16)$$

But

$$\mu = \frac{K(w - k)}{1/t}$$

and k being directly proportional to the yield value, f,

$$k = Cf \qquad (17)$$

K and C are the instrumental constants depending only on the film thickness and the area of contact.

Equation 16 now can be written in terms of the rheological concepts.

$$(T)_{1/t_p} = \frac{\mu}{Kt_p} + Cf \qquad (18)$$

Similarly for the standard oil

$$\frac{w^0{}_p}{1/t_p} = \frac{w^0}{1/t^0} \qquad (19)$$

Hence,

$$(T^0)_{1/t_p} = \frac{w^0t^0}{t_p} \qquad (20)$$

or

$$(T^0)_{1/t_p} = \frac{\mu^0}{Kt_p} \qquad (21)$$

Dividing Equation 16 by Equation 20 gives relative tack

$$(T/T^0)_{1/tp} = \frac{(w - k)t}{w^0t^0} + \frac{kt_p}{w^0t^0} \qquad (22)$$

or dividing Equation 18 by Equation 21 gives relative tack in terms of μ and f.

$$(T/T^0)_{1/t_p} = \frac{\mu}{\mu^0} + \frac{(KC)t_pf}{\mu^0} \qquad (23)$$

Since tack and relative tack will be considered in this paper primarily in reference to printing press speeds, they will be expressed simply as T and T/T^0, the subscripts being omitted.

One must be careful at this point not to visualize tack and relative tack as terms synonymous with viscosity. That would be a serious misconception. Tack, as Equation 18 shows, has an infinite number of values for each ink, regardless of its viscosity, the particular value at the moment of observation depending on the speed of the press, film thickness, and area of contact. For this reason the laboratory measurement of tack is of no particular value to either the manufacturer or the consumer of inks. It therefore becomes necessary to put the measurement of tack on a relative basis and to express the tack of an ink in its relation to a substançe of standard tackiness. This is accomplished in Equations 22 and 23.

The faster the press is operated the smaller t_p becomes; hence T increases with increasing press speeds. Theoretically, at infinite speeds tack becomes infinite. Relative tack, on the other hand, decreases slightly as the speed increases. At infinite speed T/T^0 reaches the finite value, μ/μ^0. This is a limiting value only and can be used only where high speeds are involved in the use of the ink.

The right-hand side of Equation 22 is composed of two terms. The first, $(w - k)t/w^0t^0$, involves viscosity but no instrumental constants; the second, kt_p/w^0t^0, depends on the yield value, on both instrumental constants K and C, and on the time of the press, t_p. The quantity t_p can be visualized as the time interval elapsing between contact and separation of the printing plate and the paper. In actual printing practice t_p is exceedingly small, so that for practical purposes the term kt_p/w^0t^0 can be omitted from Equation 22 if desired. This explains the important fact that in high-speed printing, viscosity becomes the dominant factor and the effect of yield value becomes negligible. The same inference can be drawn from Equation 16.

Case II. The Tack Curve Is Nonlinear. The principal cause of nonlinear flow curves is pseudoplasticity. Little of practical value is known about such curves. Fortunately pseudoplastic inks are the exception and not the rule. Investigators have used "one-point" methods for determining the viscosity of such materials: multiplying the cotangent (formed with the force axis and a line drawn through the point and the origin) by the viscometer constant. That a viscosity determined in this manner complies with the definition of the coefficient of viscosity is extremely doubtful.

For the sake of argument let the coefficient of "pseudoplastic viscosity" be defined as the instrumental constant multiplied by the cotangent of the angle formed with the force axis and a line drawn tangent to the pseudoplastic curve. Also let the intercept which this line makes on the axis be defined as a function of a "pseudoplastic yield value". It is immaterial what the physical significance of these quantities is, as long as they can be measured. The tack equation for pseudoplastics then can be derived as follows:

$$\mu_p = K\,\frac{(w - k)}{1/t}$$

where μ_p is the coefficient of pseudoplastic viscosity.

Then

$$w = T = \frac{\mu_p}{Kt} + k$$

and

$$T/T^0 = \frac{\mu_p}{\mu^0} + \frac{Kkt}{\mu^0}$$

where K is the instrumental constant already determined and μ_p is the pseudoplastic viscosity. These equations are the same in form as those derived from linear flow curves, the only difference being the introduction of "pseudoplastic viscosity" in place of "viscosity".

Unlike viscosity, pseudoplastic viscosity is a variable, decreasing with increasing speed (*3*). While the Tackmeter can determine μ_p at low rates of flow, it cannot do so at the high speeds of the printing press. For such speeds t is small and the term Kkt/μ^0 becomes relatively unimportant. This gives, as a limiting case only, and applicable to inks on the press, the convenient formula

$$T/T^0 = \mu_p/\mu^0$$

where μ_p cannot be determined on the Tackmeter and recourse must be had to a high-speed rotational viscometer for obtaining the value in poises of the pseudoplastic viscosity.

The possible effect of surface tension, so far, has not been considered. The immediate problem is whether the surface tension of the ink or of the ink vehicle influences the value of tack or of relative tack as determined by Equations 16 and 22. Each of these equations contains but two terms; the first related to viscosity, the second, to yield value. It is conceivable that surface tension might affect either term or both. If it enters the yield value term, its effect can be considered negligible in regard to printing inks, for the yield value term itself is negligibly small at normal printing press speeds. If it affects the viscosity term to any appreciable extent, it would be manifested in the measurement of t for a given w and so produce obvious irregularities in the measurement of viscosity by Equation 10. So far nothing like this has happened. It is apparently safe, then, to conclude that in the case of printing inks and ink vehicles, the only physical properties that control tack and relative tack are viscosity and yield value.

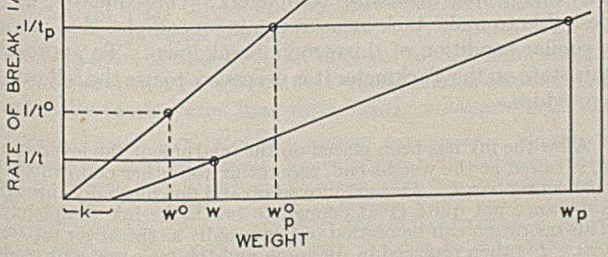

Figure 6. Tack Curves of Standard Oil and Ink

The relationship between tack and relative tack is such that if a series of inks gives a certain order of line-up for tack, the same order of line-up will exist for relative tack at the same speed. When two different inks give tack curves that cross, their tacks are equal at the point of crossing. The tacks above the point of crossing are in the reverse order from those below that point. These conditions also exist for relative tacks, though, of course, the complete formulas 22 and 23 must be used and not just their first terms, when making these calculations.

Table VI. Experimental Tack Results for Printing Inks

(μ^0 = 1.0 poise, D = 0.025 cm., 0.010 inch)

Type of Ink		Tack, T/T^0
News ink	Black	5.0
Comic news ink	Yellow	19.0
	Blue	9.0
	Red	2.0
Rotary ink	1st down yellow	884
	2nd down red	386
	3rd down black	108
	4th down blue	54.0
Rotary ink	1st down yellow	1770
	2nd down red	464
	3rd down black	312
	4th down blue	73.0
Rotary ink	1st down yellow	550
	2nd down red	370
	3rd down blue	197
	4th down black	167
Lithographic ink (tin)	Yellow	1600
	Red	1100
	Blue	800
Photogelatin ink	Blue	2500

Picking and Trapping

Picking of the paper stock occurs when an ink is too tacky for the printing speed or for the stock used. The effect of picking is to pull off part of the surface of the paper or even to rip the stock completely. Tack measurements cannot in themselves predict whether or not an ink will pick; this can be determined only by actual trial runs. When the maximum tack that can be used successfully for a given stock and press speed is once ascertained, it follows that if this tack is exceeded, picking will occur.

The control of trapping is necessary in process printing where inks of different colors are printed successively, one on top of the other. The second down ink must be trapped by the first down; otherwise it will not print. Both inks being subjected to the same pulling force at the same moment, the one that necks down faster will be trapped by the other. Hence in a series of four-color process inks the first down must have the highest tack; the second down, a smaller tack; the third down still less, and so forth. Such an order properly spaced will ensure the optimum results in trapping. Table VI includes experimental results on the relative tacks of some process inks. For experimental convenience the standard oil used for comparison was one possessing a viscosity of 20.5 poises at 30° C. The T/T^0 values in the table were recalculated to a standard oil of 1 poise by multiplying the results by 20.5. The yield value term was not used in making the calculations. The relative tack figures therefore are those for infinite speed. On account of the fact that measurements are in "relative tack" they will differ by only a negligible amount from what they would be if calculated at the finite speed of a fast press.

Table VII. Tests of Mineral Oils

Oil	Sample No.	Film Thickness *Inch*	Viscosity *Poises*	Deviation from Average %	Maximum Deviation %
Same sample and constant film thickness					
A	1	0.003	97.1	−0.52	±0.52
			97.2	+0.52	
			97.1	−0.52	
			97.2	+0.52	
B	1	0.004	57.1	−0.87	±0.12
			58.2	+1.05	
			58.0	+0.70	
			56.9	−1.22	
			57.5	−0.17	
			57.8	+0.35	
B	1	0.003	53.8	−1.48	±1.1
			54.5	−0.18	
			55.0	+0.74	
			55.0	+0.74	
			54.8	+0.38	
Same sample, film thickness readjusted each time					
A	2	0.004	95.1	−0.28	±0.2
		(readjusted)	95.5	+0.14	
		(readjusted)	95.5	+0.14	
A	2	0.003	97.0	+0.34	±0.5
		(readjusted)	96.0	−0.69	
		(readjusted)	97.0	+0.34	
B	2	0.003	55.0	+0.37	±0.5
		(readjusted)	54.5	−0.55	
		(readjusted)	55.0	+0.37	
B	2	0.004	57.2	−0.52	±0.7
		(readjusted)	58.0	+0.87	
		(readjusted)	57.4	−0.17	
Different film thickness with same sample					
A	3	0.003	96.7	+0.68	±0.7
		0.004	95.4	−0.68	
B	3	0.003	57.5	−2.3	±2.3
		0.004	54.8	+2.3	
Different samples, constant film thickness					
B	1	0.003	54.6	−0.15	±0.2
	4	0.003	54.8	+0.22	
	5	0.003	54.6	−0.09	
B	1	0.004	57.6	−0.17	±0.5
	4	0.004	57.5	−0.35	
	5	0.004	58.0	+0.52	

Discussion

This paper describes an instrument for analyzing and measuring tack. The analysis has been attained by varying the pull-resistance, the film thickness, and the area of contact individually, studying the effect of each variation and deriving therefrom a mathematical equation relating all the factors involved. This relationship is given for liquids in Equation 10, and for plastics in Equation 11. In the form of tack and relative tack of plastics like printing inks it is given in Equations 18 and 23.

It is impossible in a preliminary report of this type, where attention has been focused mainly on printing inks, to go deeply into the possibilities and limitations of the Tackmeter. As long as the material being tested can be induced to adhere to the metal finger and plate and to neck down on pulling, there seems to be no apparent upper limit to the viscosities it can handle. The range of the largest finger used on the instrument has been, so far, from 1 poise to over 30,000,000 poises, but much research must yet be carried out before the validity of these high values can be ascertained. As far as film thickness is concerned, the Tackmeter has been operated successfully with films ranging from 0.0002 to 0.050 inch (5 to 1250 microns). Bekk has claimed that films less than 10 microns behave differently from thick ones. On the Tackmeter, oil films as thin as 5 microns and even somewhat less have been used and no evidence of a change in behavior has been detected. Materials with yield value, however, can give the appearance of a change in behavior if the force employed is either less than the yield value or so close to it that the difficulty in carrying out the measurement becomes too great to permit consistent and reliable results. This possibility is greatly enhanced by the use of very thin films.

Bekk's argument is that when he plots film thickness against force, the rate of flow being maintained unaltered, the curve produced flattens out toward the force axis as film thickness decreases. It is difficult to understand how this can be interpreted as a change in behavior, for the flattening of the curve must occur even for unchangeable materials. This can be seen from the equation of flow in capillary tubes by plotting the radius against the force, a constant volume of flow being maintained. Though Bekk does not use capillary tubes, he does employ a capillary space formed between a hemisphere and a hemispherical cup of like size and curvature. The ink or material is in this space and flows either into it or out of it, according to the way the hemisphere is moving. Bekk makes no attempt to develop the formula of his flow curve and therefore offers no proof that an unchangeable material will give any different curve from the type he gets.

If a film thickness of only several molecules is to be considered, there would be, perhaps, a different law of flow from the one given in Equations 10 and 11. Printing ink films, however, are of an entirely different order of magnitude—2 to 6 microns in process printing—and there is neither theoretical reason nor experimental proof that such films behave in any abnormal manner—i. e., differently from films, say, of 0.001 to 0.010 inch or more. As it is far more convenient to work with the larger films, the Tackmeter has been designed accordingly, though its lower limit is approximately 2.5 microns.

Determining the precision and accuracy of measurements made on printing inks is complicated by the fact that such materials are invariably thixotropic and consequently it would be difficult to decide whether structural changes in the material or shortcomings in the instrument were responsible for any unsatisfactory results. Therefore stable mineral oils have been used to investigate the duplicability of results on the Tackmeter (Table VII). Several types of duplicability have been studied: (1) where the material is not removed but remains on the instrument; (2) where different samples of the same material are checked against one another (this procedure is necessary because the quantity of sample is not determined by weighing but simply by estimation); (3) by changing the setting on the micrometer and then returning it to the original setting; and (4) by changing the setting to another film thickness and allowing it to remain there. Each measurement was made from a curve of only three points. The precision, therefore, is that obtainable for ordinary routine work and by no means represents the precision obtainable if many points are used instead of three.

The limitations of the Tackmeter are in the direction of high-speed determinations. In the case of thixotropic materials various results can be obtained, depending on the amount of thixotropic breakdown that has occurred at the time of measurement. The printing press probably destroys the thixotropic structure completely; consequently it is desirable to make tack measurements on samples that are in a similar condition of thixotropic breakdown. To approach this state on the Tackmeter it is necessary to use the following procedure.

After the ink has been placed on the instrument the lever arm, *J*, is raised at the weight end, separating the other end from the connecting bar, *I*. *I* is next moved up and down rapidly through a distance not quite great enough to break the ink completely. This operation can be carried out as rapidly as the finger tap-out test. *I* is then replaced in its notch and the measurement made in the usual manner.

The method of handling pseudoplastic inks at high speeds has been discussed above. When relative tack is required at high speeds, the viscosity term above is sufficient. This can be obtained with a properly constructed and operated high-speed rotational viscometer. Such an apparatus is useful where pseudoplasticity enters or where the ink is too heavy to undergo a satisfactory thixotropic breakdown on the Tackmeter. This conclusion might lead to the question, why, then, have a Tackmeter? The answer is obvious. Neither rotational nor capillary tube viscometers measure pull-resistance and therefore they cannot show the relation of tack and relative tack to yield value and viscosity. This relationship can be determined only by an apparatus that splits or partially splits the film. The Tackmeter does this and the relationship shown in Equations 10 and 11 is the result. When Equation 11 is written in the form of Equation 23, it can be seen that relative tack at high speeds depends practically only on viscosity. This conclusion cannot be derived from either a rotational or a capillary viscometer.

Acknowledgment

The author wishes to express his indebtedness to the Interchemical Corporation for making this investigation possible, and to Ruth N. Weltmann and William A. Elbracht for valuable cooperation in carrying out this work.

Literature Cited

(1) Bekk, Julius, *Deutscher Drucker*, 44, No. 256, 450–6 (1938).
(2) Reed, R. F., "The Inkometer", Lithographic Technical Foundation, *Tech. Bull.* 2 (Research Series 4, 1939).
(3) Reiner, Markus, *Physics*, 5, No. 11 (1934) and other work.

Apparatus and Methods for Precise Fractional-Distillation Analysis[1]

New Design of Adiabatic Fractionating Column and Precision-Spaced Wire Packing for Temperature Range −190° to 300° C.

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A new column design was developed and found satisfactory over the temperature range of −190° to 300° C. with extended use of vacuum jacketing around column, flask, reflux, and all connections, and with means for compensating for residual heat leakage through vacuum jacket. New vacuum-jacketed standard-taper ground joints withstand both liquid air and 300° C. temperatures, remaining vacuum-tight and easily detachable. Flexible glass bellows are used throughout as expansion joints for differential thermal dimensional changes. The column is made of four parts to permit interchangeable use of various distilling tubes and flasks. A new form of precision-spaced wire-type packing was also developed for the fullest utilization of capillary reflux liquid films across closely spaced wire turns. This packing has tested as high as 75 plates in 35 cm. (14 inches) with the *n*-heptane and methylcyclohexane test and its low H. E. T. P. and other desirable characteristics are maintained at least up to 25-mm. diameter. Performance data are submitted for packings of various size. This type of packing is now in use in many laboratories for both low- and high-temperature fractionation.

COMPLETE and exact control of column thermal conditions and of heat input, reflux cooling, and product withdrawal is important for maximum-efficiency fractional distillation. By "maximum-efficiency fractional distillation" is meant modern high-efficiency laboratory fractionating columns and packings ranging from 50 theoretical plates upwards by test, and requiring proportionately high reflux ratios for best performance.

In another paper (*12*) illustrative data and conclusions are given on the performance of nonadiabatic fractionating columns. Actually, all laboratory fractionating columns are to a greater or lesser degree nonadiabatic, because even the best insulation is imperfect. Under certain conditions it has been experimentally proved that nonadiabatic columns test materially more plates than more nearly adiabatic columns. Under other conditions it has been possible to destroy the effectiveness of a basically 100-plate column to as low as 12 plates by supercooling or superheating it, depending on the volumes and concentrations of charge at top and bottom of the column. Present fractional distillation theory provides no adequate explanation of these findings, which have, however, been exhaustively confirmed by several years of experimental work.

In application to laboratory fractionating columns, which usually operate with a relatively large volume of charge in the kettle compared to column and condenser holdup, while super-cooling—i. e., partial condensation of ascending vapors through heat radiation from column to outside—may actually improve fractionation, although at the expense of reflux ratio, superheating may completely destroy separation no matter how effective the column may be as a contacting apparatus. In any case, for fractionation of maximum efficiency it is necessary to control the thermal surroundings of high-efficiency fractionating columns to within close limits. The insulation of such columns and the compensation of the residual heat leakage which occurs through even the best in-

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[1] Patent Notice. The Heli-Grid packing and Super-Cal column described in this paper are protected by one or more of the following patents and by pending patent applications, under which the Podbielniak Centrifugal Super-Contactor Co. is exclusive licensee: U. S. Patents 1,909,315, 1,917,272, 1,935,888, 1,967,258, 2,009,814, 2,088,385, and 2,093,644; British Patent 380,220; French Patent 721,598; Canadian Patents 343,524 and 343,525; Rumanian Patent 27,009.

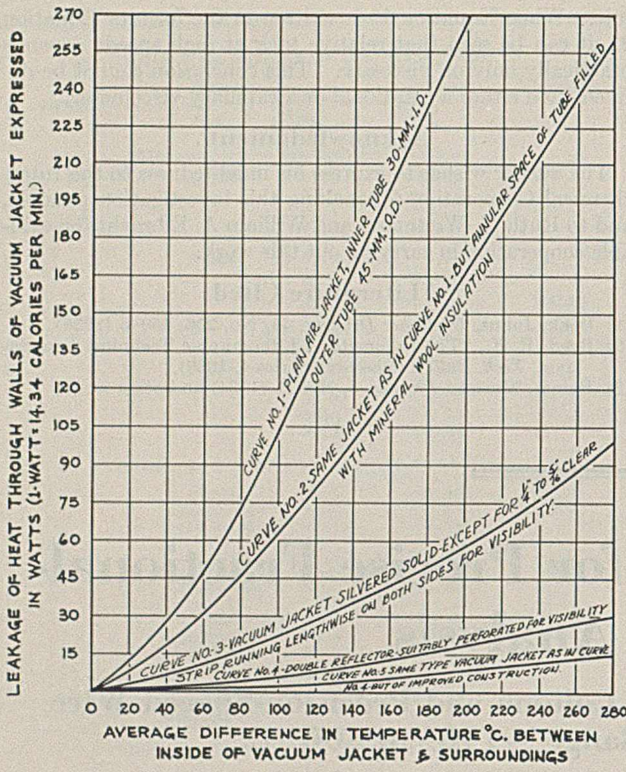

Figure 1. Thermal Insulation Effectiveness of Large-Bore Column Vacuum Jackets

Computed from experimental data on 9-mm. inside diameter jackets

sulation are essential to their best performance. Careful control of both the direction and degree of departure from the adiabatic condition is highly desirable.

Another factor also enters, in that the H. E. T. P. of most high-efficiency laboratory column packings varies with the vaporization and reflux rate as much as 200 per cent or more. It should therefore be possible to operate the columns at the proper rates to secure best balance of high fractionating effectiveness and maximum useful distilling capacity. However, in most laboratory columns 75 per cent or more of the heat input to the relatively poorly insulated distilling flask is lost to the atmosphere, and it is therefore not practicable to measure vaporization by heat input. Various devices are used to measure vaporization rate, at top or bottom of column, but these are usually of only rough accuracy, not adequate for setting the column at near its optimum rate, as determined for a particular column and a particular mixture.

Finally, the measurement and control of reflux ratio for high-efficiency columns are most important in obtaining best possible separation with a column in a given time of distillation. The reflux ratio as determined by overhead measurements is equal to the over-all reflux ratio only when the column is truly adiabatic. The importance of using an adequate reflux ratio, in conjunction with an adequate number of plates, for a desired separation, is well brought out by Rose (*13*).

Problems in Design and Construction of Adiabatic Fractionating Columns*

In an attempt to develop a fully adiabatic column for a wide range of temperatures, the selection of insulation is paramount. This is especially true of high-efficiency packings, which are usually of larger diameter to compensate for their reduced distilling capacity due to small clearances; there is more area to insulate and more dependence on the insulation.

Figure 1, computed from experimental data on a 9-mm. inside diameter series of air-jacketed and vacuum-jacketed columns as presented in a previous paper (*9*), represents the approximate residual heat leakages through a corresponding series of 30-mm. inside diameter air and vacuum jackets. The great superiority of the metal reflector–shielded vacuum jacket over any other form of column insulation is apparent. However, at 300° C. above room temperature the residual heat leakage is of the order of 15 watts, which would result in serious supercooling if uncompensated. As described in a previous paper (*10*), a miniature electric resistance wire heater may be used between the distilling tube or column proper and the sleeve-type vacuum jacket, with proper regulation, to compensate very closely for this residual heat leakage for all temperatures.

If the distilling tube for use within the vacuum jacket of Figure 1 were itself to be vacuum-jacketed, this additional vacuum jacket in series with the outer vacuum jacket might offset the increased heat leakage of the large-bore vacuum jacket, and make regulation of a miniature compensating heater between the two vacuum jackets far less critical. Such complication would not be warranted merely to replace proper compensatory heater regulation. However, the additional vacuum jacket is a by-product of a construction advantageous in several other respects.

A more serious problem came up in providing expansion joints for the large-bore vacuum jacket. For jacket bores up to about 9 mm. the inner tube of the vaccum jacket could be bowed deeply in the case of low-temperature fractionation, or left almost straight in the case of high-temperature fractionation, so that the resulting straightening or bowing of the inner jacket tube would take care of the inevitable differential expansion between the inner and outer vacuum-jacket tubes. However, for vacuum jackets of the order of 28-mm. bore, the inner tube is far too rigid to use the bowing expedient.

Figure 2 is a diagram of expansions and stresses in vacuum jackets under differential temperatures as indicated. The

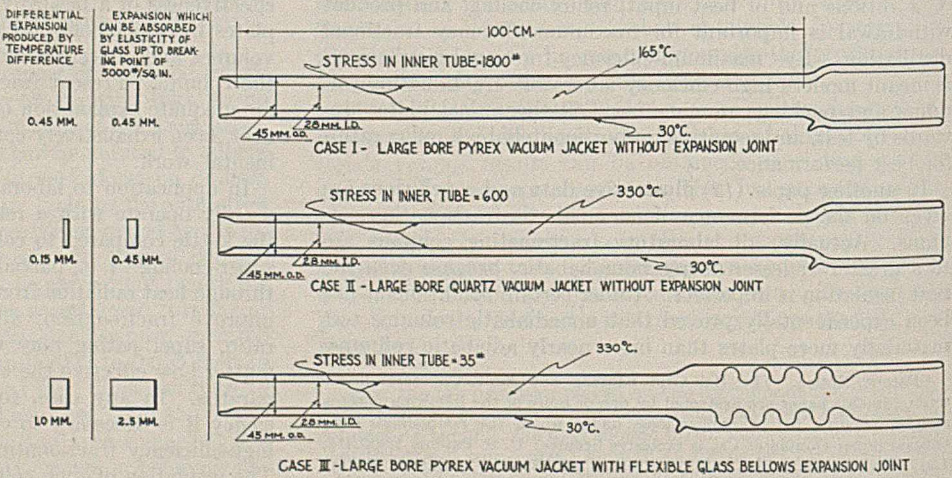

Figure 2. Differential Thermal Expansions and Resulting Stresses in Vacuum Jackets

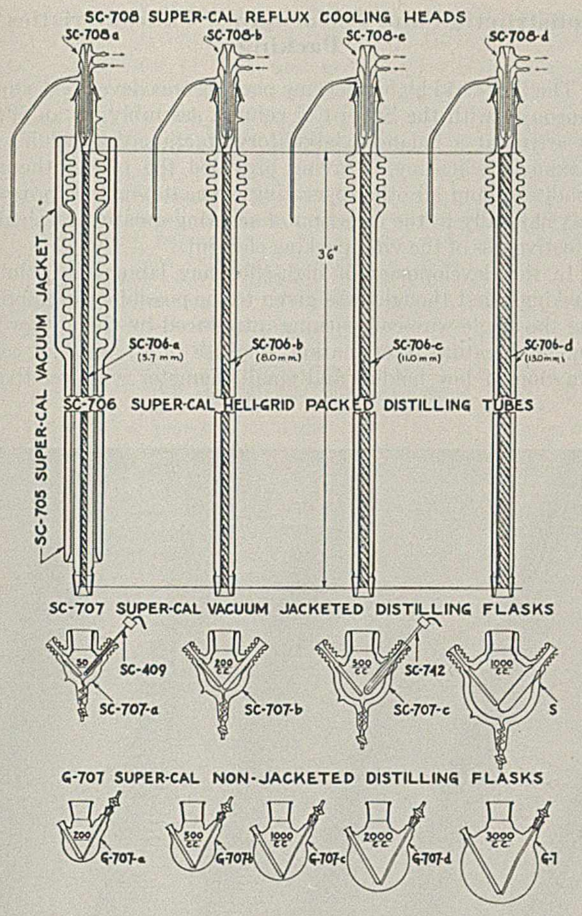

Figure 3. Super-Cal Type of Fully Adiabatic Vacuum-Jacketed Fractionating Column System

data for computation of elastic compression and stresses of glass and quartz are Morey's (7), and have been verified experimentally in this application.

The large-bore Pyrex jacket without an expansion joint cannot possibly survive about 135° C. temperature difference, as illustrated, which subjects the glass to its breaking stress, with a tremendous load on the end ring seals of the jacket. Actually, with such a severe strain, the jacket would probably break at a much lower temperature than the maximum indicated. Curiously enough, the literature contains descriptions and drawings of similar vacuum-jacketed columns without expansion joints, although intended for distillation to high temperature.

The all-quartz vacuum jacket, because of its low thermal expansion coefficient, reaches a temperature difference of 300° C. with about one third of its breaking strain (which is approximately the same as that of Pyrex). Actually, in the author's experience, such quartz vacuum jackets last indefinitely, as far as thermal strains are concerned. However, in large sizes, the cost of the quartz is prohibitive.

The third vacuum jacket in Figure 2 is Pyrex, with the incorporation of a flexible glass bellows as expansion joint in the inner tube. With proper fabricating machinery and technique, these bellows can be made amply rugged mechanically, and yet sufficiently flexible to take care of all differential expansion at 300° C. temperature difference, with more than 100 per cent safety margin and only 15.9-kg. (35-pound) strain in the inner tube. This, then, seemed the only possible and satisfactory solution of the problem of absorbing the differential expansion of a large-bore vacuum jacket, and was adopted in the columns described here.

High-Efficiency Vacuum-Jacketed Column

Figure 3 shows the Super-Cal system of interchangeable outer vacuum jacket, distilling tubes and flasks provided with vacuum jackets and ground joints, and reflux cooling heads.

Flexible glass bellows are used as expansion joints in the construction of all the column parts except the reflux cooling head, and except where inlet and outlet tubes could be bent to serve as expansion joints, as in the vacuum-jacketed distilling flasks. The flexible glass bellows expansion joint is used in the outer tube of the vacuum-jacketed distilling tubes, not in expectation of large temperature difference across these tubes in normal operation, but as an emergency provision in case of momentary large temperature differences, as when starting distillation.

The use of vacuum-jacketed standard-taper ground joints between the bottom end of distilling tubes and distilling flasks to provide a leak-tight, easily detached connection at this point has successfully overcome a very annoying difficulty in both low- and high-temperature fractionating apparatus. As rubber tubing joints or lubricated ground joints freeze at liquid air temperatures and leak, while unlubricated ground joints are not vacuum-tight at any temperature, only fused-glass joints have hitherto been satisfactory for connecting low-temperature distilling bulbs to the column. In high-temperature fractionation, corks coated with glue have been the usual but unsatisfactory solution, while ground joints cannot be relied upon at high temperatures.

With a suitable lubricant of high graphite content, the vacuum-jacketed joints between distilling tube and the vacuum-jacketed series of distilling flasks not only remain vacuum-tight at lowest obtainable temperatures, but can even be rotated at those temperatures without developing leaks. Instant interchange from one size or type of distilling bulb to another without disassembly of column has thus been made possible for low-temperature fractionation apparatus. A mercury seal, although not found necessary in practice, may be used with this type of joint to assure tightness under all vacuum conditions.

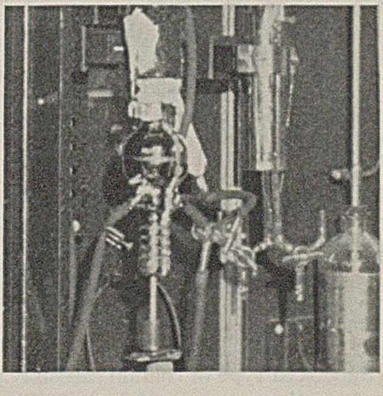

Figure 4. Low-Temperature Super-Cal Type of Distilling Flask with Built-In Precooler and Heating Well

The vacuum-jacketed joint with either the vacuum-jacketed or non-vacuum-jacketed series of distilling flasks has proved equally satisfactory for high-temperature fractionation. Sufficient temperature gradient exists throughout the long ground zone of the joint so that most of the lubricant remains at a low enough temperature to function satisfactorily.

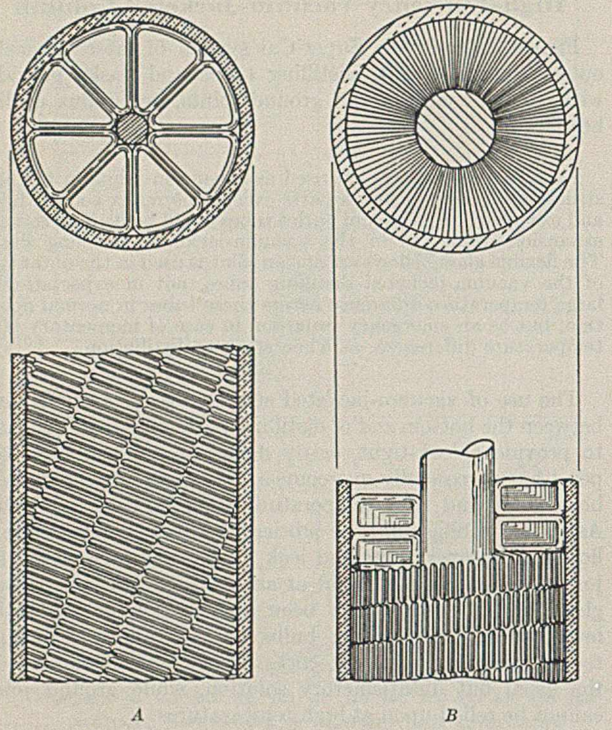

FIGURE 5. DIAGRAM OF HELI-GRID PACKINGS

A. Assembly of sector-section coils twisted around central core
B. Staircase assembly of rectangular section coils around central core

A detachable low-temperature fractionating flask must obviously carry its own vacuum jacketing, as is illustrated in Figure 4, which shows a flask of 50-cc. total capacity, with its built-in precooler element, also serving as heater well, with a cartridge-type heater, as described for the Super-Cool column (*12*).

The reflux cooling heads shown are of conventional type, for high-temperature fractionation, suitable for brine, water, or air cooling. The same remarks apply to the vacuum-jacketed upper ground joint of the distilling tubes as were made above with reference to the lower joint. The heads should be proportioned for least holdup of liquid compatible with adequate cooling surface for the capacity of distilling tube used for the lowest boiling liquids to be distilled. For low-temperature fractionation the vacuum jacket of the distilling tube terminates sufficiently below the upper end of the distilling tube to permit the use of a reflux cooling vessel and attachments as described for the Super-Cool column.

The outer tube of the vacuum-jacketed packed distilling element serves conveniently to join the upper and the lower vacuum-jacketed ground joints, without weak triple-glass seals, and to protect the weaker inner tube with its expensive packing. It also serves as a secondary (nonreflectored) insulation and as a buffer against improper regulation of the compensatory miniature resistance wire heater which is used in the annular space between the two vacuum jackets.

With the Super-Cal type of column assembly the heat lost by radiation from the vacuum-jacketed distilling flasks need not be more than a few watts, and this can be accurately allowed for, while complete compensation can be provided for in the column proper by the means described. Thus, this generalized column design provides for fully adiabatic column and still performance throughout the entire temperature range of −190° to 300° C., with no change in general design, except for adaptations of distilling flask and reflux head for low-temperature fractionation. It is actually possible, in the one column, to distill a sample ranging in composition from methane to lubricating oil, beginning with a reflux temperature of −161.4° C. at atmospheric pressure, and ending with 300° C. in the reflux at 20-mm. absolute pressure.

Construction and Performance Characteristics of Packing

The Heli-Grid high-efficiency packing was developed simultaneously with the Super-Cal column assembly, in an effort to arrive at a balanced laboratory fractionating column of maximum efficiency. Having provided the proper thermal conditions and all other operating elements, further progress was naturally in the direction of securing greatest attainable effectiveness of the vital packing element.

In the development of high-efficiency laboratory column packings, first thought was given to the possibility of improving the single wire-coil packing introduced by the author for low-temperature fractionation, because of its unusual combination of low holdup and small diameter with relatively high plates and distilling capacity. It seemed that the principle of capillary film formation between wire turns or loops spaced precisely in accordance with definite carefully worked out patterns could be extended to yield at least as low H. E. T. P.'s as packings depending on random arrangement (such as Lessing rings or single-turn wire or glass helices).

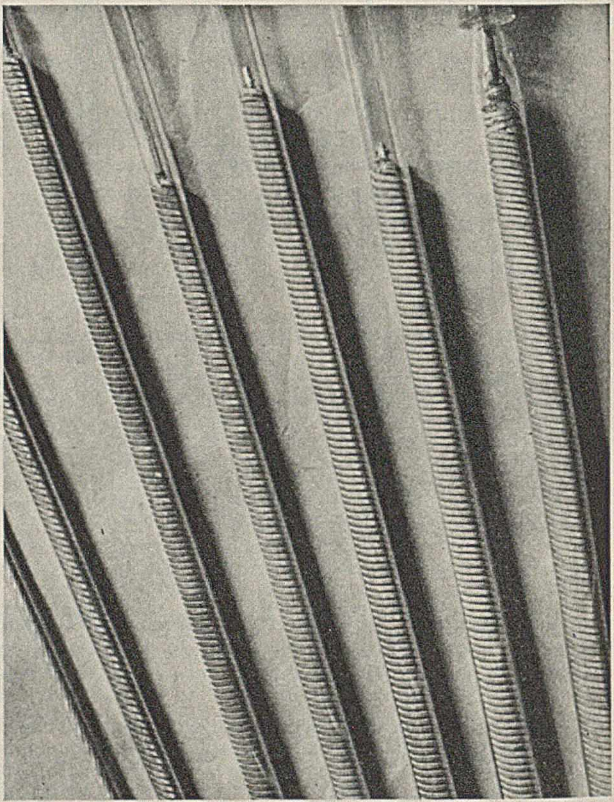

FIGURE 6. HELI-GRID PACKINGS

Starting with this basic thought, the rest of the development was entirely experimental, consisting of trying out innumerable wire patterns, sizes, spacings, loop diameters, sections, etc., in each case testing the packing variation by benzene–ethylene dichloride test mixture, and later with *n*-heptane and methylcyclohexane. Theory on surface tension phenomena was found to be of little help when dealing with liquid and vapor flows through complex wire whorls. It was necessary to concentrate on development of forming technique and tools and of special machinery for most precise and uniform execution of those packings which gave best test results, varying details of spacing, coil diameter, section shape, etc., very slightly to detect trend of change in further test results. Only correctness of form and precise execution distinguish this type of packing from a scouring wad of tangled wire.

It was found possible to develop many forms of close-clearance wire packings which showed high efficiencies, such as the two forms illustrated in Figure 5. The packing in Figure 5, *A*, consists of coils of sectorlike section, wound around each and around a very small core wire, to yield a number of uniform nonflooding vapor passageways, "lined" perfectly with capillary liquid reflux films extending between vertically adjacent wire loops. Another form of packing (Figure 5, *B*) consists of wire cage "staircases", wound around a central solid core and around each other in concentric telescoping layers, if necessary to obtain larger diameters and capacities. Figure 6 illustrates several sizes and types of Heli-Grid packings.

This type of packing has been named the Heli-Grid because of its resemblance to helical grids or filaments. Because of its capillary spacings, it acts like a metal sponge with respect to any liquid reflux seeking to channel between packing and walls of glass tube or of the solid core, and no such channeling can occur except at actual gross overflooding. Even if the packing is tilted nearly horizontal and some liquid poured into the upper end, the liquid will not channel, but will actually run spirally up and down following the capillary wire coils. In order to assure this freedom from channeling, despite nonuniformity of bore of glass tubing used, the packing is pre-tensioned as to twist in fabrication to fill the glass tubing snugly at all points, despite irregularities. Inconel, or Nichrome, is the wire material of choice, because of its high resistance to corrosion of all types and because it can be readily cleaned with sulfuric and nitric acids without injury. Wire sizes and spacings will vary with design, but usually the wire is of the order of 0.25-mm. (0.010-inch) diameter, with spacings between wire about equal to wire diameter.

As the testing of laboratory column packings has become fairly well standardized in the technical literature, it has been possible to compare Heli-Grid packings with other high-efficiency packings as to performance characteristics (Figure 7). In representing other packings every attempt has been made to use the actual data given in papers by those introducing the packings, or to compute therefrom without error or prejudice.

The author believes that in the case of analytical batch fractionating columns, neither the height nor the diameter of the column, so long as these are not excessive, is of importance, as against the desirability of high distilling capacity and number of plates with least possible holdup of sample in column. Therefore, factor A was set up to express over-all column efficiency considering all these three important factors. Bragg (*2*) has set up a similar factor, in reciprocal form, for use in his comparison of column packing types.

The H. E. T. P. of the Heli-Grid packing, as determined by the *n*-heptane and methylcyclohexane test mixture at total reflux, is the lowest yet reported in the literature, reaching 75 plates in 35 cm. (14 inches) of packing, or about 0.5 cm. (0.2 inch) H. E. T. P. As is shown in Figure 8, these low H. E. T. P.'s have been verified on 108-cm. (36-inch) packings, up to the limit of the *n*-heptane and methylcyclohexane test.

Likewise, as regards holdup per plate and factor A, Heli-Grid packings compare very favorably with other packings, throughout most of their distilling capacity range. Like many other high-efficiency low-holdup packings, the H. E. T. P. *vs.* reflux rate curve falls off rapidly with increasing reflux rate. Conversely by operating at low rates, the Heli-Grid packing attains remarkable fractionating effectiveness without the usual falling off at low rates shown by many other packings. This behavior would seem to show complete freedom from channeling of either vapor or liquid, at the lower rates.

Strangely enough, the Heli-Grid packing requires preflooding in the manner described by Fenske and others, for attainment of highest efficiency. This was not originally appreciated in

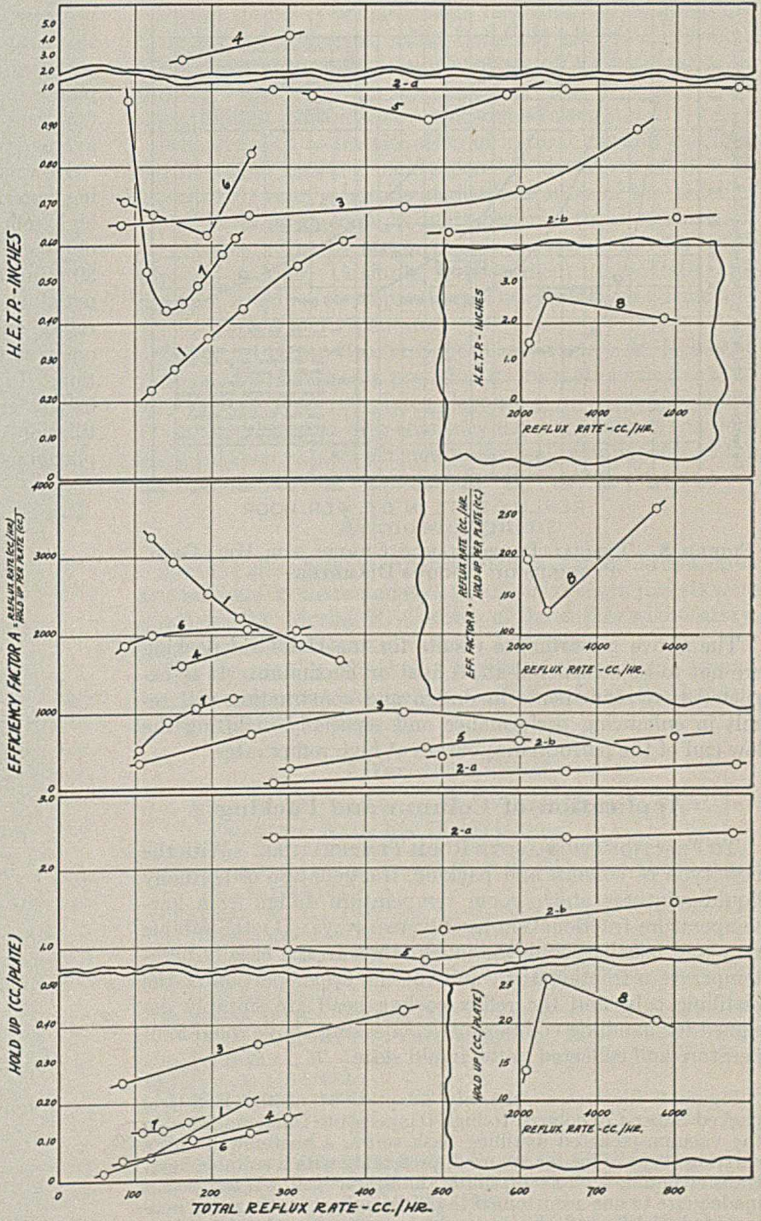

FIGURE 7. COMPARISON OF HELI-GRID WITH OTHER HIGH-EFFICIENCY LABORATORY COLUMN PACKINGS

1. Heli-Grid, 11-mm. inside diameter, 35-cm. (14-inch) section
2-*a*. Fenske, single-turn metal helices, 1.98-cm. (0.79-inch) inside diameter, 277.5-cm. (111-inch) section (*4, 17*)
2-*b*. Fenske single-turn helices, 1.55-cm. (0.62-inch) inside diameter, of No. 34 stainless steel wire, 25.4-mm. inside diameter packing, 100-mm. length of packed section (*18*
3. Purdue, spiral screen, 1.875-cm. (0.75-inch) inside diameter, 42.5-cm. (17-inch) section (*6*)
4. Spinning band, 6.7-mm. inside diameter, 540-cm. (216-inch) section (*1*)
5. Bruun 100-plate bubble cap, 195-cm. (78-inch) section (*3*)
6. Burk-Selker, concentric tubes, 14-mm. inside diameter, 150-cm. (60-inch) section (*14*)
7. Stedman, conical wire cloth, 9.5-mm. inside diameter, 60-cm. (24-inch) section (*16*)
8. Urey, rotating cone, 10.5-meter (35-foot) column (*5*)

developing the packings and it was gratifying to find that considerable improvement resulted from this procedure. Once wetted by preflooding, a packing will operate at its best efficiency throughout a distillation, until dried out by stopping distillation or otherwise.

Heli-Grid packing sizes have been worked up from 4.5-mm. (used for low-temperature fractionation) to 25-mm. diameter. Unlike certain other types of high-efficiency packings, the H. E. T. P. and factor A curves for the Heli-Grid type of packing do not deteriorate with diameter for the sizes thus far developed. This is as expected, as the design of diameter packings is varied to maintain vapor passageway length and clearances, etc., as constant as possible for all the packing sizes.

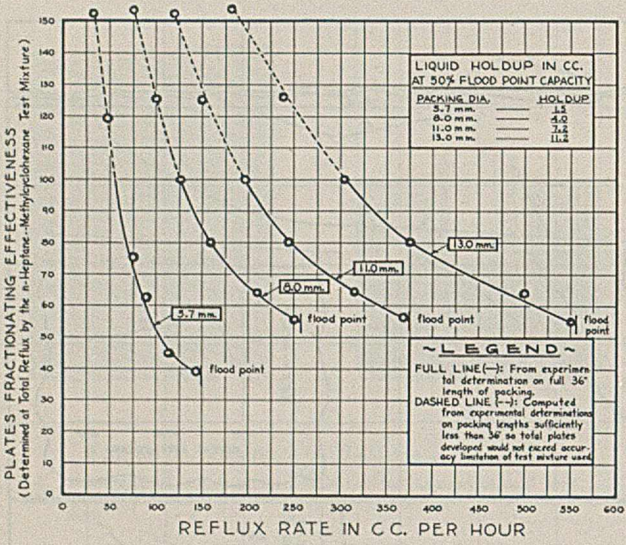

FIGURE 8. TYPICAL PERFORMANCE CURVES FOR HELI-GRID PACKINGS OF VARIOUS DIAMETERS

The above performance results for the Heli-Grid packing are not to be considered at all final or maximum. It is expected that refinements in design and construction will result in enhancing performance and especially in lifting the low end of the performance curves at high reflux rates.

Application of Column and Packing

TO FRACTIONATION ABOVE ROOM TEMPERATURE. With the new type of column and packing, fractionation of normally liquid mixtures above room temperature differs from low-temperature fractionation in only two ways: (1) the sample may and usually should be much larger in the case of high-temperature fractionation, and (2) the upper portion of the distilling tube and the reflux cooling head are suitably designed for handling components condensing above room temperature and collected in the liquid state.

Figure 3 illustrates primarily adaptations of the Heli-Grid packed Super-Cal column to high-temperature fractionation. In the vacuum-jacketed distilling flask series, a heater well and a cartridge type of heater are used, preferably with a suitable heat-transfer liquid, such as oil, filling the heater well. If this seems inadequate to one accustomed to piling on heat on the usual non-jacketed distilling flask, it should be remembered that only a fraction as much heat need be supplied through the walls of the vacuum-jacketed flask.

Figure 8 gives the performance characteristics of Heli-Grid packed Super-Cal columns, as determined by the *n*-heptane and methylcyclohexane test mixture. The packings differ mainly in distilling capacity and holdup. Best results cannot be obtained from any packing without proper thermal surroundings and close control over all distillation factors.

Figure 9 shows a complete fractionation apparatus with a Super-Cal type of column and vacuum-jacketed distilling flask, with an exact rheostat and wattmeter system for controlling and measuring heat input to flask, and with a sensitive vacuum control for use in vacuum distillation.

In this apparatus, the Heli-Grid packed Super-Cal column has been tested on a wide variety of distillable mixtures, such as high-boiling petroleum fractions, heat-sensitive essential oils, fatty acids, etc. The Heli-Grid packing loses comparatively little of its distilling capacity even down to 20-mm. absolute pressure, presumably because its bottleneck is liquid rather than vapor volume rate. Owing to its wire structure, it is possible to drain absolutely all liquid from packing towards the end of a distillation, by chilling the flask.

One interesting phenomenon observed in this work deserves at least passing mention, although full discussion must be reserved until completion of quantitative tests now in progress. It has long been tacitly assumed that the best way to operate any column is with as nearly continuous a product-withdrawal rate as possible. The computation of column plates and obtainable separations as by the Smoker equation (*15*) uses the reflux ratio obtained by dividing reflux rate by average product rate.

However, in operating the high-efficiency column and packing here described, on close-boiling binary test mixtures at high reflux ratios, very much better separations have been obtained by holding the column at total reflux for periods of 30 minutes or more, and then withdrawing a quota of product almost instantaneously, again holding the column at total reflux, and so on, than by withdrawing the product continuously at the same average rate as in the intermittent operation. In fact, the separations obtained are better than called for by either Rose's computations of batch fractional distillation curves (*13*) or Smoker's formula (*15*). The same phenomenon has long been observed in experimental work on

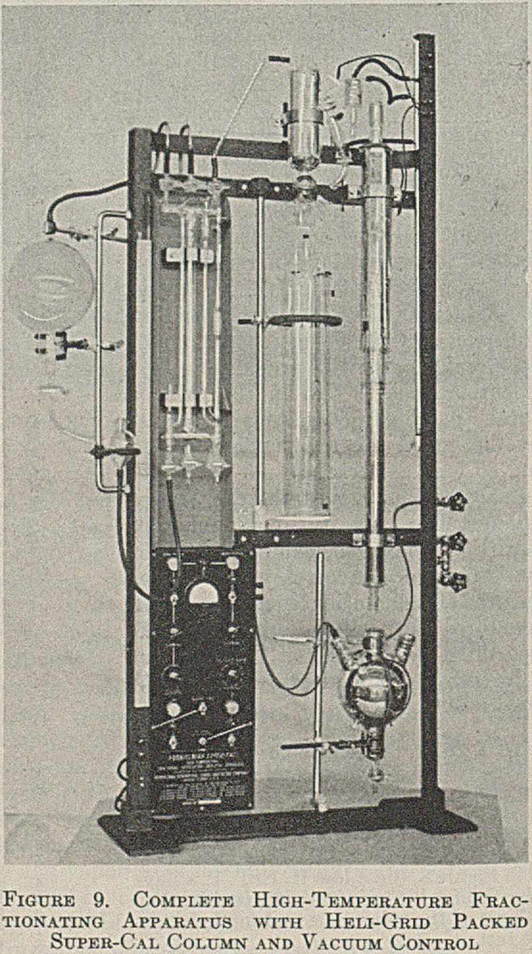

FIGURE 9. COMPLETE HIGH-TEMPERATURE FRACTIONATING APPARATUS WITH HELI-GRID PACKED SUPER-CAL COLUMN AND VACUUM CONTROL

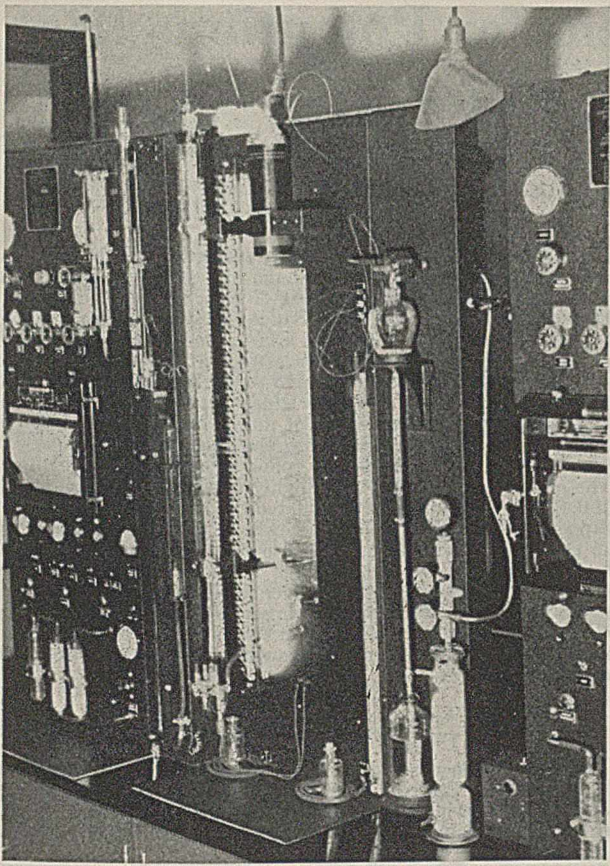

Figure 10. Hyd-Robot Automatic Recording Low-Temperature Fractionating Apparatus with Heli-Grid Packed Super-Cool Columns

centrifugal fractionators, and is now understood to be a factor in low-temperature fractionation. Like the nonadiabatic column performance phenomena mentioned above, this unexpected advantage of intermittent product withdrawal, so outstanding as to merit the nickname "the free-wheeling effect" in the author's laboratories, still is without theoretical explanation.

In application to design of the Super-Cal column, the "free-wheeling effect" makes desirable as close and accurate control of reflux cooling as possible, with lowest possible holdup in the condenser. This is contrary to the tendency displayed in the literature to use complicated reflux distributor heads of high vapor and liquid holdup.

Application to High-Efficiency Low-Temperature Fractionation. The most immediate and effective use of Heli-Grid packings within the Super-Cool type of low-temperature fractionating column (*12*) has been for the complete analysis of all the components of the cracked C_4 fraction of refinery gases, by combined high-efficiency low-temperature fractionation and supplementary chemical tests. The separation of isobutane from isobutene, and the separation of butene-1 from *n*-butane, are exceedingly difficult, and require both in theory and practice more than 50 theoretical plates and a reflux ratio higher than about 100 to 1 to obtain satisfactory separation. The wire-coil packing and its simple modifications, while satisfactory for the easier separations of hydrocarbons occurring in natural gas and gasoline (*8*), do not have sufficient fractionating power to separate components boiling as close together as 6° C., even at total reflux. On the other hand large-diameter high-holdup packings are manifestly not usable for the precise analysis of samples of condensate as small as 2 cc. of liquid.

As a matter of fact the need for a high-efficiency low-temperature packing to make complete analysis of the cracked C_4 fraction possible had become both urgent and serious, inasmuch as daily analyses of this type are a practical necessity for the efficient operation of alkylation plants for the production of high-octane aviation gasoline stock, and in catalytic cracking and other modern refining processes. The development of the Heli-Grid packing was undertaken with this exigency in mind. At this writing the Heli-Grid packing is used for complete cracked C_4 analysis in many alkylating and catalytic cracking plants in this country.

Figure 10 shows an automatic recording low-temperature fractionating apparatus, using Heli-Grid packed Super-Cool columns for the routine daily analysis of alkylate gases for efficient plant control. Apparatus of this type and their operation and performance are described elsewhere (*11*, *12*).

When applied to fractionation of natural gas and gasoline, the Heli-Grid packing makes possible the sharp separation of isobutane from *n*-butane at distillate rates of the order of 40 to 60 cc. of gaseous products per minute, as against approximately 10 to 15 cc. per minute maximum for the single wire-coil packing. A similar improvement in distillate rates has been noted for the separation of ethylene from ethane and of isopentane from *n*-pentane.

Either the Super-Cool or Super-Cal column with Heli-Grid packing thus serves as a precision microfractionating column testing from 50 to 100 plates, depending on operation, filling a need for improved high-efficiency low-temperature fractionating columns to meet the new analytical requirements of the petroleum and other industries.

Acknowledgment

Flexible glass bellows expansion joints of suitable deflection and mechanical characteristics for use in vacuum jackets were developed by Morley R. Corbett of the author's laboratory, originally in collaboration with D. J. Pompeo.

The cooperation of Alfred Viergutz of the author's laboratory on this project has been especially helpful in the development of Heli-Grid packing.

Literature Cited

(1) Baker, R. H., Barkenbus, Charles, and Roswell, C. A., Ind. Eng. Chem., Anal. Ed., 12, 468 (1940).
(2) Bragg, L. B., *Trans. Am. Inst. Chem. Engrs.*, 37, 19–50 (1941).
(3) Bruun, J. H., and Faulconer, W. B. M., Ind. Eng. Chem., Anal. Ed., 9, 192 (1937).
(4) Fenske, M. R., Tongberg, C. O., and Quiggle, Dorothy, Ind. Eng. Chem., 26, 1169–213 (1934).
(5) Huffman, J. R., and Urey, H. C., *Ibid.*, 29, 531 (1937).
(6) Lecky, H. S., and Ewell, R. H., Ind. Eng. Chem., Anal. Ed., 12, 544 (1940).
(7) Morey, G. W., "Properties of Glass", A. C. S. Monograph 77, New York, Reinhold Publishing Corp., 1938.
(8) Podbielniak, W. J., Ind. Eng. Chem., Anal. Ed., 3, 177 (1931).
(9) *Ibid.*, 5, 119 (1933).
(10) *Ibid.*, 5, 135 (1933).
(11) *Ibid.*, 5, 172 (1933).
(12) *Ibid.*, in press.
(13) Rose and Welshans, Ind. Eng. Chem., 32, 668 (1940).
(14) Selker, M. L., Burk, R. E., and Lankelma, H. P., Ind. Eng. Chem., Anal. Ed., 12, 352 (1940).
(15) Smoker, E. H., *Trans. Am. Inst. Chem. Engrs.*, 34, 165–72 (1938)
(16) Stedman, Ind. Eng. Chem., Anal. Ed., 11, 283–7 (1939).
(17) Tongberg, C. O., Lawroski, S., and Fenske, M. R., Ind. Eng. Chem., 29, 957 (1937).
(18) Whitmore, F. C., *et al.*, *J. Am. Chem. Soc.*, 62, 795 (1940).

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Multiple Electrode System for Potentiometric Titration Studies

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FOR the practical application of potentiometric titration methods to industrial analyses, it is highly desirable to select with care the electrodes to be used in following the course of the reaction.

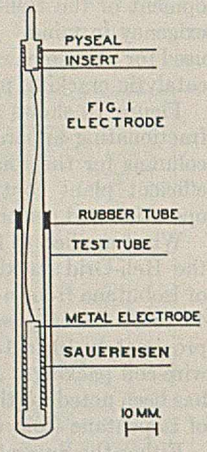

FIG. 1 ELECTRODE

A relatively large change in potential with a small change in concentration should occur in the vicinity of the equivalence point; up to the vicinity of the equivalence point the potential difference between the electrodes should remain relatively constant; the indicator electrode should reach equilibrium rapidly, so that the course of the reaction may be followed closely; and the electrodes used should not be subject to poisoning nor be attacked by the solution during the titration.

In investigating practical applications of potentiometric procedures in this laboratory it has been found expedient to make use of a flexible multielectrode system with which it is possible to determine the optimum system to be used for any specific determination under the exact conditions obtaining.

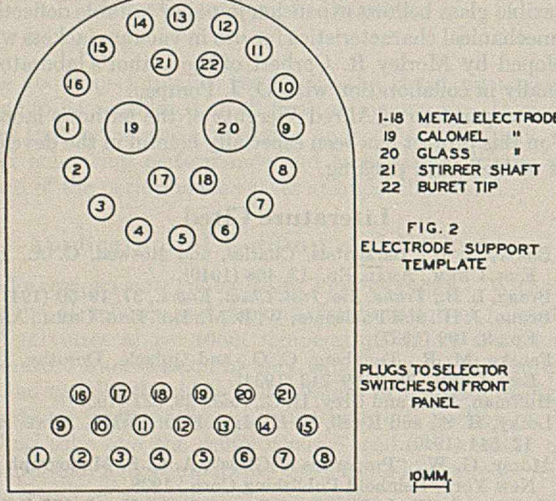

FIG. 2
ELECTRODE SUPPORT TEMPLATE

The present setup includes one reference electrode (calomel or silver chloride electrode as desired) and eighteen indicator electrodes.

Electrodes Used

The calomel and glass electrodes used are standard Beckman type electrodes with the leads modified to fit in with the rest of the wiring. The remaining electrodes (Figure 1) were prepared in several ways, determined largely by the physical limitations of the materials.

When possible (antimony, bismuth) the pure or purified metal was cast into a cylindrical rod (about 1 cm. in diameter, 5 cm. long) with a piece of copper wire (for lead) imbedded in one end. A piece of Pyrex glass tubing usually sufficed for the mold. The rod was then machined to the shape indicated in Figure 1 and sealed into a piece of glass tubing (7 mm. in outside diameter, 12 cm. long, ends ground) with Sauereisen cement No. 31. The copper wire lead was soldered to a brass insert, sealed to the opposite end of the tube with Pyseal cement, a 15-cm. length of push-back wire was in turn soldered to the brass insert, and a pin tip was connected. For metals which could not be cast (platinum, tantalum) a short length of pure wire was welded to the copper lead and then sealed into the glass tube as above. If possible, the wire electrode was coiled to expose greater surface. The machined electrodes were highly polished. A 1-cm. length of 0.47 cm. (0.19-inch) bore Scimatco rubber tubing was cut and slipped onto the glass tube as shown, so that a standard 11 × 75 mm. test tube could be slipped over the end of the electrode tip and kept in place by the rubber tubing. With the test tube in place an electrode may be shielded from contact with corrosive solutions. Solutions for preservation or cleaning of any electrode may be placed in the test tube and the electrode stored in favorable media when not in use without removing it from the electrode support.

Electrode Support

The electrodes were mounted in a Bakelite board cut and drilled as indicated in Figure 2. They were arranged on the periphery of a circle 7 cm. in diameter, so that with all electrodes and their shielding test tubes in place a 600-ml. beaker in which titrations

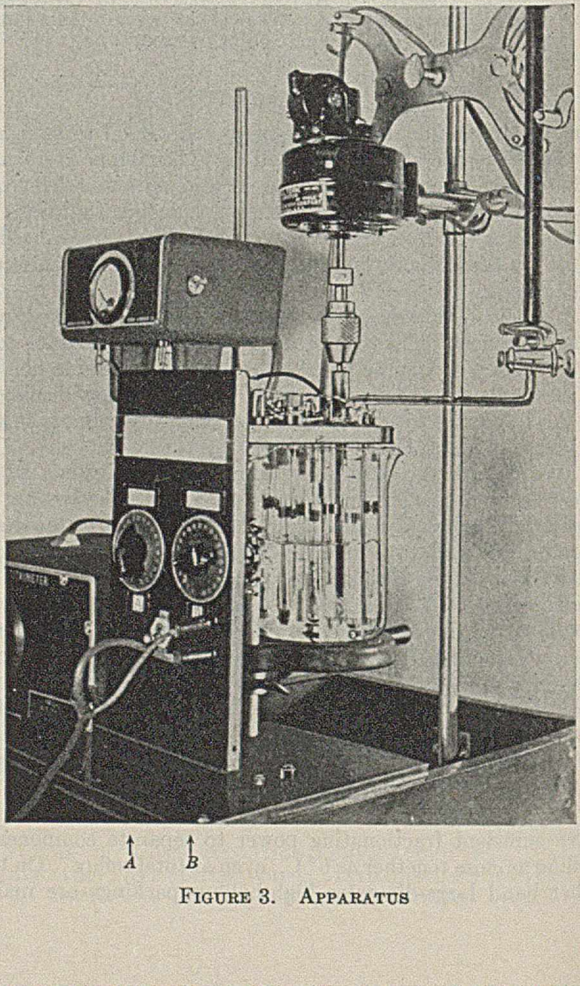

FIGURE 3. APPARATUS

may be conducted could be raised to surround them. Provision is also made in the Bakelite board for an all-glass stirrer and modified buret tip (Figure 3). In mounting the electrodes in the Bakelite board a 0.62-cm. (0.25-inch) hole was drilled through, then beveled to 0.94 cm. (0.375 inch) on the upper side. The electrode was inserted so that the top of the brass insert projected through the board and sealed in place by filling the beveled region around the glass with Pyseal. The electrodes are thus held firmly but may easily be removed by warming the cement with a hot file or small soldering iron.

Electrode Assembly

Two Centralab 23 position selector switches were mounted on the front panel and the common terminal of each was connected to individual insulated jacks (one red, one black, Figure 3) through a double-pole double-throw toggle switch. A series of jacks (taking phone tips) was then mounted on the electrode support (20 in this particular instance) and each jack was connected to the same position on both switches. Thus when the antimony electrode was installed the tip from the antimony lead was inserted in jack No. 2 and the latter in turn connected to position 2 on switches *A* and *B* (Figure 3). The calomel electrode was plugged to jack No. 5 and the latter connected to position 5 on switches *A* and *B*. The electrode leads from the titrimeter used were plugged into the red and black jacks on the front panel.

Thus, with the electrodes immersed in the solution to be studied, by setting switch *A* to position 2 and *B* to 5, with the toggle switch in the up position, the antimony electrode is connected to the red jack and the calomel to the black jack (and in turn to the titrimeter). Flipping the toggle to the down position immediately reverses the polarity, connecting the antimony electrode to the black and the calomel to the red plug. Reversal of polarity could be obtained, of course, by leaving the toggle in the up position and turning switch *A* to 5 and *B* to 2. With this flexible arrangement any pair of electrodes could be used and the polarity with respect to the titrimeter reversed at will. By including a standard reference electrode (calomel half-cell) comparative studies are simplified.

A glass electrode was included for ease in adjustment of solution pH. For example, the effect of acid concentration on a reaction may be investigated by connecting the glass and calomel electrodes to the titrimeter, adding acid from a buret until the desired pH is attained, connecting the desired indicator electrode (or electrodes) to the titrimeter by readjustment of switches *A* and *B*, and titrating with the standard reagent solution. At any point during the titration the initial electrodes may be reconnected to the titrimeter by adjustment of *A* and *B* and the pH checked rapidly.

A list of the electrodes used, with their position on selectors *A* and *B*, is mounted on the front panel for convenience. The nature of the electrodes to be used for any one study depends upon the reaction to be investigated. With this setup the best electrode pair for titration of any solution, following the five considerations outlined above, may be readily and quickly determined.

A Shaping Lathe for Graphite Electrodes Used in Spectrochemical Analysis

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THE need for a rapid and convenient means of shaping graphite electrodes for use in spectrochemical analysis of plant ash led to the design and construction of a small portable shaping lathe. This consists of two essential units, a lathe head and an electrode feeding assembly, securely held in proper relative position on a base plate.

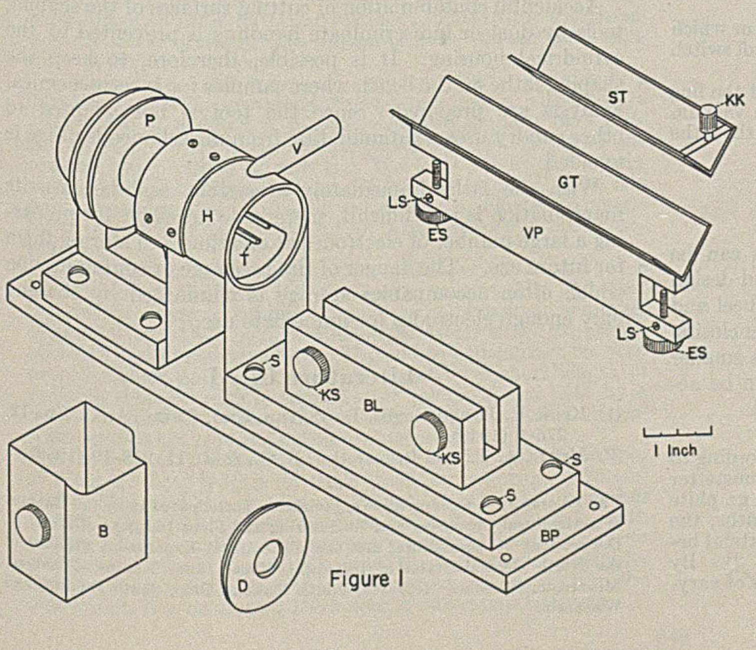

Figure I

Lathe Head

A motor-driven shaping bit mounted horizontally, and an enclosure for guarding the cutting end of the bit and collecting the graphite trimmings, are the main elements of the lathe head (Figures 1 and 2). The outer section of the shaping bit (*T*, Figure 2) forms the shaft of the rotating part and turns in two snugly fitting dustproof ball bearings (*BB*, Figure 2). A pulley wheel locked to this shaft between and in contact with the two bearings prevents thrust play in the shaping bit. The support for bearings and shaft is fastened securely to the main base plate.

A shallow cylindrical housing encloses the cutting end of the bit. A section of the underside cut away allows heavier graphite trimmings to drop into a removable bin (*B*, Figure 1). Lighter graphite dust is removed by suction through a tube fastened in the cylinder top. If the type of shaping or trimming operation does not produce large graphite chips or shells, the bin and bin enclosure can be omitted and the suction port placed on the underside of the cylindrical housing. The vacuum system will keep graphite dust from collecting.

A removable flanged disk (*D*, Figure 1), with a central opening, fits into the open end of the cylindrical housing. The central opening, while large enough to allow the entrance of the largest diameter electrode used, permits neither the operator's fingers nor the electrode carrier to come in contact with the rotating bit.

Electrode Feeding Assembly

The slide trough (*ST*, Figure 1) for carrying the electrode, the guide trough (*GT*, Figure 1) fastened to a vertical plate, and a slotted metal block (*BL*, Figure 1) make up the electrode feeding

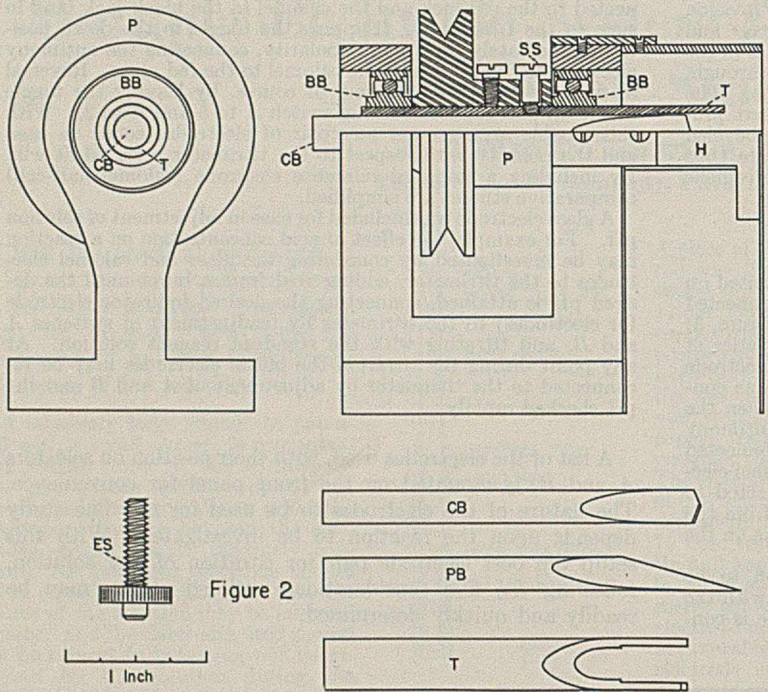

Figure 2

assembly. The sliding trough has the end away from the lathe head closed by a metal block. By means of knurled screws (*KS*, Figure 1) the vertical plate of the guide trough is clamped against an inner wall of the slotted block in such a manner that the line formed by the angle of the trough lies parallel and directly below an extension of the shaping bit axis. This forms a rigid guide for the slide trough. The contacting surfaces of the two troughs are machined true to prevent rocking or side play.

The flat plate holding the slotted block is fastened to the main base plate at each corner by steel screws. The screw holes in the upper plate are slotted at right angles to the shaping bit axis to allow sufficient lateral alignment of the guide trough. This lateral adjustment should be required only when the lathe is first assembled.

The vertical adjustment of the guide trough, necessary whenever the diameter of the electrode material is changed, is made by movement of the steel elevator screws (*ES*, Figures 1 and 2) located in each end of the vertical plate. Accidental alterations in screw settings are prevented by brass setscrews (*LS*, Figure 1). The length of the elevator screws determines the maximum and minimum electrode diameters which can be centered on the shaping bit axis.

The completed lathe assembly, a 0.05-horsepower motor which drives the shaping bit at about 1700 r. p. m., and a control switch are mounted on a wooden base.

A water aspirator supplies sufficient vacuum to collect the fine graphite dust. To prevent graphite from clogging the vacuum line or aspirator, a trap located on the wooden base near the lathe head is provided.

Shaping Tools

A variety of sizes and designs of shaping tools can be interchanged readily in the lathe described. Size and design are limited only by inside diameters of the pulley wheel and bearings, and dimensions of the cylindrical housing enclosing the bit end. Shaping bits and drills with diameters smaller than the maximum fixed by pulley and bearings can be accommodated by using sleeves or holders as adapters.

The shaping bit used in this laboratory was made according to the design and dimensions described by Myers and Brunstetter (*2*) for forming shallow, thin-walled craters in 0.31-inch graphite electrodes. In using this shaping bit in the shaping lathe, the blunt end of the inner drill (*CB*, Figure 2) is made to extend beyond the blunt end of the outer trimmer (*T*, Figure 2). By changing the length of the shaft which protrudes, craters of varying depths can be made.

Certain fixed depths of craters are obtained by using gages to set the position of the shaft. The gages are short pieces of 0.375-inch brass rod, each of which has a hole of appropriate depth drilled in one end. The holes permit passing the gages over the blunt end of the inner drill, but not over the end of the outer trimmer. The inner drill, released by turning setscrew *SS* (Figure 2) which extends through the pulley collar and outer trimmer, is seated into the outer trimmer as far as the specific gage permits.

To point the upper electrodes, a special bit (*PB*, Figure 2) is used which is interchanged with the inner drill of the shaping tool used for cupping electrodes. It is set into correct position by the use of a gage similar to ones just described.

The Chemistry Department of the University of Illinois has made further variations in shaping tools used with a copy of this lathe. For spectrochemical work done there, a facing tool and two small-diameter drills are required. Types of electrodes produced are described in an account of the spectrochemical technique used by Keirs and Englis (*1*).

Operation

For the shaping operation, the electrode is placed in the carrier with one end extending about 0.75 inch beyond the end of the sliding trough. The other electrode end lies against the closed end of the trough. While the electrode is being held down firmly in the trough by manual pressure, the carrier is moved slowly into the shaping bit by means of the knurled knob. The slide is drawn directly back to remove the shaped electrode from the cylindrical housing. Electrodes of shorter length can be accommodated by using spacers placed between the electrode and the closed end of the trough. Electrode material cut into appropriate lengths is suitable for this purpose.

Frequent rim breakage of the cupped electrodes during the shaping operation can be traced to several possible causes, such as the guide trough not in proper alignment, shaping bits which are not machined true, dull cutting edges, and low bit speeds. According to Myers and Brunstetter, bit speeds below 1300 r. p. m. cause excessive breakage.

The principal features of the lathe are the speed, accuracy, and convenience with which electrodes may be shaped. Eight or twelve cupped electrodes may be prepared per minute. Speed has been increased by omitting the operations of clamping and unclamping electrodes in a chuck or other similar device.

Accidental contamination of cutting surfaces of the shaping tools by dust or indiscriminate handling is prevented by the cylindrical housing. It is possible, therefore, to keep the shaping lathe on the bench where samples for spectrochemical analysis are prepared. Since the tool is not adapted to other sundry uses, contamination from miscellaneous usage is avoided.

With the lathe immediately accessible, and because its manipulation is not difficult, there is no necessity for preparing a large number of electrodes at one time and storing them for future use. The danger of rim breakage or contamination which often accompanies storage is eliminated by shaping only enough electrodes for immediate use.

Literature Cited

(1) Keirs, R. J., and Englis, D. T., Ind. Eng. Chem., Anal. Ed., **12**, 275–6 (1940).
(2) Myers, A. T., and Brunstetter, B. C., *Ibid.*, **11**, 218–19 (1939).

The laboratory is a cooperative organization participated in by the Bureaus of Agricultural Chemistry and Engineering and Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

An Apparatus for High-Speed Stirring

Effect of Flask Design and Some Other Factors on Stirring

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STIRRING is one of the most common practices in the laboratory and is indispensable for many reactions. Its benefits increase (*1*, *2*, *8*) as the velocity increases: Some reactions indeed occur to an appreciable extent only when the velocity becomes very great (*4*, *5*). In spite of the manifold uses to which stirring has long been put and the obvious advantages of high speed and efficiency, there has been only one apparatus (*4*) designed for operations at 10,000 r. p. m., of such construction as to be unsuitable for everyday laboratory use, and little, if any, serious study has been devoted to factors such as flask shape, stirrer design, etc., requisite for maximum effectiveness. Possibly the complexity of a subject in which an unusually large number of variables exists has deterred many would-be investigators, but the likelihood of greatly improving the yields for many known reactions and of discovering new reactions warrants a real effort to acquire knowledge of ideal conditions in an old art.

This paper gives directions for constructing a laboratory stirring apparatus which can operate at speeds near 11,000 r. p. m., yet is so simple that it can be mounted on an ordinary ring stand. Results of some studies on the type of flask suitable with stirrers of the propeller type at relatively high speeds are recorded. A simple method for comparing relative efficiencies of flasks, stirrers, and other factors has been developed. It is shown conclusively that a change in flask design has a direct bearing on efficiency of stirring and that the best flask is one from which swirling, obstructions, and pockets are largely eliminated.

High-Speed Stirring Apparatus

The apparatus consists of a motor mounted with its shaft in a vertical position, a stirrer of the propeller type supported in ball-bearing assemblies, and a flask. In all the experiments reported in this paper, a 0.04-horsepower series-wound ball-bearing motor (G. E.) with rated speed at 10,000 r. p. m. was used. It is bolted to a 0.94-cm. (0.375-inch) steel block into the center of which a 1.25-cm. (0.5-inch) steel rod is screwed, so that the motor is supported from an ordinary clamp fastener. This motor is satisfactory for many ordinary uses but lacks power to stir some mixtures at the highest speeds.

The equipment has since been supplemented by addition of a 0.25-horsepower series-wound ball-bearing motor also with a rated speed of 10,000 r. p. m., and mounted similarly on a 1.25-cm. (0.5-inch) steel block but supported by two instead of one rod and clamp device (Figure 1). The total weight of the large motor, block, and rods is about 3.7 kg. (10 pounds). The last unit is recommended for general use, since it is sufficiently powerful to stir at high speeds nearly all mixtures met in laboratory practice.

The propeller shaft is a 0.6-cm. (0.25-inch) stainless (18-8 alloy) steel rod 37.5 cm. (15 inches) long, supported by two short sections of pressure tubing (*3*) in two ball-bearing assemblies (about 2.2 cm., 0.875 inch, in outside diameter) which are placed about 15 cm. (6 inches) apart. The end-to-end contact between propeller shaft and motor shaft is closed by a short length of pressure tubing which is slipped over each end and held by a couple of turns of wire. Perfect alignment of motor and propeller shaft is not required in this arrangement.

A holder for the ball-bearing assemblies is made from two 17.5-cm. (7-inch) lengths of angle iron, the larger one 3.75 cm. (1.5 inches), and the smaller one 2.5 cm. (1 inch), held together tightly (Figure 1) by four machine bolts passed through both pieces. A little milling was necessary on the smaller angle iron in order to make it fit tightly against the ball-bearing assembly. Two sections of 1.25-cm. (0.5-inch) iron rod are tapped into the larger angle iron to support the holder in two clamp fasteners.

The propeller is made from a 5-cm. (2-inch) square piece of stainless sheet steel, No. 18 gage. A 0.3-cm. (0.125-inch) hole is first drilled in the center. The 0.6-cm. (0.25-inch) shaft is then turned down to 0.3-cm. (0.125-inch) diameter for a distance of 0.3 cm. (0.125 inch) at one end. The rod is next fitted into the hole and the two are riveted together by a few good blows with a hammer while the rod is held upright in a vise. This attachment is firm enough to permit mounting the shaft in a lathe and cutting the head to a diameter (slightly less than 2.5 cm., 1 inch) which will just pass through the neck of the flask. The disk is then slotted radially as many times as desired with a hacksaw and the segments are twisted at an angle of 45° to the shaft.

A completed assembly is shown in Figure 1. The apparatus runs smoothly and without appreciable vibration. The base of the ring stand can be anchored to the desk with screws or C-clamps, but this precaution is usually unnecessary. The noise is not unduly great, considering the high speeds involved.

The apparatus is operated with a variable transformer of 5-ampere capacity in series with the motor. The revolution rate is measured by a stroboscope (Strobotac) whose light is fixed on a marked metal disk attached to the shaft.

The small motor becomes very hot, particularly on long runs, but a blast of air directed into an opening on the underside cools it effectively. A cotton filter on the air line is usually required to remove grease.

At speeds of 10,000 r. p. m. some liquid may be forced out through the glass bearing unless it is fitted very well. In later work the authors were greatly indebted to Mr. Davidson for his suggestion of a very effective but simple rubber seal. A section of rubber tubing, 0.6 cm. (0.25 inch) in outside diameter by 0.94 cm. (0.375 inch) long, is pushed over the lower end of the glass bearing until the overhanging end of the rubber rests lightly on the propeller shaft. In this way the escaping liquid presses against the rubber and seals it more tightly. Another solution of this problem is to sink the neck far enough in the top of the flask to

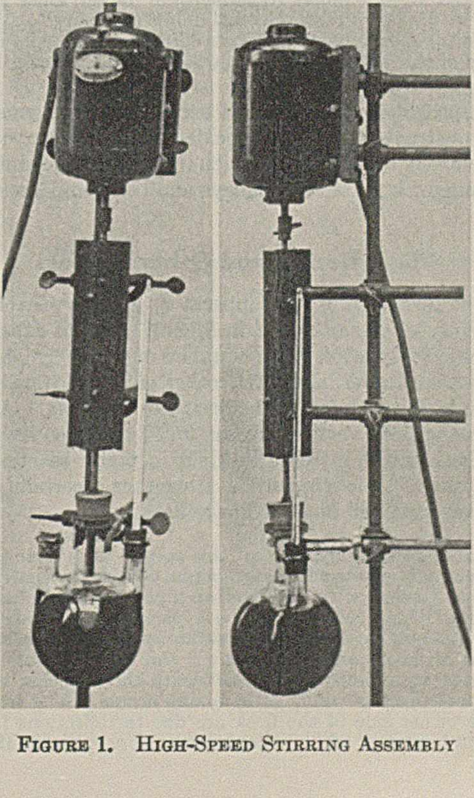

FIGURE 1. HIGH-SPEED STIRRING ASSEMBLY

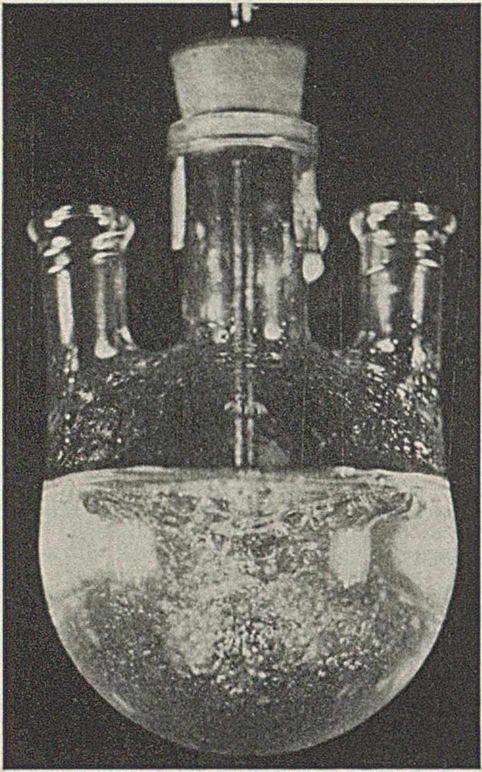

FIGURE 2. AIR AND WATER MIXTURE STIRRED IN ORDINARY FLASK

make a ring seal that directs the liquid downward. This method is very satisfactory, although the effectiveness of the flask as a vehicle for stirring appears to be reduced considerably.

Metal instead of glass propellers are used because the latter are considered dangerous at high speeds. There have been several instances in this laboratory, however, when glass has been used at 5000 r. p. m. and even higher. The glass stirrer was usually constructed from 0.6-cm. (0.25-inch) or larger glass rod. In general, its use is not recommended unless necessary to avoid corrosion and then only with adequate safeguards to avoid injury if a section of the glass breaks and goes through the flask.

The apparatus as a whole is exceedingly convenient and easily constructed. It is a decided simplification over the one previously described (*4*) which included a substantial iron pipe framework, numerous pulleys and belts, and a special location.

Flask Design and Other Factors

The performance of this apparatus, using a stirrer of the propeller type, was observed in several series of experiments in which the type of flask, number of propeller segments, position of propeller, and a few other variables were studied. Major interest centered in the design of the flask. A special flask having deep vertical creases (*6*, *7*) has been responsible for a considerable increase in yield in many reactions and, in one case (*7*), for eliminating altogether a certain product which was obtained in an ordinary flask.

The comparative efficiency of this special flask over the common one in mixing air and water can be observed visually in Figures 2 and 3, taken with an Edgerton high-speed flash lamp, with exposure of $^1/_{30,000}$ second. In both pictures, the propeller was moving at 11,000 r. p. m. All conditions were identical save for the type of flask used. In Figure 2 the characteristic swirling and vortex are plainly visible. Beneath the propeller is a relatively quiet place in which little mixing occurs. The two bright spots on either side of the flask are due to reflections from the photographic lamp. The little ring on the propeller shaft above the liquid surface is composed of drops of liquid which have fallen on or climbed up the shaft. Figure 3 shows the effect in the creased flask. Uniform mixing is secured. The positions of the creases are shown by the reflections as bright lines of the edges. The circular spot a little below the neck is the roughened place for pencil marking present on all commercial flasks.

In addition to this visual evidence, it was found that the oxidation of toluene by permanganate at 10,750 r. p. m. for 30 minutes in the ordinary flask was so slight as to produce no temperature rise over the 1.6° C. due to mechanical agitation. With a creased flask other factors being constant, a total temperature rise of 12.3° was noted, of which 7° was the result of chemical heat.

The unusual successes which have attended use of this creased flask warranted study of the effect of additional variations from this type. The four varieties considered in this study are labeled as:

O An ordinary 3-necked flask with four vertical creases
S Same as *O* but with powdered glass sintered to the bottom in order to act as an abrasive
I Same as *O* but with the bottom pushed inward about 2.5 cm. (1 inch) in the form of an inverted funnel which is about 4.4 cm. (1.75 inches) in diameter at the bottom
P Same as *O* but with the bottom pushed outward in the conventional pear shape

The *O*, *I*, and *P* flasks are pictured in Figure 4. All were made from commercial 500-ml. 3-necked Pyrex flasks. Four vertical creases were made in each to a depth of about 2.5 cm. (1 inch) at the deepest point. Save for the four distinctions made above, construction of each was as nearly identical as could be accomplished by a competent glass blower. A large Thiele tube was also used as a flask in a few experiments.

Measurement of Efficiency

Efficiency was judged on the basis of the temperature rise, starting from room temperature, with the vessel shielded by

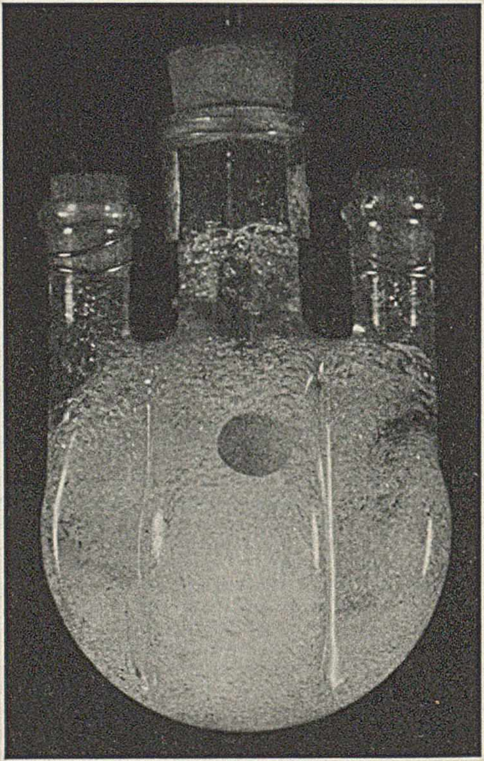

FIGURE 3. AIR AND WATER MIXTURE STIRRED IN CREASED FLASK

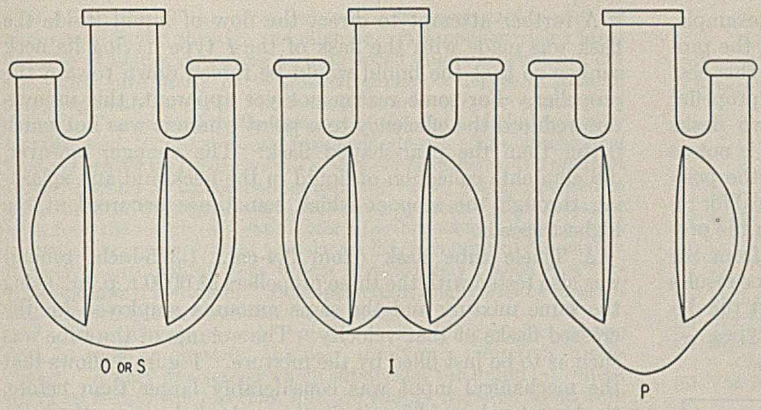

Figure 4. Types of Flasks Used in Tests

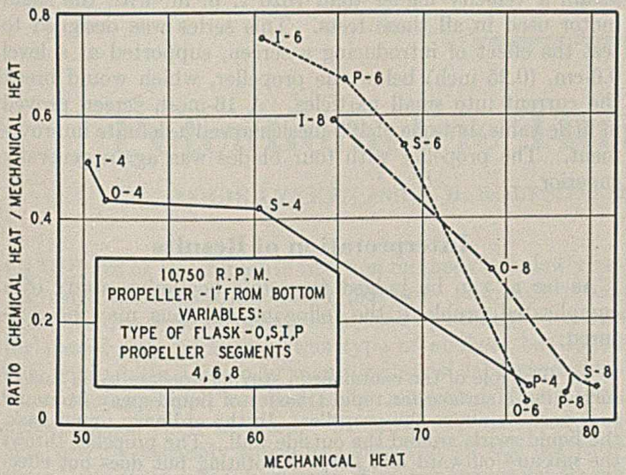

Figure 5. Effect of Varying Flasks and Stirrers at 10,750 R. P. M. as Tested by Evolution of Heat in Oxidation of Toluene

an insulated can. The reaction was the permanganate oxidation of toluene (at 10,750 r. p. m.) or xylene (at 6000 r. p. m.) over a 30-minute period. Part of the total temperature rise is due to the mechanical effect of stirring, so that an independent experiment, identical save for the absence of permanganate, was necessary. The respective areas on a time-temperature graph were then estimated. Numerical values for chemical and mechanical heats used in all graphs in this paper are merely these areas which are proportional to the true heat units. The total temperature increase was as much as 27° C. in the studies at 10,750 r. p. m.

This method has the great advantage of rapidity, so that a large number of observations can be made of many factors. Interpretation of data, however, is subject to the criticism that production of mechanical heat will automatically increase the total chemical heat according to the general expectation that a chemical reaction is doubled for every 10° temperature increment. Fortunately any such effect is negligible compared with the greater influence which the flask exerts on the efficiency of agitation.

Effect of Variables

Figure 5 pictures the ratio of chemical to mechanical heat plotted against mechanical heat for a study of the oxidation of 25 ml. of toluene by 2 grams of potassium permanganate in 300 ml. of water at 10,750 r. p. m.

The propeller was, in all cases, placed 2.5 cm. (1 inch) above the bottom of the flask. For the *I* flask, the bottom was taken to be the flat top of the conical indentation. The positions on the graph marked *I*-4, *S*-6, *P*-8, etc., refer to the test made on the *I* flask using the propeller with four segments, that in the *S* flask with the propeller having six segments, and that in the *P* flask with a propeller having eight sections. Lines have been drawn between points representing different flasks in which comparable conditions were present—for example, *O*-4, *S*-4, *I*-4, and *P*-4 are connected.

Points to the upper left represent high efficiency, a high chemical effect with a minimum of mechanical energy expended; while points to the lower right represent low efficiency, small chemical heat in spite of a relatively large mechanical effort. The results show clearly that in every series the *I* flask was superior. With one exception the pear-shape flask, *P*, was the most ineffective of the lot.

Lines could also have been drawn between points representing different propellers for otherwise comparable conditions—e. g., *I*-4, *I*-6, and *I*-8. In such a comparison the eight-bladed propeller gave poor results, although in every series but one it produced the largest mechanical heat. The performances of the four- and six-bladed stirrers were in general very good. If a line be drawn diagonally towards the northeast, so as to separate the six best from the six worst conditions, the *I* flask and the four-bladed propeller are represented three times each among the better group. These results are contrasted with the occurrence of the *P* flask (twice) and the 8-bladed propeller (three times) in the poorer half. The single occurrence of the eight-bladed propeller among the better group can be attributed to its being used with the best flask; likewise the single appearance of the four-bladed propeller with the poorer group can be explained on the ground that it was used with the poorest (*P*) flask. The results are in general striking, particularly in view of the later discovery (Figure 6) that the position of the stirrer at 2.5 cm. (1 inch) from the bottom was far from ideal.

Figure 7 shows a parallel study at 6000 r. p. m. of the oxidation of 25 ml. of xylene by 16 grams of potassium permanganate with 4 grams of sodium hydroxide in 300 ml. of water. The position of the propeller was again 2.5 cm. (1 inch) from the bottom. This figure exhibits the clear superiority of the

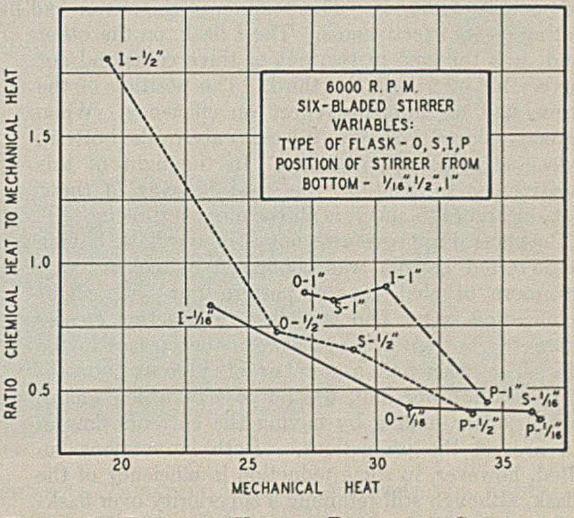

Figure 6. Effect of Varying Position of Stirrer as Shown by Evolution of Heat in Oxidation of Xylene

four-bladed propeller with every flask tried—(for example, compare *I*-4, *I*-6, and *I*-8 or *S*-4, *S*-6, and *S*-8) and the pronounced difference between the *I* and *P* flasks with this best (No. 4) stirrer. The series with the six-bladed propeller shows also a marked difference between these two flasks (*I*-6 and *P*-6) but the superiority of *I* over *O* and *S* is not so evident. It should be remembered, however, that the position of the stirrer in this set of experiments is not ideal for revealing any superior qualities present. Indeed, when the propeller is moved to a position 1.25 cm. (0.5 inch) from the bottom (Figure 6) other conditions being the same, the results with the six-bladed propeller confirm in every respect the decided superiority of the *I* flask over the three other types.

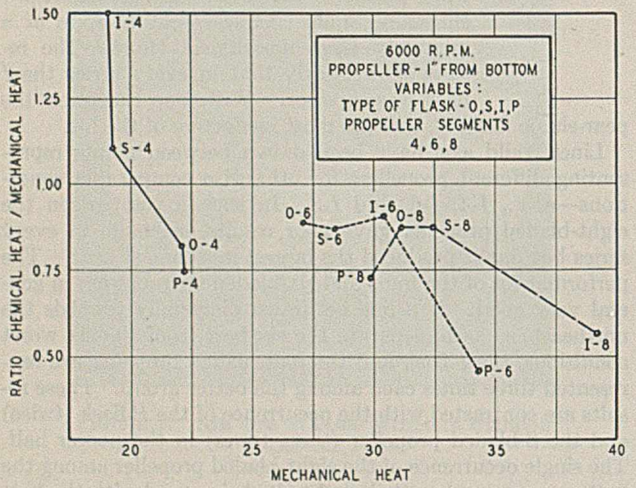

Figure 7. Effect of Varying Flasks and Stirrers at 6000 R. P. M. as Shown by Evolution of Heat in Oxidation of Xylene

The erratic results (Figure 7) with the stirrer having eight segments are attributed both to its general ineffectiveness and unfavorable position. The mechanical heat generated by this stirrer, however, is 50 to 100 per cent larger than that realized by the four-bladed one.

Figure 6 depicts the effect of varying the position of the propeller with six segments at 6000 r. p. m. The same mixture was used as in the preceding test at this velocity. The results are decisive. The pear-shaped flask was, in all cases, the poorest of the lot. The position of the stirrer had little bearing on its effectiveness. The *I* flask, on the other hand, was the best in two out of three cases and not appreciably inferior in the third. The position of the stirrer had an immense effect on efficiency. When correctly placed 1.25 cm. (0.5 inch) above the bottom, a decided superiority resulted. In the light of this sensitiveness to position, the good showing of the *I* flask, in Figures 5 and 7, is all the more surprising.

The general improvement noted in the flask having the inverted bottom was confirmed by constructing two more of that general pattern but with slight modification. One had two deep intersecting creases across the bottom spaced between the creases in the side. The other had a number of Vigreux indentations in the lower half, the purpose of which was to promote more mixing by having the currents flow in and around the projections. Both innovations resulted, however, in some reduction in efficiency of the *I* flask, although still retaining a superiority over flasks *O*, *S*, and *P*. Even minor obstructions such as Vigreux points interfered with the proper functioning of the flask.

A further attempt to direct the flow of liquid inside the flask was made with the flask of the *I* type having its neck sunken so that the liquid would be forced down toward the propeller. For some reason not yet apparent, this innovation reduced the efficiency to a point where it was not much better than the pear-shaped flask. The change, however, did eliminate collection of liquid in the neck and any splashing through the stopper which sometimes occurred at the highest speeds.

A Thiele tube flask (from 3.4-cm., 1.375-inch, tubing) was also tested with the three propellers at 6000 r. p. m., using the same mixture and the same amounts employed for the creased flasks at that velocity. The volume of the tube was such as to be just filled by the mixture. Figure 8 shows that the mechanical input was considerably larger than before, the lowest value of 36 units in this series being near the highest value of 39 in Figure 7. So great was the power required to stir the mixture in this apparatus that it was impossible to attain a velocity higher than 7620 r. p. m. with the small motor used in all these tests. This series was designed to test the effect of introducing a screen, supported at a level 0.6-cm. (0.25 inch) below the propeller, which would break the current into small particles. A 16-mesh screen proved of little value, but one of 100-mesh showed a definite improvement. The propeller with four blades was again generally superior.

Interpretation of Results

As far as can be judged from this beginning study of a complicated problem, the following opinions may be ventured:

A. The role of the container in stirring appears to be that of furnishing a surface for rapid transfer of liquid away from and to a position above the propeller. In the ordinary round flask, the liquid swirls around the outside wall. The propeller throws the mixture outward and keeps it rotating but does not effectively mix the components. The creased flask directs the liquid flow upward, from whence it falls again upon the stirrer to be hurled once more in fast-moving currents from the propeller.

The additional superiority of a creased flask with an indented bottom is due to the further facilitation of movement of liquid within the flask. The effect is similar to that of streamlining. The pocket immediately below the propeller where liquid can collect and escape mixing is eliminated.

The poor results with the pear-shaped flask come from interference of the movement of the liquid. The propeller churns the liquid at the bottom, does a great deal of mechanical work in trying to force the liquid around an unnatural and difficult path, and is unable to perform its proper function of mixing because the flow of liquid is impeded.

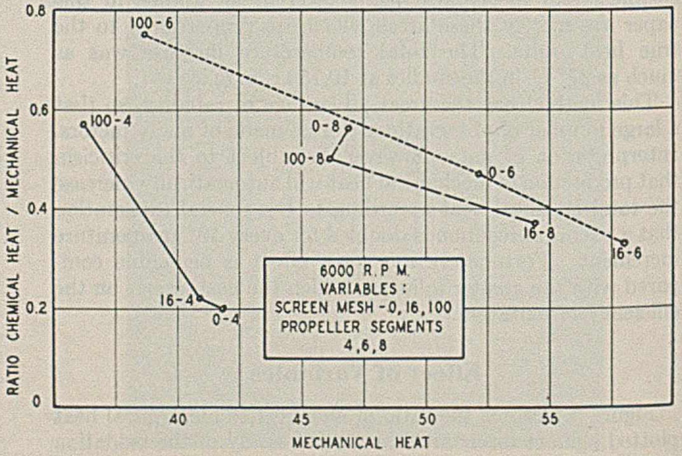

Figure 8. Effect of Varying Stirrers and Screens in a Thiele Tube as Measured by Heat Evolution in Oxidation of Xylene

B. The role of the propeller can be to generate fast-moving currents of liquid through the mixture. A propeller with a large number of blades operating at high speed might conceivably cut the liquid into many parts and accomplish a degree of mixing. Each segment, however, needs enough surface to serve as a good driver. The general ineffectiveness of the eight-bladed propeller at 6000 and 10,750 r. p. m. was pronounced. The mechanical heat generated by its use was in nearly every instance the greatest (sometimes by 50 to 100 per cent) of the three, yet it appeared to whirl around in a generally ineffective manner. The propeller with four blades gives a satisfactory performance. Even a good propeller, however, cannot translate a large amount of the energy it receives into useful work unless it is properly placed in a correctly designed container. Such principles might well be of practical importance in large-scale apparatus.

C. Impediments, whether points on the inner surface of the flask or walls to constrict the flow, result in a reduction in efficiency. A very fine screen which subdivides the liquid into small particles assists the reaction, but the energy required to operate a stirring apparatus of that type is very much greater and the ratio of chemical to mechanical heat is less than in a properly designed flask.

Acknowledgment

The authors are indebted to I. Amdur for very helpful suggestions in handling the data.

Literature Cited

(1) Brunner, E. J., *Z. physik. Chem.*, 47, 56 (1904).
(2) Friend, J. A. N., and Dennett, J. H., *J. Chem. Soc.*, 121, 41 (1922).
(3) Hershberg, E. B., Ind. Eng. Chem., Anal. Ed., 11, 170 (1939).
(4) Huber, F. C., and Reid, E. E., Ind. Eng. Chem., 18, 535 (1926).
(5) Milligan, C. H., and Reid, E. E., *Ibid.*, 15, 1048 (1923).
(6) Morton, A. A., Ind. Eng. Chem., Anal. Ed., 11, 170 (1939).
(7) Morton, A. A., Olson, A. R., and Blattenberger, J. W., *J. Am. Chem. Soc.*, 63, 314 (1941).
(8) Van Name, R. G., and Edgar, G., *Z. physik. Chem.*, 73, 97 (1910).

Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology, No. 248.

Potentiometric Titration Stand Assembly

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THE use of electrometric titration methods has slowly become a common laboratory practice. Although potentiometric titrations have long been used by academic workers for special determinations, this type of analysis has found only limited application in many industrial laboratories because the apparatus has had to be assembled largely from miscellaneous parts at hand. Generally, this resulted in a cumbersome assembly which was inconvenient and unwieldy to use in routine determinations. Also, experience has shown that the use of loosely assembled equipment requires that a considerable part of the operator's time be spent in maintenance.

In designing the assembly described here, every effort was made to produce a titration stand which could be used for routine as well as special determinations. It was recognized that a satisfactory assembly must be as easy to use as the ordinary apparatus required for indicator titrations. The buret clamp, stirring motor, beaker cover, and electrode support have been semipermanently attached to the vertical supporting rod. The table supporting the titration beaker has been designed to be the only easily movable part on the stand. The buret may be readily removed from its support and the electrodes may be conveniently removed and replaced.

During two years of continued use at Emeryville, five such titration stands have been found satisfactory and convenient for routine titrations. They are durable, are easy to maintain, are simple to operate, have a neat appearance and, although unitized into compact units, are sufficiently flexible for most electrometric titrations.

Apparatus

A photograph of one form of the assembly is given in Figure 1 and some details of construction are shown in Figures 2 to 4. The customary "universal" clamps have been replaced by metal connector-blocks containing holes of appropriate size and headless Bristo setscrews. No attempt has been made to use the same connector-block for all purposes. A modified thermometer clamp replaces the customary buret holder or clamp. A thick piece of polished Bakelite is used as a combination electrode support, beaker cover, and buret-tip support. The titration vessel, which is a 250-ml. tall-form electrolytic-type beaker, is supported on a Bakelite table attached to a friction clamp. The glass, propeller-type stirrer is supported and operated by a small variable-speed motor; the Eastern Engineering Company variable-speed stirrer, Model 1, has proved satisfactory. The motor and rheostat are conveniently mounted on the same support, as shown in Figure 3 (left).

Pencil- or stick-type electrodes are used throughout; whenever a salt bridge is used, contact is made with the titration medium through a ground-glass joint. The durable, permanent Beckman glass and calomel electrodes, manufactured by the National Technical Laboratories, have been found ideally suited for use in the titration assembly. For convenience, metallic electrodes—i. e., silver, platinum, and tungsten—have been mounted, as shown in Figure 2 (left), so as to be easily interchanged with the Beckman electrodes.

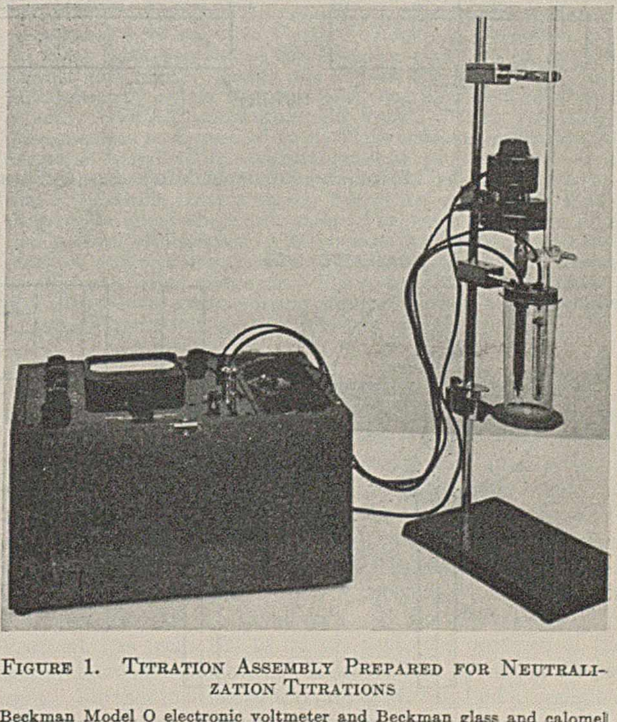

Figure 1. Titration Assembly Prepared for Neutralization Titrations

Beckman Model O electronic voltmeter and Beckman glass and calomel electrodes

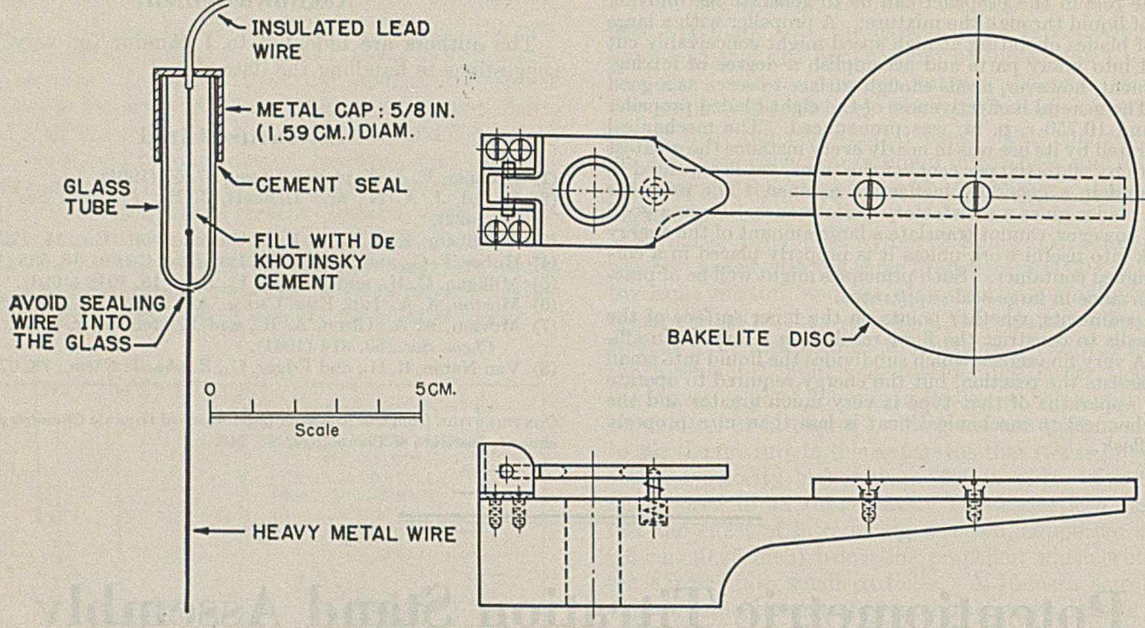

FIGURE 2. METAL ELECTRODE (*left*) AND MOVABLE BEAKER SUPPORT (*right*)

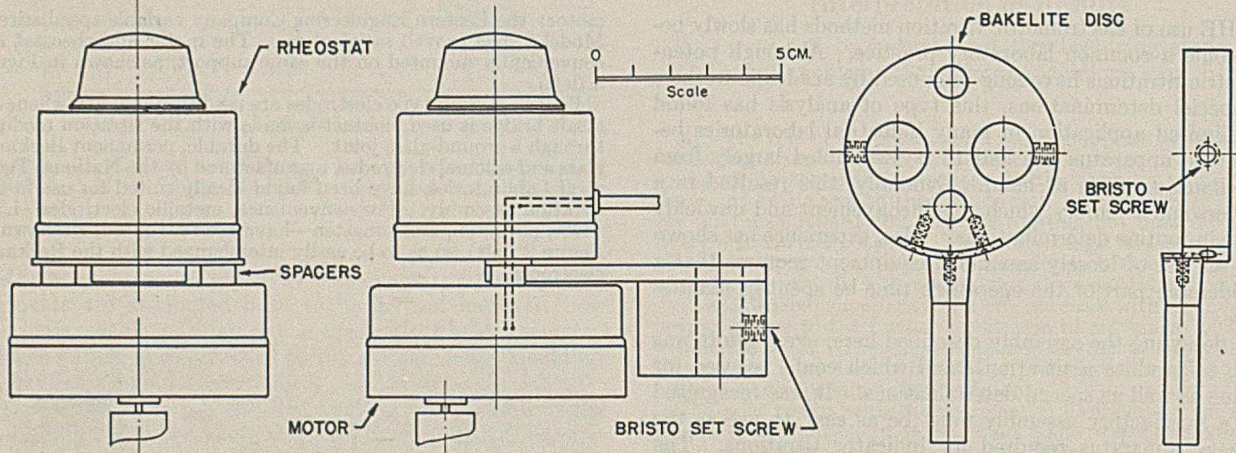

FIGURE 3. MOTOR AND RHEOSTAT MOUNTING (*left*) AND COMBINED ELECTRODE HOLDER AND BEAKER COVER (*right*)

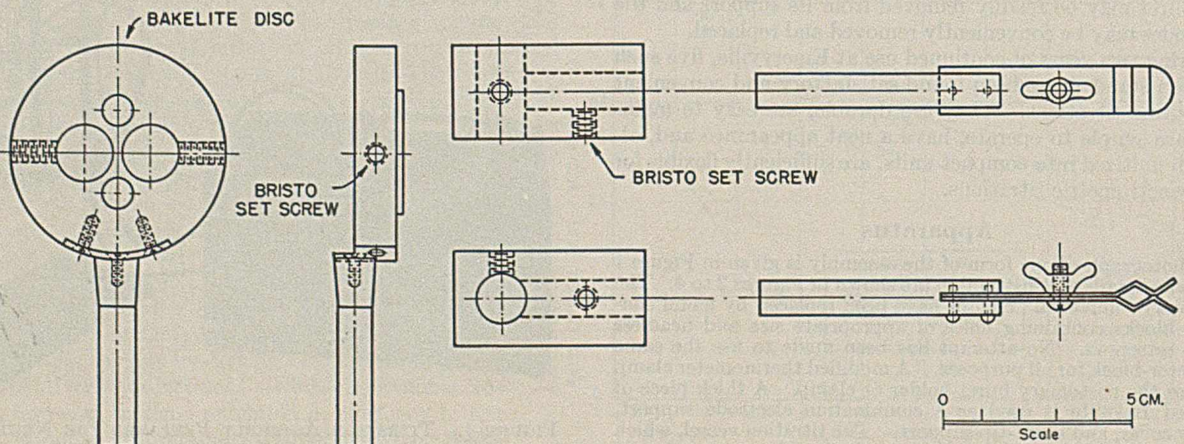

FIGURE 4. ELECTRODE SUPPORT DISK FOR SEMIMICROTITRATIONS (*left*) AND SUPPORT BLOCK AND BURET CLAMP (*right*)

The assembly is made on any 1.25-cm. (0.5-inch) ringstand rod. The various metal parts are made of brass and subsequently chromium-plated. This plating has proved satisfactory as a protection against attack by the laboratory fumes and affords a durable, neat finish.

The apparatus may be readily adapted to semimicrotitrations, of 5- to 10-ml. initial volume of solution, by changing the Bakelite electrode support disk and using a special titration cell in place of the tall-form beaker. The Bakelite disk of Figure 3 (right) is replaced by the one shown in Figure 4 (left), in which the holes are brought closer together. The modified disk has a small raised portion, 33 mm. in diameter, on the underside. The special titration cell is made from Pyrex glass tubing 34 mm. in inside diameter; it is sealed off flat at one end and is cut to give an internal length equal to 11.2 cm. The blades on the glass propeller stirrer are ground down to be 12 to 13 mm. in diameter. The regular Beckman electrodes and stirrer are adjusted so that they almost touch the bottom of the special cell when the latter is in position on the stand. The buret is made with a 15-cm. (6-inch) tip that has a 10- to 15-mm. offset about 12 cm. from the end tip.

Magnetic Stirrer for Use in the Cup Type of Moisture-Transfusion Apparatus

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THE cup type of moisture-transfusion apparatus is the chief means used for determining the passage of moisture under a relative humidity gradient through paper, impregnated paper, film material such as cellophane, and thin sections of wood.

Water, an aqueous solution of sulfuric acid, or a saturated salt solution in equilibrium with a specific relative humidity is poured into the bottom of a cup. The membrane material to be studied is sealed across the top of the cup. The cup is then weighed and the loss or gain in weight with time determined when the cup is exposed to a lower or higher relative humidity than that set up within the cup.

This simple technique is subject to one serious source of error, especially for relatively permeable membranes—namely, vapor is not supplied to the lower surface of the membrane as rapidly as it can pass through the membrane, and moisture is not removed from the upper surface of the membrane as rapidly as it passes through the membrane. Part of the relative humidity gradient thus occurs through the air on each side of the membrane. This situation can be readily corrected on the outer surface of the membrane, when humidity rooms or chambers are used, by blowing air across the surface with an electric fan, or rapidly passing air over the surface from a humidification train.

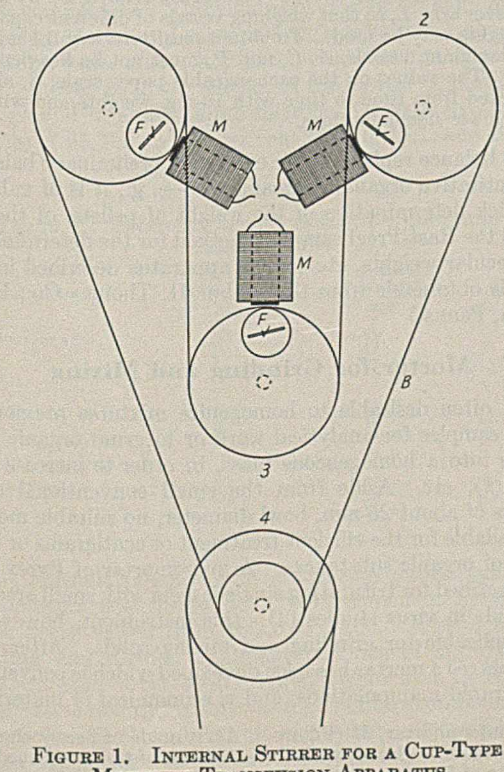
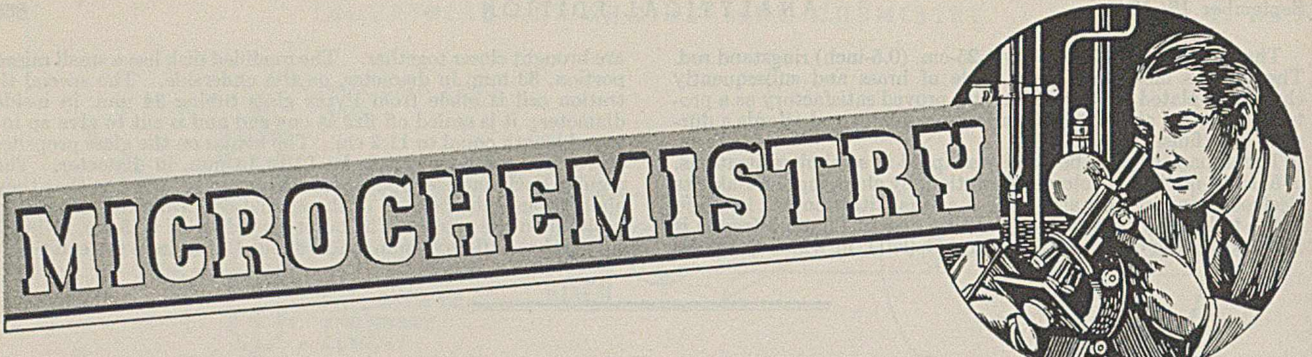


FIGURE 1. INTERNAL STIRRER FOR A CUP-TYPE MOISTURE TRANSFUSION APPARATUS

The device shown in Figure 1 was designed to correct this same difficulty within the cup. It does not interfere with making a vapor-tight seal of the membrane. It permits easy removal of the cups for weighing and does not increase the weight of the cups sufficiently to decrease the accuracy of weighing. It consists of four horizontally mounted pulleys. Pulleys 1, 2, and 3 serve as the supports for three moisture-transfusion cups, in this case glass crystallizing dishes, which are slightly smaller in diameter than the pulleys. The cups may be clipped to the pulleys so as to be readily removable. The three pulleys are rotated by a continuous belt, *B*, by pulley 4.

Rings made by bending 18-gage sheet-iron strips 1 cm. wide into circular cylinders 3 cm. in diameter were completely covered with tinfoil on the circular surfaces as well as on the ends to make sealed drums, *F*. Small tinfoil vanes, *V*, were sealed horizontally on the top face of the drums. These drums, which served as the stirrers, weighed only 5 grams each. They were floated on the liquid in the crystallizing dishes, after which the membranes were sealed to the top. Three electromagnet coils, *M*, taken from old electric doorbells, were mounted so that the magnet surface just cleared the side of the crystallizing dish. These electromagnets were operated from the secondary of an ordinary doorbell transformer (18 volts). When the pulleys were operated at a speed of about 60 revolutions per minute, the drums, *F*, were held in a position near the electromagnets as the pulleys and crystallizing dishes rotated. Because of the friction of the drum stirrers on the side of the crystallizing dishes, they rotate about their own axes. The vane, *V*, on the drum thus rotates with respect to the base on which the apparatus is mounted and also with respect to the crystallizing dish, causing an efficient stirring of the air. The rotation of the crystallizing dish with respect to the stirring drum, *F*, also adequately caused a continual formation of a new liquid surface.

The apparatus was set up in various relative humidity rooms for making the measurements. An electric fan was directed across the membrane faces. Good check values were obtained when similar membranes were used on each of the crystallizing dishes with a liquid giving the same relative humidity inside each. When the stirring drum was left out of one of the crystallizing dishes, the rate of loss of moisture from that dish was materially less than from the other dishes. When four thicknesses of noncoated Cellophane No. 600 were used for the membrane and the relative humidity gradient was from 100 to 80 per cent, the presence of the stirrer increased the rate of moisture loss by about 70 per cent. Further increase of the rate of stirring had a negligible effect upon the rate of loss of moisture.



Systematic Qualitative Organic Microanalysis

Improved Apparatus for Micropreparative Work

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IT HAS been shown by the author (*1–3*) that the qualitative schemes for the identification of organic compounds developed by Mulliken (*9*) and Shriner and Fuson (*10*) operate with equal efficiency if small amounts of materials are available; systematic studies, however, were necessary in order to select the most suitable procedures for such a scheme of qualitative organic microanalysis. The first step to be taken in the process of identification is the purification of the organic compound to a degree commensurate with the stability, the amount of sample available, and the accuracies established for determination of the physical constants. The principal procedures of this preliminary step are again applied in the final step of the identification—i. e., the preparation of a characteristic derivative.

During the investigations on procedures for the purification of centigram and milligram amounts of organic substances (*2*) various kinds of apparatus have been developed or modified in order to obtain satisfactory results within a reasonably short time; three of these are described here in detail.

Improved Balance for Micropreparative Work

Standard as well as microchemical balances have been applied in the preparation of derivatives, estimation of yields, determination of solubility, semiquantitative elementary analysis (*1, 2*), etc. A small, sturdy, portable, and inexpensive instrument which permits rapid weighing of 1-mg. samples to within 0.1 mg. is needed for this work.

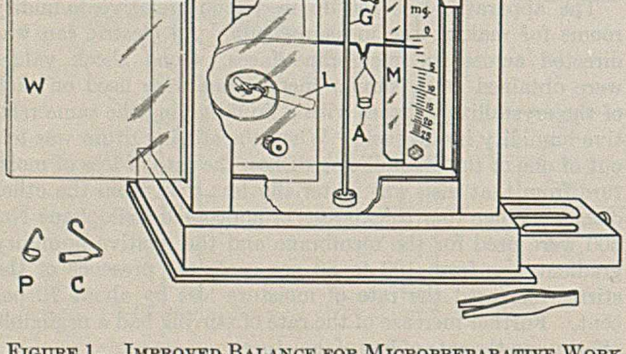

FIGURE 1. IMPROVED BALANCE FOR MICROPREPARATIVE WORK

The balance of Friedrich (*7*), a modified Emich-Salvioni balance (*6*), has been further improved. A wooden case 195 × 65 × 155 mm. (Figure 1) is mounted on a base, which contains a drawer for the weighing accessories, such as the forceps or the weighing vessels; the front window, *W*, is closed during the weighing in order to protect the spiral spring, *Sp*, from draughts. The mirror, *M*, beside the exchangeable paper scale, *S*, both of which are mounted on a glass plate, minimizes the error due to parallax when determining the position of the pointer. The aluminum-painted background facilitates the reading. Guide posts, *G*, keep *Sp* in place when the load is varied.

The weighing vessels vary in form according to the procedure in which they are used. Aluminum dish *A* serves for weighings in general preparative work. Platinum dish *P* is recommended for the ignition test and semiquantitative residue determinations (*1, 2*), and glass capillary *C* is suitable for transferring the weighed substance into sodium fusion tubes in the semiquantitative elementary analysis (*1, 2*).

Most weighings are made by difference; the spiral spring comes quickly to rest, and a single weighing is accomplished within a minute. The tension of spring *Sp* is adjusted by means of the lever arm, *L*, so that weighing vessels of different capacities and weights may be used. To obtain sensitivities of 0.1 mg. the empty weighing vessels, *A*, *C*, and *P*, must not be heavier than 80 mg. The values on the exchangeable paper scale, *S*, should be checked from time to time with 10-mg. weights and wires of known lower denominations.

This balance replaces more expensive preliminary balances in quantitative organic microanalysis—e. g., it is of value in the quick determination of the weight of pellets, of the solvent in the Rast-Pregl camphor method for the determination of molecular weights, etc. (The apparatus described in this paper is obtainable from the Arthur H. Thomas Co., Philadelphia, Penna.)

Mortar for Grinding and Mixing

It is often desirable to homogenize mixtures previous to taking samples for analytical work or to grind organic compounds into a homogeneous mass, in order to increase solubility (*2*), etc. Aside from the small conventional agate mortars of about 25-mm. bowl diameter, no suitable mortars are available for the efficient treatment of centigrams or milligrams of organic substances. A micromortar of Pyrex glass was described for triturating single insects with small amounts of liquids in virus studies (*4*); this instrument, however, is not applicable for grinding and mixing solids. After some attempts (*5*) a mortar has been developed which is convenient, allows rapid manipulations, and is economical of material.

The micromortar, *M* (Figure 2, *A*), is made of heavy chemical porcelain and is glazed, with the exception of the roughened outside base of 50-mm. diameter which assures a firm support on the table during grinding operations. The inside has the form of an inverted cone 15 mm. in length, the opening being 20 mm. wide, narrowing to 7 mm. To prevent loss of material the lip is eliminated.

The unglazed base of the pestle, *P*, is 6 mm. wide. The radius of curvature of the bottom part of the mortar, r_m (Figure 2, *B*), is designed to ensure close contact between the material and the acting surfaces of both mortar and pestle; a pestle with a base of a slightly smaller radius of curvature, r_p, than that of the mortar is used.

If freedom from small contaminations is of vital importance or hard substances are to be ground, as in mineral analysis, the recently introduced sillimanite (Mullite, Coors, U. S. A.) is recommended in preference to porcelain.

The efficiency of the micromortar was tested in two ways: Weighed amounts of substances of varying hardness were ground in the mortar to a fine powder for about 5 minutes. The powder was removed with a microspatula and weighed again on an ordinary balance. A few results are reported in Table I.

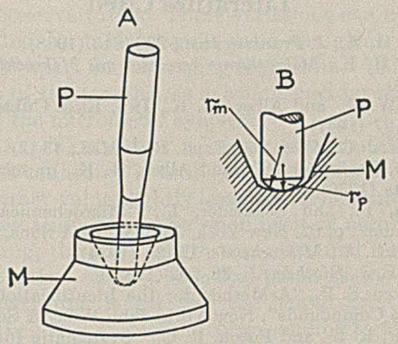

FIGURE 2. MICROMORTAR WITH PESTLE (*A*) AND RATIO OF CURVATURES OF PESTLE AND MORTAR (*B*)

Low recoveries of 30 and 50 per cent were observed on exceedingly soft, hygroscopic, and highly charged (finely powdered) compounds. The high recoveries of sea sand in Table I are characteristic of materials with a hardness above 6 in the Mohr scale, since they become contaminated with material removed from the surface of the mortar or pestle. Sea sand ground in a sillimanite micromortar as above gave recoveries of 95, 93, and 93 per cent of 25.0, 18.1, and 10.5 mg. used.

TABLE I. RECOVERY OF MATERIAL ON GRINDING IN MICROMORTAR

Substance	Taken (Original) *Mg.*	Recovered (Powdered) *Mg.*	Recovery %
Benzoic acid	50	44	88
	20	17	85
	10.0	6.4	64
	5.0	2.6	52
KH_2PO_4	50	42	84
	20	17	85
	10.0	8.0	80
	5.0	4.0	80
Sea sand	50	48	96
	30	28	93
	11.4	11.6	102

The efficient mixing of heterogeneous substances in the micromortar was tested on a two-component system, the ratios being varied from 100:1 to 1:100. After 3 minutes' grinding and mixing, 2 aliquot portions of approximately one third each of the total original weight were taken, and a quantitative determination was made of one compound, or of a characteristic element in this compound. Potassium dihydrogen phosphate and sodium oxalate were selected for the experiments in Table II, because they had given approximately identical recoveries in grinding experiments. The degree of uniformity of the final product was determined by analyzing each aliquot portion for phosphorus, using the colorimetric procedure of King (*8*).

TABLE II. EFFICIENCY OF MIXING TWO SOLID COMPOUNDS IN MICROMORTAR

Components of Mixture Weighed Out		Approximate Ratio	Deviation of P Found from P Calculated in Aliquot Portions	
KH_2PO_4	$Na_2C_2O_4$			
Mg.	*Mg.*		%	%
3.0	100	1:100	−2.8	−9.5
9.3	99	1:10	+0.7	+2.3
50.0	50.0	1:1	−0.4	+1.8
100	10.0	10:1	+0.7	−1.4
100	1.5	100:1	+0.3	−0.4

Appreciable errors were noticed only when very small amounts of the component to be analyzed were ground with large amounts of the admixed material, ratio 1 to 100. The results on the ratio 100 to 1 may be taken as an indication of the accuracy and precision of the phosphorus determination.

Combined Separatory and Sedimentation Funnel

Many procedures for separation, isolation, or purification of organic constituents involve extraction; a study of continuous extractors for solids has been reported recently (*3*). A special problem is the separation of a mixture of several liquids, in which the components are isolated by consecutive washings with several portions each of water, alkali, acid, and organic solvents. After extraction or washing a careful separation of the layers becomes a difficult task in an ordinary funnel, especially if a precipitate is formed during the process. The upper layer should not be "poured out" of the top, as this leads to unavoidable loss of material. The treatment of a solid compound in successive steps with different organic solvents—e. g., in the determination of solubility—is also difficult without a special separatory funnel.

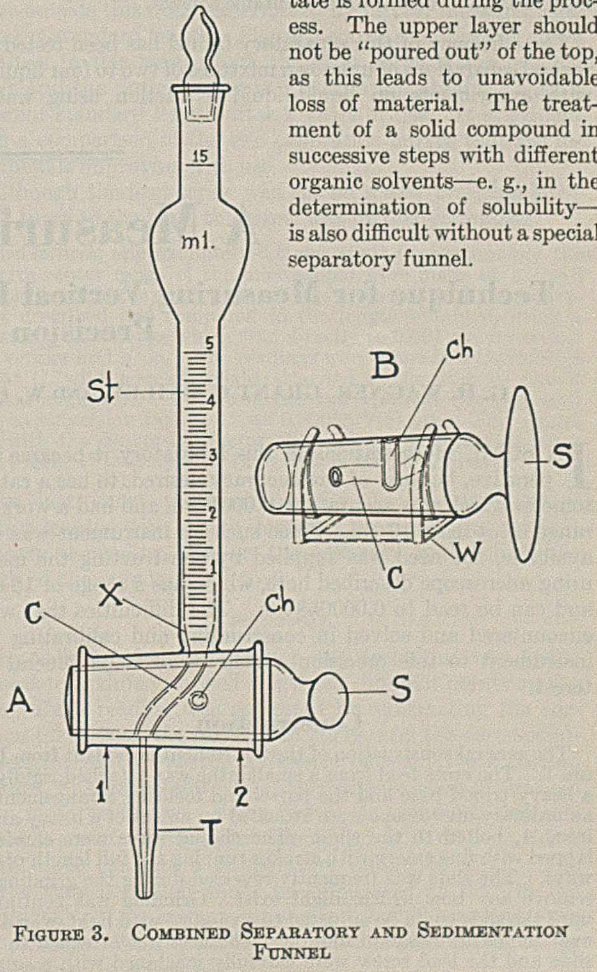

FIGURE 3. COMBINED SEPARATORY AND SEDIMENTATION FUNNEL

The combined separatory and sedimentation funnel, Figure 3, is a useful apparatus for the above-mentioned procedures. The dimensions are best chosen according to the problem; the ones given here are recommended for milligram and centigram amounts of solids, and milliliters or less of liquids. The calibration on the cylindrical stem, *St*, permits the estimation of used volumes and volume changes. *St* has an inner diameter of from 7 to 8 mm., and is graduated to 5 ml., each milliliter being subdivided into 0.1 ml.; it extends into a bulb of 10-ml. capacity, which is closed with a ground-glass stopper, the total capacity of 15 ml. being indicated by a mark on the upper neck. (Funnels have been used with stems graduated to 10 ml. and extending into a bulb giving a capacity of 25 ml.) The lower end of the stem is gradually reduced, at *X*, within a length of from 15 to 20 mm. to 3 to 4 mm. inner diameter, thus forming a smooth cone.

The hollow stopcock, *S*, with an average diameter of about 20 mm. is equipped with a bent capillary, *C*, 3 to 4 mm. in diameter, leading to the tip, *T*, 15 to 20 mm. long (Figure 3, *A*). With stopcock *S* (Figure 3, *B*) turned 90°, the opening of the stem coincides with that of the cylindrical sediment collector, *Ch*, 3 to 4 mm. in inner diameter and 10 to 12 mm. long, having a capacity of 70 to 150 cu. mm. The size of *S* may seem excessive for the small amounts of material handled, but this is necessary to prevent leakage, as in most cases no grease is used between positions 1 and 2 (Figure 3, *A*). Grease-collecting grooves in positions 1 and 2 were tried, but they merely complicated the apparatus.

The technique of manipulating this separatory funnel is simple. If the liquid with higher density is in the range of about 100 cu. mm., it is collected in the sediment collector, *Ch*, by settling; the stopcock is turned into position *A*, and the lighter liquid is removed through capillary *C* and tip *T* without disturbing the liquid in *Ch*. After turning back the stopcock into position *B*, the treatment is continued with a fresh portion of solvent. Finally, stopcock *S* is pulled out from the separatory funnel and placed in a small wire rack, *W* (Figure 3, *B*); the liquid is removed from the chamber by means of a fine capillary pipet.

The same procedure is applied for solid sediments, which are dried in the sediment collector, weighed, and removed with a microspatula or dissolved in a suitable solvent.

The efficiency of this separatory funnel has been tested on several separations of unknown mixtures of two to four liquids, with experiments on liquid-liquid extraction using water, ethyl alcohol, ethyl ether, amyl alcohol, petroleum ether, carbon tetrachloride, benzene, etc., with processes necessitating a salting-out with sodium chloride, magnesium sulfate, or potassium carbonate, and with percolation experiments on fibrous materials (drugs) packed in the stem, etc.

Emulsions which are difficult to break up usually collect in a thin layer on the interface of two immiscible liquids. After the lower layer has been carefully drained through the capillary, the emulsion in some instances settles out overnight in the sediment collector and can easily be removed.

Acknowledgment

A part of these investigations was carried out in the microchemical laboratory of the Biochemical Research Foundation of the Franklin Institute, Philadelphia, Penna. The author wishes to express his thanks to J. T. Bryant for his assistance in the experiments.

Literature Cited

(1) Alber, H. K., *J. Franklin Inst.*, 226, 813 (1938).
(2) Alber, H. K., *Mikrochemie vereinigt mit Mikrochimica Acta* (in press).
(3) Batt, W. G. and Alber, H. K., Ind. Eng. Chem., Anal. Ed., 13, 127 (1941).
(4) Bugher, J. C., *Proc. Soc. Exptl. Biol. Med.*, 43 (2), 422 (1940).
(5) Emich, F., Schally, E., and Alber, H. K., unpublished experiments (1930).
(6) Emich, F., and Schneider, F., "Microchemical Laboratory Manual", p. 62, New York, John Wiley & Sons, 1932.
(7) Friedrich, A., *Mikrochemie*, 15, 35 (1934).
(8) King, E. J., *Biochem. J.*, 26, 292 (1932).
(9) Mulliken, S. P., "A Method for the Identification of Pure Organic Compounds", New York, John Wiley & Sons, 1904.
(10) Shriner, R. L., and Fuson, R. C., "Systematic Identification of Organic Compounds", 2nd ed., New York, John Wiley & Sons 1940.

Presented before the Division of Microchemistry at the 99th Meeting of the American Chemical Society, Cincinnati, Ohio.

A Measuring Microscope

Technique for Measuring Vertical Distances up to Several Centimeters with a Precision of 0.00005 Cm.

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IN SOME investigations in this laboratory it became imperative, because of the accuracy desired, to use a cathetometer which was accurate to 0.0001 cm. and had a working range of at least 10 cm. Since such an instrument was not available, the need was supplied by constructing the measuring microscope described here, which has a range of 16 cm. and can be read to 0.000058 cm. The difficulties that were encountered and solved in constructing and calibrating the instrument to this precision should be of some general interest.

Construction

The general construction of the instrument is evident from Figure 1. The cross feed from a small lathe was attached rigidly to a heavy tripod base and the barrel and focusing arrangement of an ordinary microscope were attached by means of a heavy angle iron, *A*, bolted to the slide. The sliding ways were carefully lapped with fine emery with strokes running the full length of the ways. The slide was frequently reversed during the grinding to remove any bow which might exist. Grinding was continued until the slide could be adjusted to a snug fit with light even drag over the entire range of motion. The lead nut attached to the slide and the lead screw were carefully machined with a square thread, 12 turns to the inch. The lead screw was fitted by means of a tapered pin with a steel collar by which the weight of the slide was carried on the adjustable brass bearing, *B*. The position of *B* was adjusted so that the lead screw lined up perfectly with the direction of motion of the slide and there was no tendency to bind at any point. A pointer on the slide permitted reading the number of turns of the lead screw on a fixed scale, and a graduated disk on the lead screw and vernier read to 0.1° of arc.

Lengths could be read with a precision of 0.001 cm. merely by taking one turn of the lead screw equivalent to 0.21 cm. (0.083 inch). However, in order to obtain the next significant figure, further calibration and a consistent technique were required.

Testing and Leveling the Instrument

A 40-gram weight was suspended by means of a 1.5-mil nickel wire in water to minimize vibrations. The microscope was focused on the wire and leveled by means of the leveling screws until the wire remained in focus, and the vertical cross hair of the eyepiece did not deviate more than half the width of the wire, while traveling over the range of the instrument. This insured a vertical alignment with a deviation of less than 0.025 mm. (0.001 inch) and also showed that the sliding ways were not warped appreciably at any point. Since the two cross hairs in the eyepiece were perpendicular, alignment of the vertical cross hair parallel to the wire served to make the other cross hair horizontal.

Reading Technique

Because of the weight of the slide it was necessary to use a heavy oil on the lead screw to prevent wear. Many different grades of lubricant were tried. With temperatures from 23° to 27° C., the best results were obtained with medium heavy cup grease on the slide and S. A. E. 120 lubricant applied freely to the lead screw. This gave a film which had a thickness much greater than the limit to which the microscope was being read. It was found that the thickness of the oil film could be kept constant and the reading of a given fixed point could be duplicated to 0.1° by means of the following technique: Flood the screw with oil while the slide is at the bottom of the screw, run the slide to the top, apply more oil to the screw, run slide back to the lowest point on the instrument, and raise to the point being read. It was very important in the process of taking a reading that the cross hair did not go past the index so that the motion of the slide had to be reversed. Using this technique, any error greater than 0.1° in measuring length results from imperfections in the lead screw.

Imperfections in Lead Screw

Periodic Errors. Periodic errors are imperfections in the screw which are repeated monotonously at corresponding points on successive turns. These variations can be successfully eliminated by taking readings on the given length at four points 90° apart and averaging the results. This uniform displacement of the length was accomplished by moving the cross hairs in the micrometer eyepiece.

Longitudinal Variations. Longitudinal variation in the lead screw was calibrated in terms of a fixed length which was given an arbitrary value slightly less than its measured length, so that the deviations would be small positive numbers.

In calibrating, the fixed length was measured from a turn near the top of the screw which was taken as the reference turn. The measured length less the length arbitrarily assigned was taken as a correction corresponding to the turn in which the lower reading was taken. The standard length was then lowered by successive steps each equal to its length; cumulative deviation was plotted against the turn number corresponding to the lower reading. A smooth curve drawn through these points was a first approximation of the calibration.

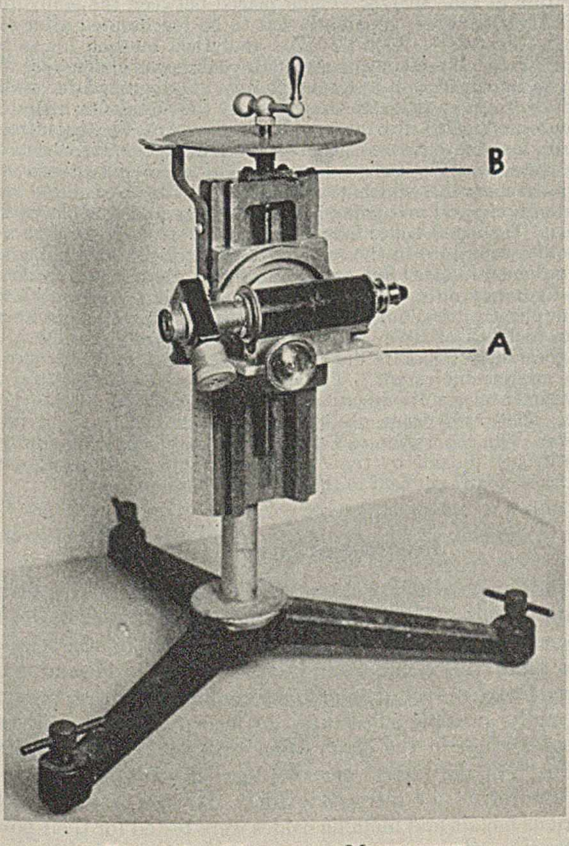

Figure 1. Measuring Microscope

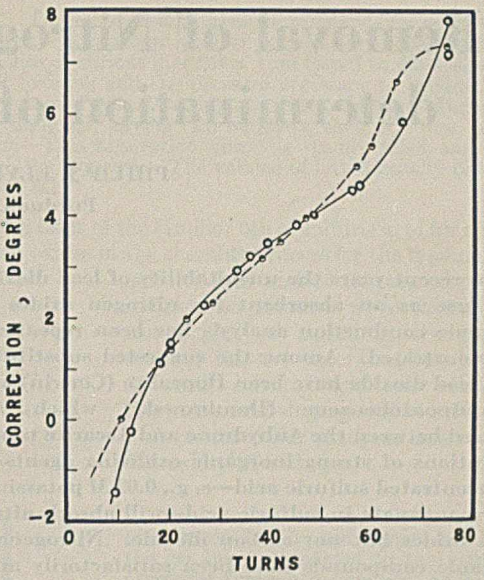

Figure 2. Longitudinal Calibration Curves

From measurements with shorter lengths it was found that the central portion of the screw was uniform. This corresponds to a linear portion of the calibration curve as it was plotted. In this range other reference points may be accurately established and the deviation at other points on the curve outside this range determined by further measurements with the standard length. Figure 2 shows a calibration curve obtained in this way, where the solid curve is the original curve and the dotted curve is a calibration obtained with a different standard length after 2 years of use. It is evident from a comparison of the two calibration curves that the instrument is improving with use.

Although the lead screw was cut on a new precision lathe at 12 turns to the inch, the screw was further calibrated:

> Two indices, approximately 6.5 cm. apart (approximately the uniform center range of the microscope) were made on a small quartz fiber and the exact distance was measured with the instrument described and compared to the length obtained, using a measuring microscope which read directly to 0.001 cm. by means of a vernier and scale. The readings were made in a thermostat at 25° C. with a small weight attached to the fiber to give it vertical alignment. A ratio of the two readings (uncorrected) gave a conversion factor, $1^\circ \equiv 0.0005879(8)$ cm. This agrees well with the conversion factor obtained by assuming 12 turns to the inch, $1^\circ \equiv 2.540005/12 \times 360 = 0.00058796$ cm.

The instrument therefore permits the measurement of relative lengths with a high degree of precision, the absolute accuracy depending also on the accuracy with which the length of the standard is known.

Precision

The validity of the calibration and technique was tested by measuring different fixed lengths at different points on the scale. Each reading was corrected by subtracting the correction taken from the calibration curve, and the corresponding length, which was the difference between the corrected readings, was corrected for the thermal expansion of the lead screw when necessary. Using 25° C. as standard, this correction for thermal expansion amounted to 0.0001 cm. for a length of 10 cm. and a temperature difference of 1°. The lengths thus corrected could be duplicated to 0.1° in the middle range of the instrument and to 0.2–0.3° near the ends of the range. When possible the extreme ends of the range were avoided in actual use.

Removal of Nitrogen Oxides in Semimicrodetermination of Carbon and Hydrogen

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Purdue University, Lafayette, Ind.

In recent years the unsuitability of lead dioxide for use as an absorbent for nitrogen oxides in organic combustion analysis has been repeatedly demonstrated. Among the suggested substitutes for lead dioxide have been Hopcalite (Corwin) and *p*-aminoazobenzene (Dombrowski) which are placed between the Anhydrone and Ascarite tubes. Solutions of strong inorganic oxidizing agents in concentrated sulfuric acid—e. g., 0.02 *M* potassium permanganate in sulfuric acid—will absorb nitrogen oxides but not carbon dioxide. Nitrogenous organic compounds have been satisfactorily analyzed, using sulfuric acid solutions of potassium permanganate in a special absorption vessel following the Anhydrone tube.

In a search for a substitute for lead dioxide that could be used either in the combustion tube or in the absorption train various metals and metallic oxides have been tested for their ability to decompose or absorb nitrogen dioxide from mixtures of nitrogen dioxide and air.

ONE of the serious sources of error in present methods for the determination of carbon and hydrogen is the use of lead dioxide to remove the nitrogen oxides from the products resulting from the combustion of organic compounds containing nitrogen (*2, 6, 15, 25, 26, 41, 42, 43*). These oxides must be removed prior to the absorption of carbon dioxide, since their acidic nature will cause their absorption by the alkaline reagents used for absorbing the carbon dioxide and consequently will lead to high results for carbon. Various absorbents, which will not react with the nitrogen oxides in the gas stream of combustion products, may be used for the water formed. These nitrogen oxides can be removed by absorption by a suitable substance or reduction to free nitrogen.

Lead Dioxide and Proposed Substitutes

Lead dioxide, long used in macroanalysis (*13, 20*), was retained in his microanalytical procedure by Pregl, who called it "the most critical reagent" in the method (*39*). The use of lead dioxide in both micro- and macroanalysis has been studied critically by numerous investigators (*2, 6, 7, 9, 15, 20, 21, 24, 41, 42, 43*). The mechanism of the absorption of nitrogen oxides by the lead dioxide was investigated by Kirner (*19*) who summarized previous work on this topic. Specific sources of error (*3, 14, 23, 25, 26, 27, 30, 39*) are the tendency of lead dioxide to absorb carbon dioxide when dry and to give it off again in the presence of small amounts of water or of the combustion products of organic compounds containing nitrogen, halogen, or sulfur, and the gradual absorption and elimination of water from the lead dioxide. Boëtius (*4*) and Niederl and Whitman (*35*) consider the time and amount of gas specified by Pregl for the purpose of sweeping out the combustion gases insufficient for the complete removal of the water from the lead dioxide. These sources of error are more or less eliminated by keeping the lead dioxide at a temperature of 180° to 200° C., in which range the vapor pressure of water–lead dioxide system has a constant value, which is high enough to minimize the absorption of carbon dioxide and low enough to guard against storing up appreciable amounts of water (*22, 39*).

The various absorbents and reagents for the removal of the oxides of nitrogen suggested in the literature have been tested by Corwin (*6*) and their advantages and disadvantages studied. Most of the substitutes proposed for lead dioxide have been metals intended to reduce the oxides of nitrogen to elementary nitrogen. Müller and Barck (*29*) studied the decomposition of nitric oxide when heated with various metals. The most efficient reducing agent for the oxides of nitrogen seems to be metallic copper, first used by Gay-Lussac (*17*). The use of copper in combustions taking place in oxygen, however, necessitates the introduction of a freshly reduced copper spiral for each determination. The latter was avoided by Benedict (*1*) who burned a weighed sample of high carbon content with each nitrogen-containing sample, the combustion of the former producing the freshly reduced copper surface needed to reduce any oxides of nitrogen formed by the second sample. A more satisfactory solution of the problem involving the use of metallic copper was proposed by Niederl and Whitman (*34*) who burned the sample in an atmosphere of nitrogen, using the combustion tube filling recommended by Pregl (*38*) for the micro-Dumas method. The oxygen for the combustion was supplied by copper oxide mixed with the sample. Lindner (*24*) also used a combustion tube containing copper spirals, employing nitrogen as the transport gas and oxygen or air in the actual combustion. After four or five runs Lindner's copper spirals had to be renewed. Pregl (*37*) claims that metallic silver, suggested by Dennstedt (*8*) and Dubský (*11*), is incapable of decomposing the higher nitrogen oxides. Untreated Raney nickel-aluminum catalyst, kept at 200° to 250° C., has been found by Gardella and Baldeschwieler (*16*) to be effective in removing nitrogen oxides in macroanalysis.

Perkin (*36*) suggested replacing the lead dioxide used in macroanalysis with potassium chromate. Corwin (*6*) found that dry Hopcalite could be substituted for lead dioxide as an absorbent for the oxides of nitrogen. The Hopcalite, maintained at a temperature of 125° to 175° C. and placed between the Anhydrone and Ascarite tubes, apparently has to be regenerated after each run by heating to 300° C. The analytical method for carbon and hydrogen based on the use of Hopcalite was claimed by Corwin to be superior in accuracy to any micromethod for carbon and hydrogen previously described in the literature. In 1940 Dombrowski (*10*) also proposed an absorbent for the nitrogen oxides inserted between the tubes containing the absorbents for the water and the carbon dioxide. The adsorbent used was *p*-aminoazobenzene, which was moistened with a saturated solution of boric acid and potassium dichromate and was placed in a special U-shaped tube, followed by a layer of magnesium perchlorate contained in the same U-shaped tube. This filling had to be renewed after five or six analyses. Dombrowski's results for hydrogen on five nitrogen-containing compounds, each run in duplicate, using magnesium perchlorate as water absorbent, were high, on an average, by 0.23 per cent, indicating that the magnesium perchlorate did not absorb the oxides of nitrogen to any appreciable extent. This latter fact was confirmed by the experimental results described below. Corwin (*6*) claims, however, that Anhydrone absorbs nitrogen dioxide but not nitric oxide. The absorption of 1 per cent of the nitrogen in a sample as nitrogen dioxide by the Anhydrone would cause an apparent increase of 0.37 per cent in the hydrogen content.

Purpose of Investigation

The purpose of the investigation reported in this article was twofold. First, a simple absorbent for the oxides of nitrogen was sought which could be used outside the combustion tube; this would avoid the use of lead dioxide and would permit the use of a simplified combustion tube packing. Secondly, possible substitutes for lead dioxide were investigated for use in the combustion tube or in the absorption train. For the former purpose, various solutions were tried as absorbents for nitrogen oxides; for the latter purpose, various metals and metallic oxides were tested for their power to remove nitrogen oxides from a stream of gas.

Preparation of Mixtures of Oxides of Nitrogen and Oxygen

In anticipation of testing the absorptive capacity of many materials for oxides of nitrogen, a permanent setup was constructed for generating nitric oxide, measuring a definite volume, and mixing with oxygen in any desired proportions. The apparatus, shown in Figure 1, is an adaptation of the nitric oxide generator described by Kirner (*19*), although a different reaction was used.

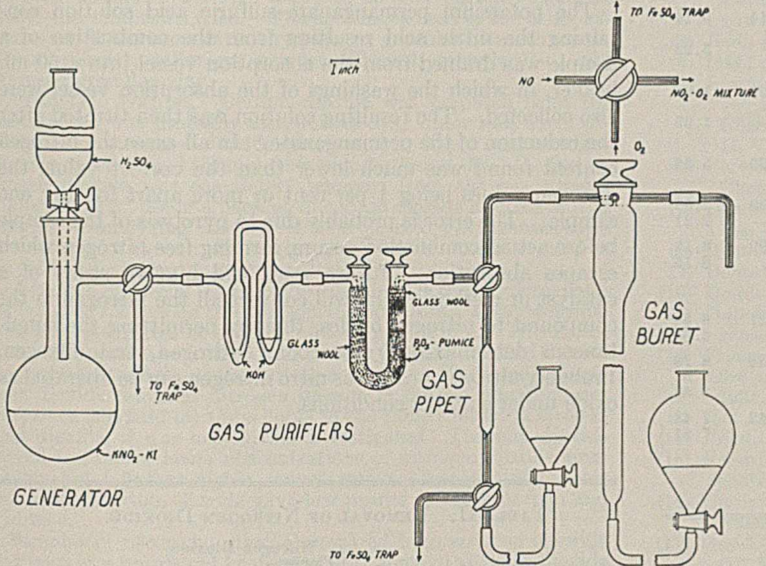

Figure 1. Apparatus for Preparation of Nitrogen Dioxide–Oxygen Mixtures

Nitric oxide was made in the generator by the action of dilute sulfuric acid on a 1 to 1 molar solution of potassium nitrite and potassium iodide (*44*). The nitric oxide was washed and dried by passage through saturated potassium hydroxide solution and through phosphorus pentoxide mixed with pumice. Small volumes of nitric oxide were measured out in the calibrated gas pipet (volume = 2.5 cc.) while large volumes of nitric oxide were measured out directly in the gas buret (volume of the upper bulb = 50 cc., volume of the lower calibrated tube = 50 cc.), where the samples of nitric oxide were diluted with oxygen and from which the gas mixture was led to the reagent being tested for removal of nitrogen oxides. Before using, the apparatus was cleared of air by flushing with nitric oxide. The samples of nitric oxide taken were absolutely colorless. On the addition of oxygen brown nitrogen dioxide was formed. Mercury was used as confining liquid in the gas pipet and gas buret, and ferrous sulfate solutions were used in the traps designed to keep the nitric oxide from getting into the air. The generator and purification train were kept filled with nitric oxide when the apparatus was not being used.

Under the condition of the experiments, using an excess of oxygen, the nitric oxide would be changed completely to nitrogen dioxide in the gas buret. As has been pointed out (*18*, *19*, *28*, *40*) nitrogen dioxide and nitrogen are the probable end products from a properly conducted combustion of a nitrogen-containing compound.

Absorption of Nitrogen Dioxide by Solutions

For the experiments involving the use of an absorbing solution, absorption vessels of various shapes and sizes were tested.

Each type was placed in the combustion train, as it would be in practice, to determine how much resistance it offered to the flow of gas. Those possessing too much resistance for operation were discarded. A capillary bubbler seemed best suited to the need. Capillaries of various diameters were tested to determine the extent of foaming and the pressure necessary to produce a satisfactory flow of gas. An all-glass vessel, shown in Figure 2, was finally designed, having two bubblers, each of 1-mm. orifice, in tandem. This absorption vessel is readily filled and emptied through the stopcock. The volume of liquid usually present was about 10 ml.

On the basis of the familiar use of sulfuric acid for absorbing nitrogen oxides in the chamber process for the manufacture of sulfuric acid and of the use of potassium dichromate solution as an absorbent for the oxides of sulfur in the analytical method for the determination of carbon in steel, sulfuric acid and solutions of inorganic oxidizing agents in sulfuric acid were selected for study as absorbents for the oxides of nitrogen.

In the experiments described the mixture of nitrogen dioxide and oxygen was led from the gas buret connected to the nitric oxide generator through a capillary glass tube to the absorption vessel described, then through a bubbler into a Mariotte bottle. The bubbler contained an indicator solution of diphenylamine which gives a blue coloration with nitrogen dioxide. By this device the failure of the absorbing solution to remove nitrogen dioxide from the gas stream could be instantly detected. A blue color appeared on passing 0.01 mg. of nitrogen dioxide directly into the diphenylamine solution.

Concentrated sulfuric acid was unsatisfactory as an absorbent for nitrogen dioxide. A saturated solution of potassium dichromate in concentrated sulfuric acid was found to be satisfactory. When 1500 cc. of a 50 per cent nitrogen dioxide mixture were passed through at the rate of 5 cc. per minute, no nitrogen dioxide was detected in the scrubbed gas. To determine whether or not this absorbent would also absorb carbon dioxide, the absorption tube was placed in the combustion train between the Anhydrone and Ascarite tubes and analyses were made on standard substances. The results for carbon and hydrogen were satisfactory. Suitable experiments showed that nitrogen dioxide is either not absorbed or only negligibly absorbed by Anhydrone under the usual conditions of gas flow and nitrogen oxide concentration.

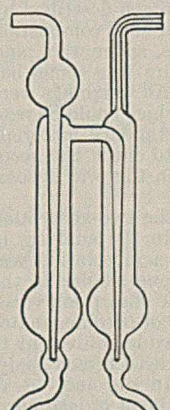

Figure 2. Absorption Vessel

By similar experiments sulfuric acid solutions, 0.02 *M* in potassium permanganate, 0.1 *M* in potassium persulfate, or saturated with ceric sulfate, were each found to give satisfactory removal of nitrogen dioxide from nitrogen dioxide–oxygen mixtures, ranging in concentration to 50 per cent nitrogen dioxide and in rate of flow to 10 cc. per minute. As a general procedure, it is safe to assert that any nonvolatile oxidizing agent in sulfuric acid which is relatively stronger as an oxidizing agent than nitric acid can be used to remove nitrogen dioxide from the gas stream.

Table I. Determination of Carbon and Hydrogen

Compound	Absorbent Used	Carbon Calculated %	Carbon Found %	Hydrogen Calculated %	Hydrogen Found %
Benzoic acid	Potassium dichromate[a]	68.88	68.83	4.95	5.11
	Potassium permanganate[b]		69.06		4.97
d-Mannitol	Potassium dichromate[a]	39.55	39.58	7.74	7.83
Glycine	Potassium dichromate[a]	32.00	32.19	6.71	6.81
	Potassium permanganate[b]		31.95 32.13		7.07 7.00
p-Nitrotoluene	Potassium dichromate[a]	61.31	61.59	5.14	5.14
	Potassium permanganate[b]		61.15		5.23
3,5-Dinitrobenzoic acid	Potassium dichromate[a]	39.63	39.53	1.90	1.97
	Potassium permanganate[b]		39.70		1.95
Thiourea	Potassium permanganate[b]	15.78	15.87	5.29	5.36
p-Nitrobromobenzene	Potassium permanganate[b]	35.67	35.30 35.61	1.99	2.03 2.31
Ephedrine hydrochloride	Potassium permanganate[b]	59.55	59.50 59.38	7.99	8.18 8.15
Research substances					
$C_8H_{20}O_4N_2$	Potassium permanganate[b]	37.04	37.07 36.80	6.21	6.54 6.58
$C_7H_{13}O_3N$	Potassium permanganate[b]	52.81	52.75 52.98 52.86	8.23	8.28 8.51 8.58
$C_7H_{14}O_4N_2$	Potassium permanganate[b]	44.20	44.36 44.37	7.42	7.43 7.81

[a] Saturated solution in concentrated sulfuric acid.
[b] 0.02 *M* solution in concentrated sulfuric acid.

Analysis, Using the Proposed Absorbent

Various nitrogen-containing compounds were analyzed, using either a saturated solution of potassium dichromate in concentrated sulfuric acid or a 0.02 *M* solution of potassium permanganate in concentrated sulfuric acid to remove the nitrogen oxides from the combustion products.

The analyses were carried out on a semimicro scale, using 10- to 20-mg. samples. A combustion apparatus of the conventional type for the determination of carbon and hydrogen described by Niederl and Niederl (*31*) was used with the simplified combustion tube filling, consisting only of platinum gauze, silver wool, and copper oxide (*32*). The combustion procedure was somewhat modified because of the larger samples (*33*). All weighings were made on a Becker No. 360 semimicrobalance which could be read to 0.01 mg. Many analyses were made on standard materials such as benzoic acid and *d*-mannitol, in order to check the accuracy of using this semimicrotechnique. When this was accomplished, experimental work was started.

The absorption vessel was placed between the two absorption tubes containing Anhydrone and Ascarite. In the analyses in which the potassium permanganate–sulfuric acid solution was used, an absorption tube containing Anhydrone similar to the water-absorption tube was inserted between the absorption vessel and the Ascarite tube. A single 10-ml. filling of permanganate–sulfuric acid solution will absorb nitrogen dioxide equivalent to 0.07 gram of nitrogen and should suffice for at least fifteen analyses. The analyses are shown in Table I. In the analyses of samples containing halogen or sulfur, a 6-cm. layer of lead chromate was inserted before the copper oxide in the combustion tube, except that for the analysis of the ephedrine hydrochloride the lead chromate was mixed with the copper oxide.

Simultaneous Determination of Carbon, Hydrogen, and Nitrogen

It seemed probable that the nitrogen oxides absorbed in the sulfuric acid containing a strong oxidizing agent would be converted to nitric acid. If this were true, and if all the nitrogen in the sample were burned to oxide, then it remained only to determine the nitric acid in the absorption vessel to have a quantitative method for the determination of nitrogen simultaneously with carbon and hydrogen. With this in mind a method was devised for the determination of nitric acid in concentrated sulfuric acid which would be applicable to solutions containing permanganate, since permanganate was the oxidizing agent most readily destroyed without destruction of the nitric acid. The method of Bowman and Scott (*5*) for the determination of nitric acid in oleum and in mixed acids was adapted for use on a semimicro scale.

The potassium permanganate–sulfuric acid solution containing the nitric acid resulting from the combustion of a sample was drained from the absorption vessel into a 50-ml. beaker, in which the washings of the absorption vessel were also collected. The resulting solution was then titrated after the reduction of the permanganate. In all cases the nitrogen content found was much lower than the correct value, the nitrogen values being 1 per cent or more apart for any one sample. The error is probably due to pyrolysis of the sample before actual combustion occurs, forming free nitrogen which escapes absorption. Future work will involve study of a catalyst or method which will convert all the nitrogen in the compound to nitrogen oxides, thereby permitting the simultaneous determination of carbon, hydrogen, and nitrogen. Probably nitrogen present as nitro nitrogen can be liberated as oxide under suitable conditions.

Table II. Removal of Nitrogen Dioxide

	Temperature ° C.	Nitrogen Dioxide Concentration %	Rate of flow Cc. per min.	Result
By Metals				
Aluminum	180	5	5	Partially effective
Antimony	300	2	5	Unsatisfactory
Bismuth	Below melting point	2	4	Unsatisfactory
Nickel	180	5	3	Partially effective
Silicon	300	2	1	Unsatisfactory
Silver	300	2	3	Partially effective
Tellurium	300	2	5	Unsatisfactory
Tin	180	2	5	Unsatisfactory
Zinc	180	2	5	Unsatisfactory
By Metallic Oxides				
Cerium dioxide	300	2 to 50	1.5	Complete
Lead dioxide	180	2	5	Incomplete
Manganese dioxide	180	2 to 50	5	Complete
Thorium dioxide	180	5 to 10	5	Complete
Zirconium dioxide	180	5	5	Complete
	180	10	5	Partially effective
	"Red heat"	5 to 20	5	Complete

Removal of Nitrogen Dioxide by Metals and Metallic Oxides

In studying the effectiveness of various metals and metallic oxides in removing the nitrogen dioxide from a mixture of nitrogen dioxide and oxygen, the gas mixture was passed through a 15-cm. tube, cut from the tapered end of a combustion tube, which contained the substance under study, then through a bubbler containing diphenylamine indicator solution, and into a Mariotte bottle. The piece of combustion tube was held in a glass heating mortar, so that by use of *p*-cymene or mineral oil the substance being tested could be held at a temperature of 180° or 300° C. A thermometer was placed in the heating mortar containing the mineral oil. In some experiments, the heating mortar was removed and the tube was heated directly by a Bunsen burner and wing tip. The substance being tested was packed in a 6-cm. layer in the tube, supported at either end of the layer by asbestos plugs. In some cases the substance had asbestos plugs inserted in it at 2-cm. intervals to prevent channeling.

The conditions used and the results obtained are summarized in Table II. An unsatisfactory result indicates that the substance in the state tested failed to remove the nitrogen dioxide from the gas stream at the concentration of nitrogen dioxide, rate of flow, and temperature tried. Failure to remove nitrogen dioxide was indicated by the appearance of a blue color in the diphenylamine solution.

Metals. Aluminum powder or nickel powder failed to remove the nitrogen dioxide completely from mixtures of nitrogen dioxide and oxygen. Mixtures of aluminum and nickel powders in the proportions 1:3, 1:1, and 3:1 were no more satisfactory at 180° or 300° C. A coil of silver wire and a silver-asbestos contact mass were found to be only partially effective under the conditions tried. The specimens used in the other experiments listed were antimony powder, granular bismuth metal, silicon powder, tellurium powder, 30-mesh granular tin, and 20-mesh granular zinc.

Metallic Oxides. Cerium dioxide was prepared from the oxalate and was probably contaminated by other rare earth oxides. When nitrogen dioxide mixtures, 2 to 50 per cent nitrogen dioxide, were passed through this preparation at 300° C., the nitrogen dioxide was completely removed from the gas stream. Unfortunately, use of a packing of cerium dioxide in place of lead dioxide in analyzing samples of benzoic acid gave consistently low results for carbon, although cerium dioxide has been used as an oxidation catalyst in macroanalysis (*12*).

A sample of special lead dioxide intended for use in microanalysis failed to remove all the nitrogen dioxide from a 2 per cent mixture passed through at the rate of 5 cc. per minute. This is further confirmation of Corwin's statement (*6*) that dry lead dioxide does not completely absorb nitrogen oxides. Powdered manganese dioxide removed nitrogen dioxide in 50 per cent mixtures but, since it is said (*6*) to be liable to the same sources of error as lead dioxide, it was not further investigated Thorium dioxide served to remove lower concentrations of nitrogen dioxide completely but failed at higher concentration. Analysis of benzoic acid using thorium dioxide gave low results for both carbon and hydrogen.

Samples of zirconium dioxide, prepared from zirconyl chloride and kept at a bright red heat, seemed to remove nitrogen dioxide completely. Analysis of 3,5-dinitrobenzoic acid, using zirconium dioxide at a red heat in place of lead dioxide, gave results for carbon which were high by an amount approximately equivalent to the nitrogen in the sample if it had been absorbed as nitrogen dioxide by the Ascarite. Analysis of the same compound using a permanganate-sulfuric acid solution between the Anhydrone and Ascarite tubes gave satisfactory results for carbon. Analysis of the permanganate-sulfuric acid solutions for nitrogen gave low results. The hydrogen results were satisfactory in all cases.

Summary

The defects in the use of lead dioxide in organic combustion analysis and suggested substitutes for lead dioxide are discussed.

It is believed that the method used for the determination of carbon and hydrogen in nitrogen-containing compounds has been improved by substituting for the lead dioxide in the combustion tube a sulfuric acid solution of potassium permanganate, or of some other oxidizing agent, which is placed between the absorption tubes used for water and carbon dioxide. Potassium permanganate and sulfuric acid are readily available in any laboratory and are considerably cheaper and more convenient to use than other proposed nitrogen oxide absorbents which are similarly placed in the absorption train, while apparently equally efficient. If a method can be found for converting all the nitrogen in the sample to nitrogen oxides, the proposed method will suffice for the simultaneous determination of carbon, hydrogen, and nitrogen. An added advantage of the proposed method is that it permits the use of a simplified combustion tube filling, whether or not compounds containing nitrogen are being analyzed.

In seeking a substitute for lead dioxide which could be used in the combustion tube or in the absorption train, various metals and metallic oxides have been tested for their ability to decompose or absorb nitrogen oxides. Although some of the metallic oxides satisfactorily remove oxides of nitrogen, their use is excluded since unsatisfactory carbon and hydrogen values are obtained when they are present.

Acknowledgment

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Literature Cited

(1) Benedict, F. G., *Am. Chem. J.*, 23, 334–52 (1900).
(2) Boëtius, M., "Über die Fehlerquellen bei der mikroanalytischen Bestimmung des Kohlen- und Wasserstoffes nach der Methode von Fritz Pregl", Berlin, Verlag Chemie, 1931.
(3) *Ibid.*, pp. 57–9.
(4) *Ibid.*, p. 62.
(5) Bowman, F. C., and Scott, W. W., J. Ind. Eng. Chem., 7, 766–9 (1915); Furman, ed., "Scott's Standard Methods of Chemical Analysis", 5th ed., Vol. 2, pp. 2214–19, New York, D. Van Nostrand Co., 1939.
(6) Corwin, A. H., paper presented at Rochester Meeting, Am. Chem. Soc., Sept. 9, 1937.
(7) Dennstedt, M., "Anleitung zur vereinfachten Elementaranalyse", 3rd ed., Hamburg, O. Meissner, 1910
(8) Dennstedt, M., *Ber* , 30, 2861–2 (1897).
(9) Dennstedt, M., *Z. anal. Chem.*, 42, 417–27 (1903).
(10) Dombrowski, A., *Mikrochemie*, 28, 136–40 (1940).
(11) Dubský, J. V., "Vereinfachte quantitative Mikroanalyse organischer Substanzen", Leipzig, Veit & Co., 1917.
(12) Fisher, H. L., "Laboratory Manual of Organic Chemistry", 3rd ed., pp. 249–50 New York, John Wiley & Sons, Inc., 1931.
(13) *Ibid.*, p. 292 (footnote).
(14) Friedrich, A., *Mikrochemie*, 10, 329–54 (1931).
(15) Friedrich, A., "Praxis der quantitativen organischen Mikroanalyse", Leipzig and Vienna, F. Deuticke, 1933.
(16) Gardella, M. J., and Baldeschwieler, E. L., Esso Laboratories-Research Division, Linden, N. J., private communication.
(17) Gay-Lussac, J. L., *Ann. Chim.*, [1], 95, 184 (1815); 96, 53 (1815); quoted by Benedict (*1*).
(18) Kirner, W. R. Ind. Eng. Chem., Anal. Ed., 7, 366–8 (1935).
(19) *Ibid.*, 10, 342–6 (1938).
(20) Kopfer, F., *Z. anal. Chem* 17, 28 (1878).
(21) Lindner, J., *Ber.*, 59, 2561-73 (1926).
(22) *Ibid.*, 59, 2806–12 (1926).
(23) *Ibid.*, 63, 1396–1405 (1930).
(24) *Ibid.*, 65, 1696–1706 (1932).
(25) Lindner, J., *Chem. Fabrik.*, 6, 277 (1933).
(26) Lindner, J.. *Mikrochemie*, 25, 197–207 (1938).
(27) Lindner, J., *Z. anal. Chem.*, 66, 305–70 (1925).
(28) Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 8, p. 210, New York, Longmans Green and Co., 1928.
(29) Müller, E., and Barck, H., *Z. anorg. allgem. Chem.*, 129, 309–20 (1923).
(30) Niederl, J. B., and Niederl, V., "Micromethods of Quantitative Organic Elementary Analysis", New York, John Wiley & Sons, 1938.
(31) *Ibid.*, pp. 80–117.
(32) *Ibid.*, p. 88.
(33) Niederl, J. B., Niederl, V., Nagel, R. H., and Benedetti-Pichler, A. A., Ind. Eng. Chem., Anal. Ed., 11, 412–14 (1939).
(34) Niederl, J. B., and Whitman, J. B., *Mikrochemie*, 11, 274–300 (1932).
(35) *Ibid.*, p. 276.
(36) Perkin, W. H., *J. Chem. Soc.*, 37, 121 (1880).
(37) Pregl, F., "Quantitative Organic Microanalysis", 2nd English ed., tr. by Fyleman, p. 34, Philadelphia, P. Blakiston's Son & Co., 1930.
(38) *Ibid.*, pp. 81–95.
(39) Pregl, F., and Roth, H., "Quantitative Organic Microanalysis", 3rd English ed., pp. 34–5, tr. by Daw, Philadelphia, P. Blakiston's Son & Co., 1937.
(40) Richardson, A., *J. Chem. Soc.*, 51, 397–403 (1887).
(41) Weil, H., *Ber.*, 43, 149 (1910).
(42) Weygand, C., "Quantitative analytische Mikromethoden der organischen Chemie in vergleichender Darstellung", pp. 70–163, Leipzig, Akademische Verlagsgesellschaft, 1931.
(43) Weygand, C., and Hennig, H., *Chem. Fabrik.*, 9, 8–10 (1936).
(44) Winkler, L. W., *Ber.*, 34, 1412 (1901).

Presented before the Division of Analytical and Micro Chemistry at the 101st Meeting of the American Chemical Society, St. Louis, Mo.

MODERN LABORATORIES

The American Tobacco Company Research Laboratory

CLAIBORNE E. BROGDEN, American Tobacco Co., Richmond, Va.

THE research facilities of The American Tobacco Company were greatly expanded with the completion of its new building at 400 Petersburg Turnpike, Richmond, Va. The building was designed by Francisco and Jacobus, of New York, and erected by the Wise Contracting Company of Richmond. The cost of the building and fixed equipment was approximately 95 cents per cubic foot.

The building, which consists of one story and full basement, measuring 135 by 110 feet, is of modified Georgian design, the exterior of buff brick with limestone trim. The exterior doors and sash are of wood painted white. The interior shows the influence of the Williamsburg restoration. The vestibule is paneled in teakwood, the lobby wainscoted to the ceiling and painted in old ivory. The library, which occupies 38 by 41 feet in the center of the building, consists of a conference room, from both sides of which open reading alcoves with bookstacks between. The room is finished in matched walnut panels. The executive and general offices are wainscoted in walnut or paneled in wood, painted ivory. The ceilings of the library and offices are acoustically treated. The floors of the vestibule and lobby are of marble, the library of teakwood with ebony inlay, the private offices carpeted.

LABORATORIES. The laboratories on the first floor are arranged in units, or suites, around the building. These units correspond to the divisions under which the research department is administered—tobacco, essential materials, cigaret paper, physical standards, tobacco smoke, factory service, and biological. The laboratories are 24 feet in depth and vary from 9 feet to 35 feet in width. Ceiling heights vary from 10 to 15.5 feet. The walls are of glazed terra-cotta to a height of 5 feet 9 inches with painted plaster above. Laboratory floors consist of $^3/_{16}$-inch air-pad rubber over concrete. Lighting is furnished by daylight fluorescent tubes operating on three-phase 208-volt circuits.

LABORATORY FURNITURE AND SERVICES. Laboratory furniture is of birch flush construction finished in "burley" brown, with the exception of the biological division, which is furnished with white enameled lead-coated steel. Table tops are 1.625-inch birch, finished in black satin acid-alkali resistant enamel, excepting under hoods. Table tops under hoods are of black serpentine stone 1.625 inches thick. Balance table tops are of 1.625-inch enameled asbestos composition, which provides added weight and stability.

Hardware and fittings are made of brass, satin chrome-plated, excepting under hoods, where special acid-resistant alloy is used. All are of severely plain design for ease of maintenance. Services in each laboratory include steam, hot and cold water, compressed air, gas, vacuum, 120- and 208-volt alternating current, and distilled water. All service lines are fully enclosed, so that only the fixtures are visible. Brass pipe is used throughout the building for hot and cold water. Ceramic drains for waste are used, except for lead connections from the floor level to laboratory sinks.

Sinks and drainboards of one-piece construction are of black vitrified ceramic ware, set in mastic at the joints with table tops to prevent moisture reaching unprotected surfaces. Acid-proof ceramic drip trays, connected to the acid drainage system, are provided beneath all sinks, so that traps and wall pipes may be serviced without damaging furniture or floors by contact with corrosive liquids. These trays also serve as an excellent storage for stock bottles of concentrated acids.

In addition to housing all mechanical equipment in connection with the building, the basement is provided with laboratories and other rooms for special equipment. Laboratory furniture in the basement is of lead-coated steel finished in a pearl gray enamel with impregnated asbestos tops.

One room, 32 by 35 feet, is equipped with semiworks digesters, beaters, sheet formers, and other equipment for fabricating cigaret paper from raw material. This room has a separate ventilating system for exhausting directly to the outside. A processing room, equipped with all services for use with small-scale factory machinery, occupies about 2000 square feet of floor space. A drying and milling room for tobacco and other samples has been provided, as well as a special room for pulverizing coal and related samples. The grinding mills are housed in hoods connected with rotoclones which remove 98 per cent of the dust, returning clean air to the rooms. One laboratory is equipped with a Kjeldahl wet-ashing unit provided with a Duriron vent directly to the roof. Moisture ovens having a capacity of over 500 samples a day occupy one room. A machine shop equipped with lathes, drill presses, and other necessary shop facilities occupies 24 by 30 feet.

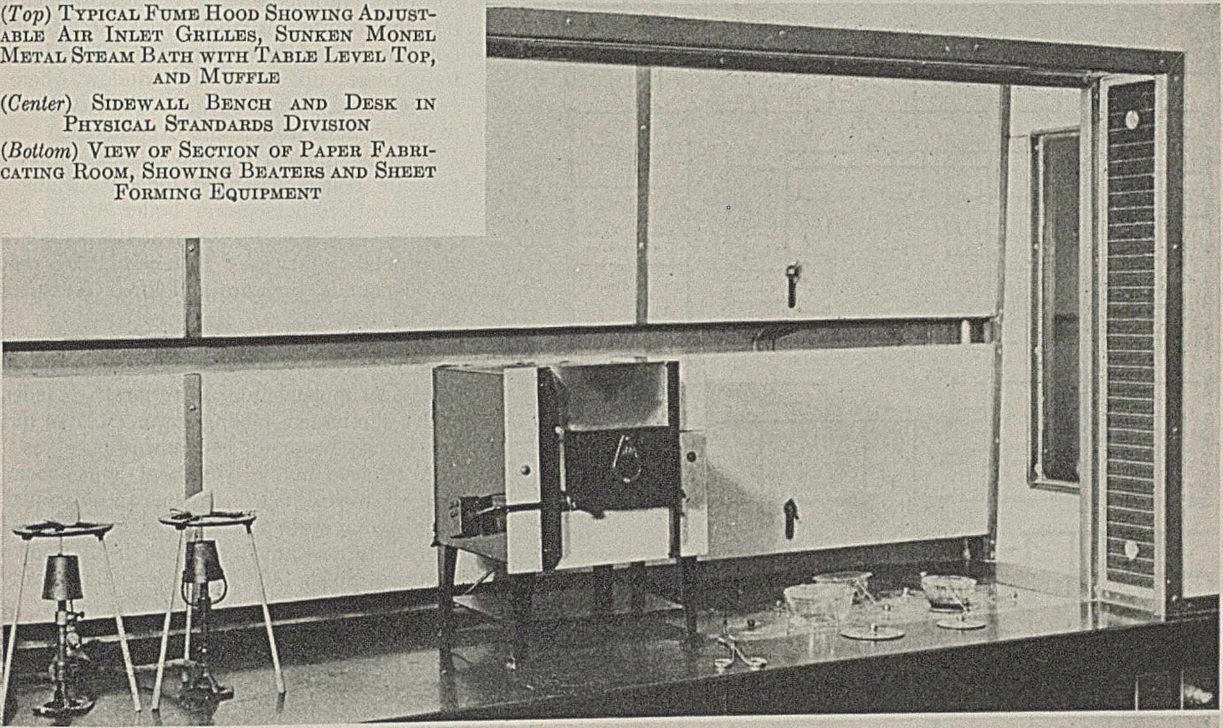
Stockrooms for glassware and chemicals, a storeroom for samples which are retained for reference, stationery stock room, record vault, shipping room, glassware washroom, sterilizing room, as well as locker rooms and showers for employees, are also located in the basement.

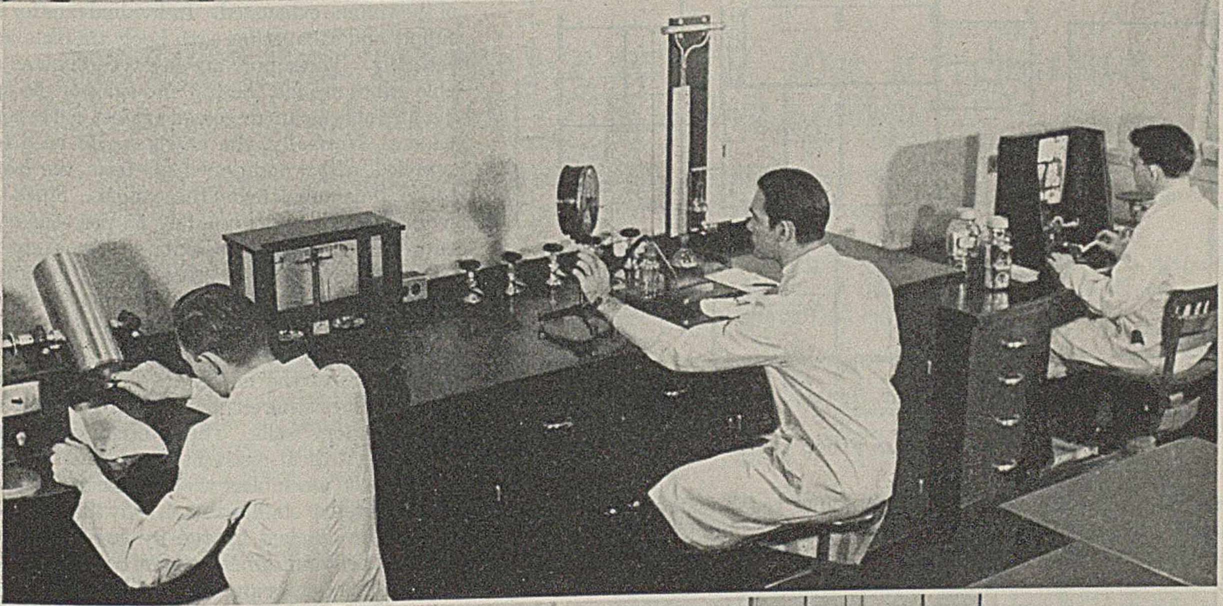
HEATING AND AIR CONDITIONING. The main floor is completely air-conditioned with controls in individual rooms or suites. The system is designed for both winter and summer conditioning—that is, dry bulb temperature and humidity will be automatically controlled throughout the year. All the air supplied to the laboratory through the air-conditioning system is thoroughly washed by means of a spray-type de-

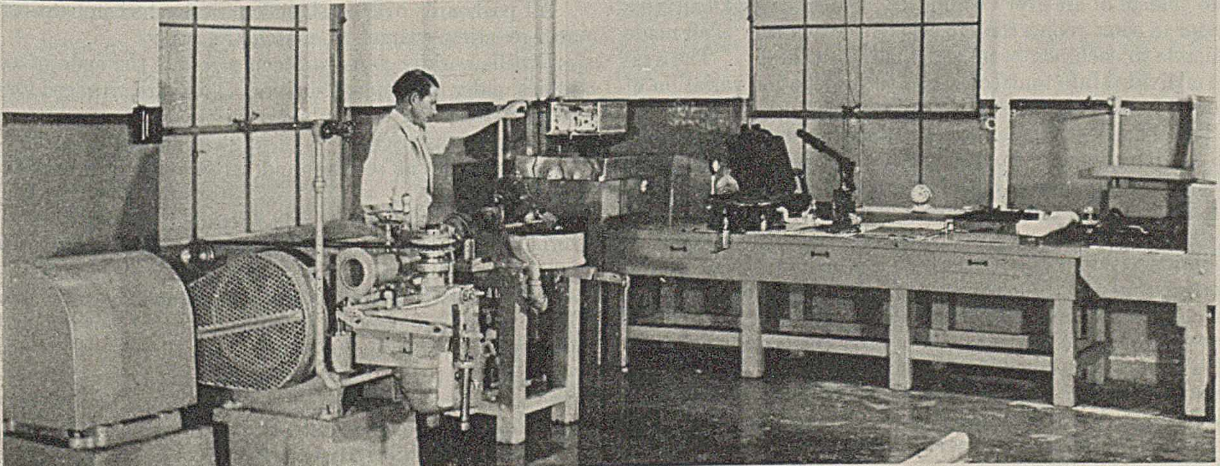
(*Top*) Typical Fume Hood Showing Adjustable Air Inlet Grilles, Sunken Monel Metal Steam Bath with Table Level Top, and Muffle

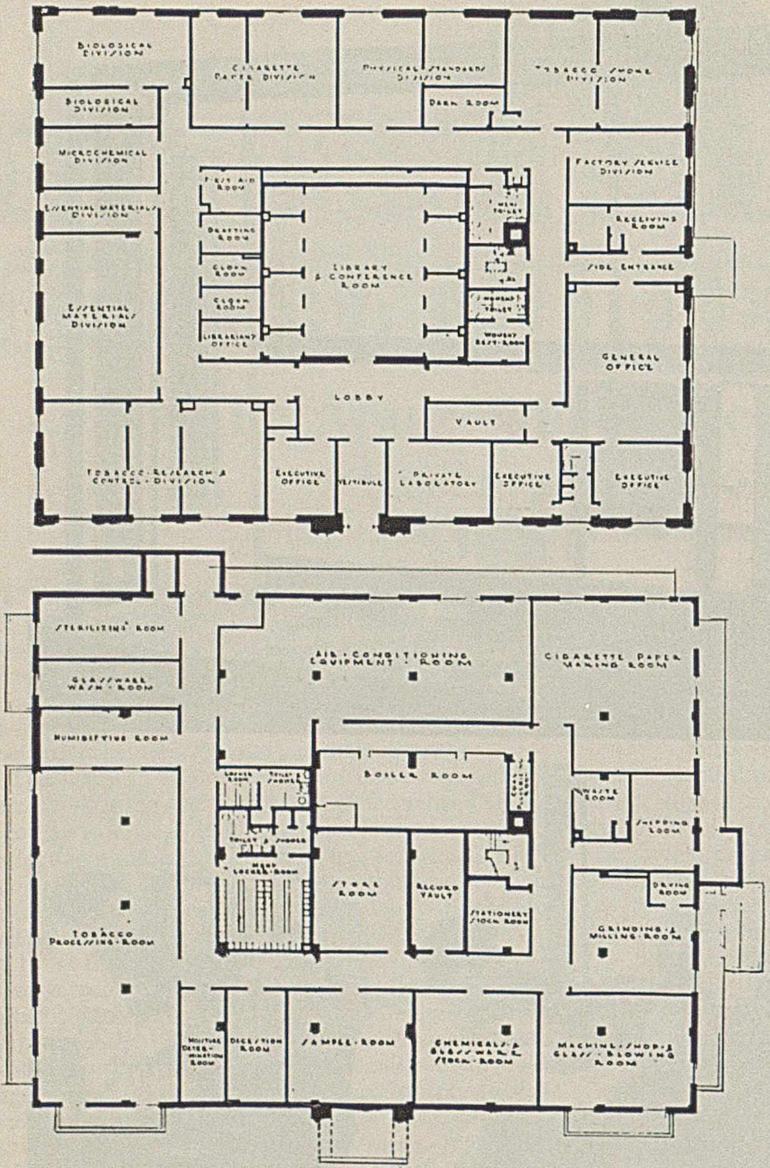
(*Center*) Sidewall Bench and Desk in Physical Standards Division

(*Bottom*) View of Section of Paper Fabricating Room, Showing Beaters and Sheet Forming Equipment









Floor Plan of Main Floor and Basement

humidifier, then filtered. The dehumidifier is fabricated of stainless steel, ensuring freedom from corrosion and minimum maintenance costs. The fan supplying conditioned air to the first floor has a capacity of 28,000 c. f. m., equivalent to a complete change of air every 6 minutes. Since the heat load is far greater in some rooms than in others, the quantity of air made available to each has been regulated accordingly. The system is divided into fourteen zones to provide for variation of internal heat load from laboratory equipment and of external load as the direct rays of the sun travel around the building.

Requirements vary from comfort conditions in the offices to very accurate control of both temperature and relative humidity—for example, measurement of the physical characteristics of cigarets and tobaccos requires the maintenance of relative humidity within ±0.5 per cent and similar exactness in temperature control. Smoke research, while demanding less precise control, requires more flexibility, with facilities for changing relative humidity over a fairly wide range and maintaining it at any prescribed level during a series of experiments. Since the duties of each division are specialized, facilities have been provided which are peculiar to its needs. Individual rooms are equipped with special humidifying equipment for control at various levels. The conditioned air is introduced into the laboratories through adjustable openings in the window sills. The air, therefore, passes up across the window where the greatest heat change occurs. This avoids direct drafts on both worker and experiment.

Heat is supplied by two 36-horsepower low-pressure boilers arranged for oil burning. An additional 10-horsepower boiler of the Scotch Marine type generates steam at 100 pounds' pressure for laboratory use. In general this is reduced to 40 pounds' pressure and lower pressures for special uses.

Refrigeration is furnished by three compressors, each having a capacity of 40 tons of ice daily. They are supplemented by evaporative condensers which eliminate a cooling tower or large quantities of city water for condensing purposes.

A tobacco humidifying and aging room, insulated with 4-inch cork, has an individual air-conditioning system designed to control a dry-bulb temperature at any prescribed level from room temperature to 140° F. and to maintain any desired relative humidity up to 90 per cent.

An important and novel feature of the air-conditioning system is the development of air-conditioned fume hoods—that is, they are provided with a supply of air equivalent to about 90 per cent of the volume exhausted. Individual fans for both supply and exhaust for each hood are installed in the attic. The supply air enters through adjustable grilles around the top and sides of the opening and acts as an air screen against the escape of vapors. Normally, the hoods would need to be supplied with conditioned air from the laboratories, thus unbalancing the system. Since their requirement is approximately 35 per cent of the entire air-circulating capacity of the system, it would have been necessary to add a greater amount of refrigeration to accommodate this additional load. Their practicability has been fully demonstrated by use.

Exteriors of the hoods are finished in baked acid-alkali resisting enamel of a color to blend with the laboratory walls. The interiors of the hoods are lined with heat-resistant glass with Monel trim.

Titration assemblies are of special design, the frames being constructed of stainless steel. At the back of the assembly is an opalescent glass lighted by fluorescent tubes which provide permanent uniform lighting of correct intensity, well adapted to reading burets and end points.

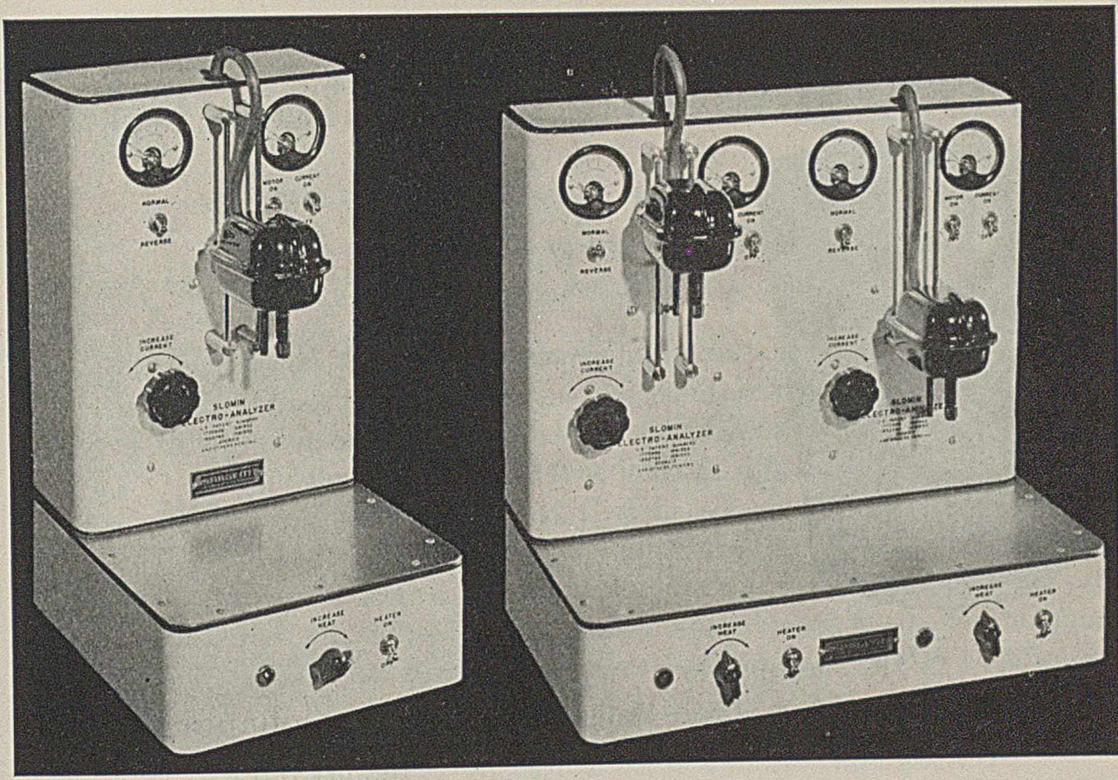
All pegboards over wash sinks are finished in light-colored acid-resisting enamel to match the walls.

Distilled water tanks are concealed at the ends of center tables under the reagent shelves. They are arranged for easy removal for filling with only the cock exposed.

Waste receptacles of stainless steel are attached inside of swinging doors at recesses and tables, wholly concealed but easy of access.

Service fixtures are of one special design to ensure uniformity in appearance. All parts subject to wear are easily replaced with stock parts. Fixtures for air, vacuum, and steam are fitted with throttling nuts to ensure ease of control. Hand wheels are of black Bakelite of two-piece sanitary type with the proper initial to identify the service.

Fluorescent tube lighting was selected because of its high degree of efficiency, especially important in an air-conditioned building. The average intensity of illumination in the laboratories is 35 foot-candles.



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Literature on Request

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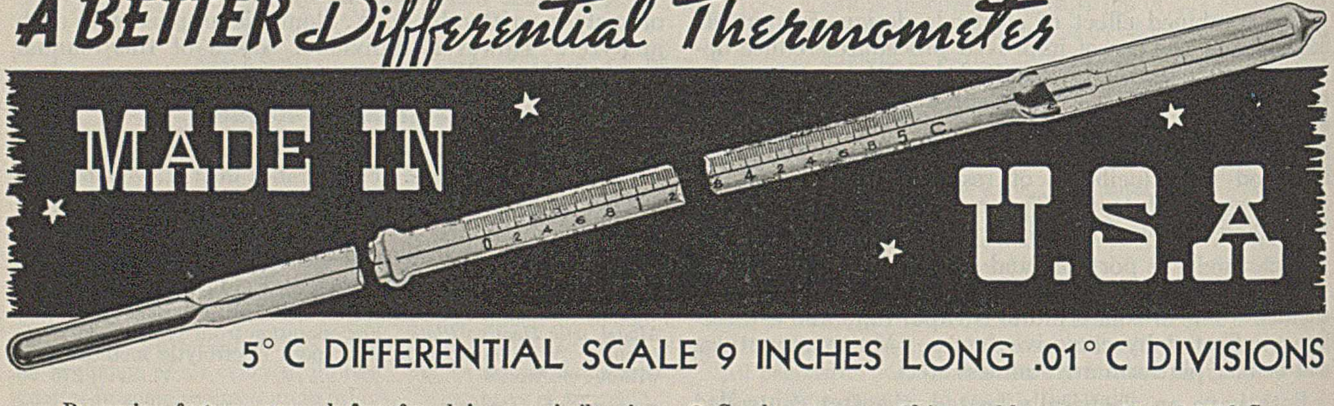
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Identification of Sulfonic Acids

REAGENT—Benzyl-iso-thiourea Hydrochloride
METHOD—Determination of melting points
REFERENCE—Chambers and Watt, *J. Org. Chem.*, *6*, 376 (1941)

Benzyl-iso-thiourea hydrochloride forms with aromatic sulfonic acids crystalline derivatives, the melting points of which are useful for the identification of the acids. The method is satisfactory for both mono- and di-sulfonic acids, if other functional groups are not present. Relatively impure acids may be used. Certain isomers also may be distinguished.

The advantages of the procedure are the rapidity of the operation, the ease of recovery of the acids, and the well-defined physical properties of the salts. The reagent is available as a stock compound, as *Eastman 2124 Benzyl-iso-thiourea Hydrochloride, MP 176-177°.*

Write for an abstract of the article listed above; a table of the melting points of 34 sulfonic acids is included. . . . Eastman Kodak Company, Chemical Sales Division, Rochester, N. Y.

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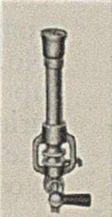
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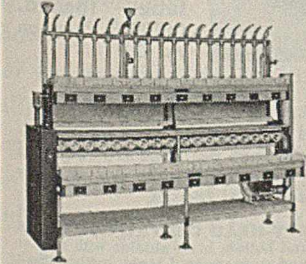
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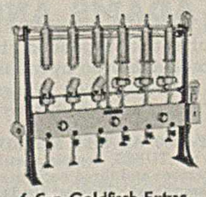
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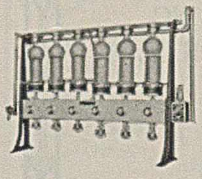
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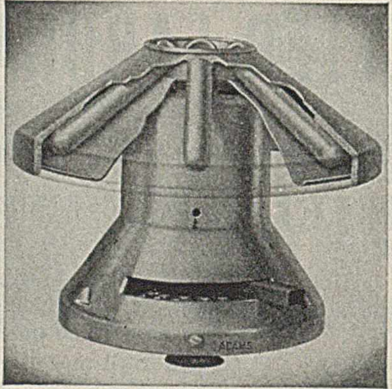

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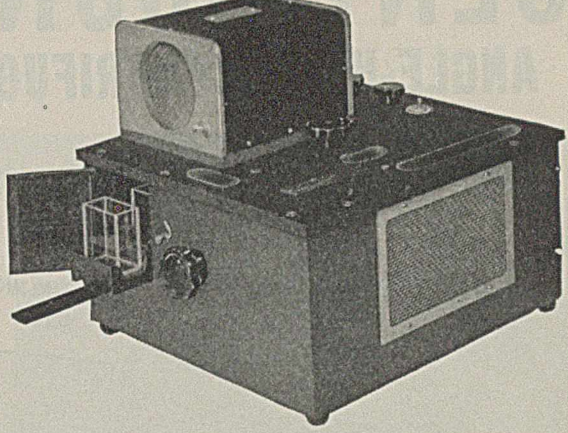

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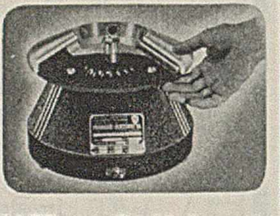

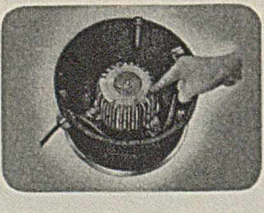

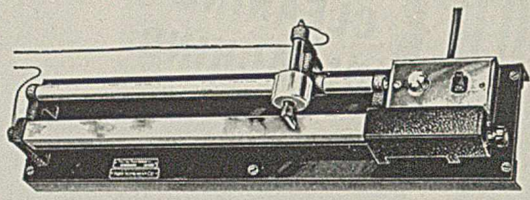

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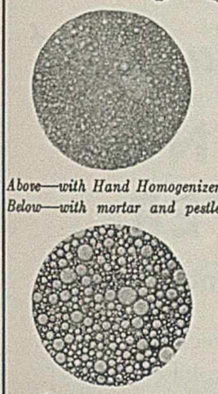

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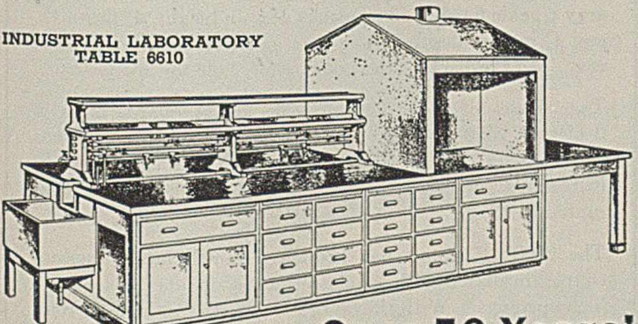

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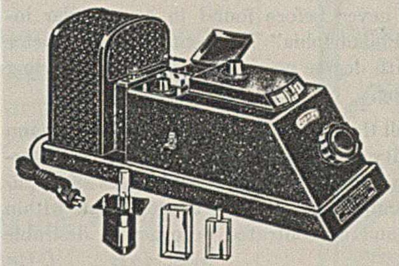

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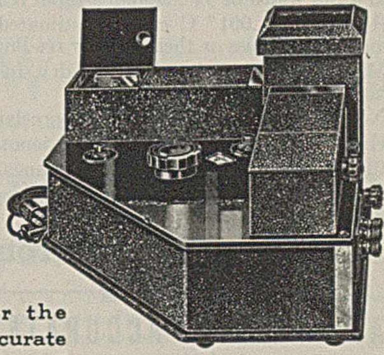

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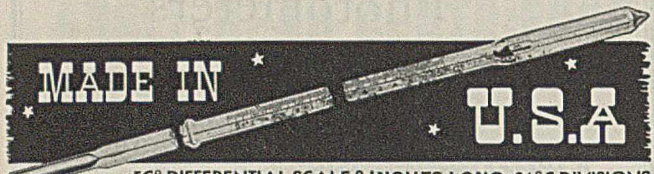
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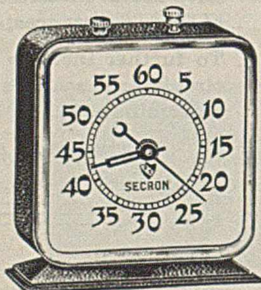
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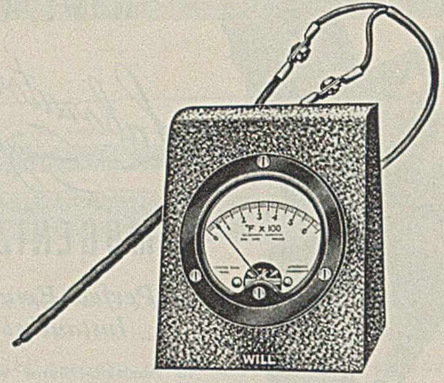
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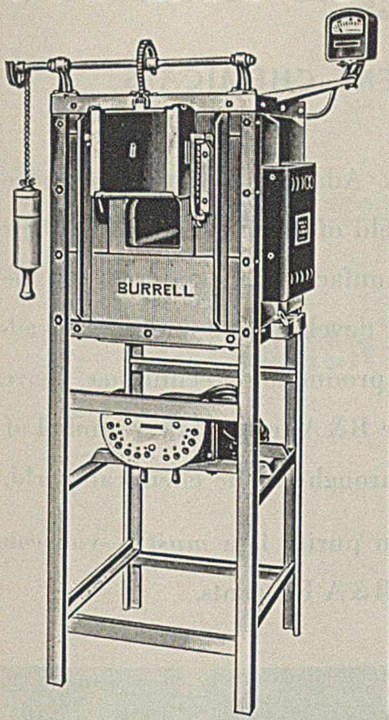
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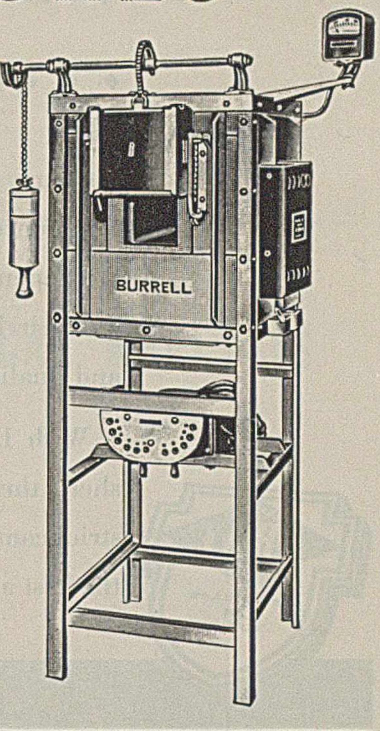
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