Not in the Textbooks

A HIGHLIGHT of the recent summer symposium held at Ohio State University was a short dinner talk by Charles W. Foulk, who retired from active teaching at the university some time ago. Dr. Foulk is widely recognized as one of the real pioneers of modern analytical chemistry.

His philosophical discussion, entitled "These Things Are Not in Textbooks," contains much food for thought by modern analysts, and we quote extensively from it:

Why were the early analytical chemists so slow in using the generalizations of physical chemistry? It was a physical chemist—Ostwald—who about 60 years ago wrote that readable book, "The Scientific Foundations of Analytical Chemistry." Ostwald, it may be remembered, had a theory of indicators which was wrong. But the analytical chemists either did not see it or if they did, they kept silent. It was an organic chemist, Stieglitz of Chicago, who gave us the true explanation of these chamelionlike substances.

Other illustrations could be given, but these suffice. It shows, at least, that the grass on the analytical side of the fence was green. Otherwise the physical, organic, and colloid chemists would not have climbed over to browse in the luxuriant pasture.

I have a theory as to why analytical chemists were so slow in these matters. Maybe it's more plausible than correct, like Ostwald's theory of indicators; but here it is.

The analytical chemist did not need theory to tell him whether a newly devised method would give accurate results. There is an experimental method that gives him the answer. He simply prepares in a pure state a portion of the substance to be determined, puts a weighed amount of it into a mixture, to simulate the sample of material he has. If necessary, he even does the paradoxical thing of using pure impurities in this synthetic sample. Then he analyzes the sample and if he gets back what he put in he knows his method is good. In no other field of chemistry grows a plant of such nearly universal application as this procedure.

But, good as it is, this method has a serious weakness. It leaves too little to the imagination. However, times are changing. Analytical chemists are now studying the behavior of substances as analytical chemists from an analytical chemical standpoint. In this they, of course, use when necessary the knowledge and techniques of other fields. The work of Kolthoff is a brilliant example of this. What prompted this distinguished chemist to engage in this field I do not know, but I venture the guess that it was curiosity, scientific curiosity. That is the driving force in the mind of the scientist, the pillar of fire that leads him to the promised land of discovery. But on this journey he must be helped by his scientific imagination. These two qualities of mind are closely related.

Now I want to say something about scientific curiosity and scientific imagination. In the later years of my teaching I sometimes told graduate students that they could give themselves an intelligence test which would show whether they were going to make their mark in creative work. And I always emphasized that they need not tell anyone how it came out. Here is what I told them: "Think back over the last six months or so and see if you were ever curious enough about some question that arose in your mind, a question that no professor asked you; just something that aroused your attention and made you so curious about it that you made a little experiment in the laboratory or looked it up in the library, all on your own. If that does not happen at least once in six months you haven't much scientific curiosity—and maybe you'd better search your mind for other talents—financial ability, for example."

But curiosity is a forked road. The left fork is wide and full of people who talk much and say little. Some are curious about what Mrs. Jones paid for her new hat and some are curious about just what Mr. Doe did that time he was in New York. The right fork has few people on it. They are curious about the ways of nature and the road is lighted from time to time by flashes of imagination. It sometimes happens that news of discoveries reaches the left fork and arouses intense curiosity there.

Scientific imagination is a much misunderstood term. Most people—even some scientists—think it means wrinkling the brow and coming forth with a great generalization of the kind that made Newton and Einstein famous. That indeed is scientific imagination—at its very highest. But what shall the rest of us do as we play on the shore of the great ocean of truth? I think I know the answer. It is a homely one: Scientific imagination in its simplest form consists merely in thinking of something that no one else has yet thought of. Now, do not think that this is trivial; and above all things, do not think that it is easy. If it were easy, we would all be Nobel Prize winners.

Here is another point that is not in the textbooks. It can be called studying the problem before trying to solve it. If one of your students has a research problem, tell him to study it first as a problem. The tendency of the beginner is to confuse *what* is to be done with *how* it is to be done. The tools and techniques of science are numerous. The best ones to use cannot be selected without a clear idea of *what* is to be done with them.

Secondly, warn this hypothetical beginner against reading into a problem conditions that are not in it. Another bad habit is the mixing together in the mind of facts and observations with their interpretation. Let me say something about observation. Frank Gilbreth, the motion study engineer, had a perfect definition of a good observer. He said: "A good observer sees what he is not looking for if it is there and does not see what he is looking for if it is not there." He added two other statements which, he said applied to young engineers. I rather think they apply to young chemists, too. Gilbreth said: "Only about 5% of young engineers are good observers and only about 5% of the good observers are good recorders."

Thirdly, if you reach a dead end and can think of nothing more to do, do what I once heard Ostwald say, "try a *Kater Versuch.*" *Versuch* means experiment, and *Kater* means "tom cat." From this the German etymologists readily derived the meaning—a blind experiment. That is, try something whether it makes good sense or not.

Separation of Cracked Gasolines by Chromatographic Adsorption

ADSORBENT CHARACTERISTICS AND REGENERATION TECHNIQUES

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The accurate engine evaluation of the hydrocarbon group constituents of cracked gasolines depends upon a satisfactory method for separating these stocks into saturate, olefin, and aromatic portions. The National Bureau of Standards has developed a method for accomplishing the desired separation on a small scale for analytical purposes by means of chromatographic adsorption on silica gel. However, application to the separation of quantities of material large enough for engine testing has required an extensive study of the variables involved. The adsorbent characteristics and regeneration techniques necessary for the most efficient and economical operation of a large-scale adsorption column are the subject of this paper. Of the commercially available adsorbents examined, a silica gel supplied by the Davison Chemical Company had the greatest capacity for adsorbing toluene from iso-octane and was most responsive to repeated regeneration. Most alkyl benzenes in the gasoline boiling range appear to be adsorbed to about the same extent by silica gel (20 ml. per 100 grams from a 20% by volume solution in iso-octane); the capacity of a silica gel for adsorbing olefins, in the same range of molecular weights, increases in order straight-chain olefin < branched-chain olefin < cyclic olefin; the "average olefin" is adsorbed to the extent of about 10 ml. per 100 grams from a 20% by volume solution in iso-octane. The amount of gel required to separate a given volume of a solution containing saturates, olefins, and aromatics can be calculated fairly accurately by taking into consideration the percolation temperature, the change in capacity with concentration of the material to be adsorbed, and the exaggerated effect of olefins in reducing the capacity of the gel for aromatics. The volume of solution that can be separated over a given weight of adsorbent is increased about 0.4% for each degree centigrade lowering of the temperature of the column. Polymerization of olefins during passage over silica gel can be prevented by using gels that have been tempered or reactivated at about 100° C. and by cooling the column below 0° C. during percolation. The Davison gel can be regenerated at least eight times in small glass columns with less than 15% drop in capacity; extended contact of gel and eluting agent at high temperatures and pressures must be avoided to prevent premature deactivation of the adsorbent. Decrease of gel capacity by contact with a polar solvent under regeneration conditions is less pronounced with acetone than with other eluting agents tested.

THE purpose of this investigation is to develop a practical method for separating gasolines into the principal hydrocarbon classes: saturates, olefins, and aromatics. It is desirable that such a method make possible the recovery of representative samples of the three hydrocarbon classes in sufficient quantities to permit study of physical and chemical properties as well as engine performance. A knowledge of these properties of the fuel constituents will not only help in explaining the properties and engine behavior of various types of gasolines but may also serve as a guide in refinery operation and commercial gasoline blending. Precision distillation of the hydrocarbon classes separated from various refinery stocks may be useful in determining sources for specialty products.

Chemical methods for carrying out this separation almost always result in nonrepresentative samples due to varying reactivities within a hydrocarbon class and to side reactions such as isomerization and polymerization. The physical method which seems most readily adaptable to the problem is chromatographic adsorption.

The National Bureau of Standards has reported the successful use of silica gel in an adsorption method for removing aromatics from petroleum stocks (6). This analytical procedure for separating aromatics from straight-run petroleum distillates is now in extensive use; a similar method for separating olefinic gasolines

has also been suggested (8). These same laboratories have more recently reported (7) the assembly and testing of a 52-foot adsorption column. Lipkin et al. (5) have described a method of separating aromatics from saturates in the gas oil and lubricating oil range. Allibone (1) has used the chromatographic adsorption technique for separation and analysis of high-boiling petroleum fractions. The analysis of small samples of shale-oil naphthas by the silica gel adsorption technique has been described by Dinneen et al. (2).

The separation of a hydrocarbon mixture by selective adsorption depends upon the fact that the tendency for hydrocarbons to be adsorbed on silica gel decreases in the order: aromatics > olefins > saturates. When an appropriate mixture of these three types of hydrocarbons is passed into a column of gel and eluted with a suitable polar solvent, the fractions collected appear in the following order: pure saturate, saturate-olefin mixture, pure olefin, olefin-aromatic mixture, and pure aromatic. The Bureau of Standards' analytical methods are based upon the use of a sufficiently fine gel and narrow column so that the volume of intermediate cuts is small compared to the total; the composition can then be estimated fairly accurately from a plot of the volume collected versus the refractive indexes of the various cuts.

At this point in the development by the Bureau of Standards, the method showed considerable promise as an analytical tool, but major drawbacks appeared when the selective adsorption technique was considered as a means of separating all three hydrocarbon classes on a relatively large scale. Foremost among these

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was the extreme length necessary for an adsorption column having both the desired capacity and separation efficiency. Another important problem, the polymerization of certain types of olefins during passage over the gel, was also demonstrated by the Bureau of Standards.

In order to develop satisfactory equipment and techniques for separating all types of refinery gasolines on a scale that would yield relatively large volumes of representative samples of the three hydrocarbon classes, it was necessary to study more thoroughly the factors affecting the over-all process. These process variables have been divided into factors which influence properties of the adsorbent, regeneration of the adsorbent, and the degree of separation (separation efficiency) obtainable. The most important properties of an adsorbent in this process are (1) capacity, which determines the quantity of a given mixture that can be separated over a given weight of adsorbent and which, in turn, influences equipment size, and (2) catalytic behavior, which may cause alterations in the structure of certain hydrocarbons in the mixture being separated. The factors affecting the degree of separation will influence the dimensions, design, and operation of the adsorption equipment. A study of regeneration is important from the standpoint of adsorbent economy and time required for a given number of separations.

A summary of the information gained from a study of adsorptive capacity, polymerization activity, and regeneration of the adsorbent is reported here. Another paper (3) covers the factors that influence the efficiency of separation and the design and operation of larger scale equipment.

PROPERTIES OF ADSORBENT

Adsorptive Capacity. COMPARISON OF COMMERCIAL SILICA GELS AND OTHER ADSORBENTS. One of the principal problems in developing a separation process of this type is the selection of a solid of high adsorptive capacity—i.e., the capacity of the solid for selectively adsorbing one type of hydrocarbon in mixtures with other types. The capacity of the adsorbent will determine the size of the equipment and the amount of time necessary to effect a given separation. Previous investigations have indicated that some types of silica gel are superior to other adsorbents in this particular application.

The adsorptive capacities of several types of commercially available silica gels and other types of adsorbents have been determined. These capacities, expressed in milliliters of toluene per 100 grams of adsorbent, were measured by percolating a 20% by

Table I. Adsorptive Capacities of Commercial Silica Gels and Other Adsorbents

Source	Designation	Approximate Mesh Size Range	Adsorptive Capacity[a]
	Silica Gels		
Davison Chemical Corp.	659528-2000	28–200	20.1
	659520-650	Coarser than 60	21.0
	Intermediate	32% w. 100–200 52% w. through 200	15.1
	8595150	27% w. 100–200 70% w. through 200	14.0
	NBS analytical gel	8% w. 100–200 66% w. 200–325 26% w. through 325	19.4
	Part 12-08-09-01	28–200	20.3
	Part 11-08-09-01	28–200	19.8
International Minerals & Chemical Corp.	. . .	40–200	17.3
	. . .	28–200	17.5
	Other Adsorbents		
Aluminum Ore Co.	Activated alumina, F-20	Coarser than 80	4.0
Attapulgus Clay Co.	Bauxite	28–200	5.5
	Louisiana bentonite	28–200	2.9
	Fuller's earth	28–200	4.5

[a] Ml. of toluene per 100 grams of adsorbent from 20% v. toluene in iso-octane.

Table II. Effect of Particle Size of Davison 659528-2000 Silica Gel on Capacity

Mesh Size	Capacity, Ml. of Toluene/100 G.
28–200	20.0
60–200	19.7
100–200	19.9
Through 200	19.6

volume solution of toluene in iso-octane over a known weight of adsorbent contained in a 1 × 40 cm. column. (A 20% solution of aromatic was used here, because olefin and aromatic concentrations of cracked gasolines usually fall in this concentration range and gel requirement calculations can be made with less extrapolation.) A low rate of percolation was maintained in order that this operating variable should exert no influence. The effluent from the column was collected in small fractions until its composition, as determined by refractive index measurements, coincided with that of the original mixture. The volume of pure iso-octane that would have been collected had the break between the components been infinitely sharp was calculated by assuming additivity of the refractive index. The quantity of toluene adsorbed by the gel is that quantity which in the original solution was associated with the iso-octane rendered aromatic-free. The volume of toluene adsorbed from a cut of volume V and refractive index N (n_D^{20}) is given by the formula:

$$\left[1 - \frac{\frac{10^4(N - 1.3915)}{210}}{4} \right] V$$

The capacities and approximate mesh size range of the various adsorbents are shown in Table I. These capacities were determined by assuming linear blending of iso-octane and toluene and are in error by approximately 1% on the high side as a result. All measurements were made at room temperature which may be taken as 25° ± 2° C.; this variation in temperature has a negligible effect on the results. Because the isotherms for the adsorption of toluene from iso-octane by various gels are similar in shape, the capacities determined at 20% by volume give a reliable comparison. From the data in Table I it is seen that the adsorptive capacities of various commercial gels differ appreciably; however, the coarser Davison gels gave almost identical values of about 20 ml. per 100 grams and both International gels gave about 17.5 ml. per 100 grams. The adsorbents other than silica gel have very small capacities for selectively adsorbing aromatics. The Bureau of Standards (6) has reported the capacities of activated carbon, Filtrol, alumina, magnesia, and Florosil for toluene; all these adsorbents except carbon have less than 50% of the adsorptive capacity of silica gel. Carbon compares favorably with silica gel on a weight basis but is appreciably inferior on a volume basis.

The adsorptive capacity of a silica gel for aromatics does not depend on particle size, as can be seen from the data in Table II, where capacity values are given for Davison 659528-2000 gel screened into various mesh size ranges. After screening, the gels were tempered several hours at 110° C.

EFFECT OF HYDROCARBON STRUCTURE. *Binary Solutions.* In order to effect a clean-cut separation of the different hydrocarbon classes in a solution, it is necessary to employ a column of adsorbent which has sufficient capacity to adsorb selectively all the olefins and aromatics present. The adsorptive capacity of silica gel depends not only on the structure of the hydrocarbon being adsorbed and its concentration in the solution but also on the nature of the solvent from which the adsorption takes place. To be able to approximate the volume of gasoline of known composition that can be separated over a given weight of gel, it is necessary to know the capacity of the adsorbent for different types of olefins and aromatics; the effect of concentration on the capac-

Table III. Adsorptive Capacity of Davison 659528-2000 Gel for Aromatics from 20% by Volume Solutions in Iso-octane

Aromatic Hydrocarbon	Adsorptive Capacity, Ml. of Aromatic/100 G.
Toluene	19.8
o-Xylene	19.9
m-Xylene	20.1
p-Xylene	19.7
n-Propylbenzene	20.8
Cumene	20.7
tert-Butylbenzene	19.8
p-Cymene	19.0
Phenylcyclohexane	19.2

ity (adsorption isotherm); and the effect of varying the solvent from which the olefins and aromatics are adsorbed.

The data in Table III show the capacity of a commercial gel for adsorbing various aromatics from iso-octane. These values were obtained by percolating 20% by volume solutions of the aromatics in iso-octane over Davison 659528-2000 gel at room temperature. The results indicate that there is a slight difference in the capacity of the gel for the various aromatics; however, it can be assumed for practical purposes that the aromatics occurring in 400° F. end point gasoline are adsorbed to the same extent as toluene.

In order to determine the effect of the nature of the solution from which adsorption occurs and to illustrate the effect of concentration, the isotherms for the adsorption of toluene from several types of olefins at room temperature have been obtained. These are given in Figure 1. International 40- to 200-mesh gel was used in the experiments; the isotherm for toluene in iso-

Table IV. Capacity of International Gel for Toluene from 20% by Volume Solutions in Various Saturates at 2° C.

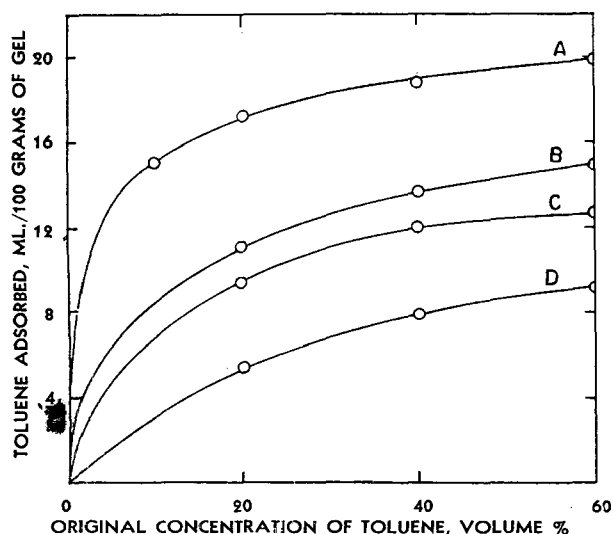| Solvent	Capacity, Ml./100 G.
n-Pentane	18.3
n-Heptane	18.2
n-Nonane	18.2
2,2,3-Trimethylbutane	18.3
Methylcyclohexane	15.5

Figure 1. Adsorptive Capacity of International Silica Gel for Toluene from Solutions of Toluene in Various Pure Olefins

A. Toluene in iso-octane (included for comparison)
B. Toluene in trans-3-heptene
C. Toluene in diisobutylene
D. Toluene in cyclohexene

octane is given for comparison. From the adsorption isotherms in Figure 1 it is seen that toluene is much more strongly adsorbed from a straight-chain olefin, trans-3-heptene, than from a cyclic olefin, cyclohexene.

From the isotherms in Figure 1 it can also be predicted that the three types of olefins of about the same molecular weight will be adsorbed to greater extents from a given saturate in the order: cyclic olefin > branched-chain olefin > straight-chain olefin. This is shown to be the case by the isotherms in Figure 2, where the effect of molecular structure and concentration on the adsorptive capacity of International gel for olefins from iso-octane is plotted.

The National Bureau of Standards has determined the capacities of a number of aromatics from solutions in various saturates. The available data indicate that the capacity of a gel for toluene increases as the molecular weight of the paraffinic solvent increases, and the capacity for toluene from a naphthene is appreciably less than the capacity from a normal paraffin of approximately the same molecular weight. Table IV gives some data obtained in these laboratories which verify the latter relation; however, there appears to be no effect of structure or molecular weight in the case of the C_5-C_9 paraffin hydrocarbons.
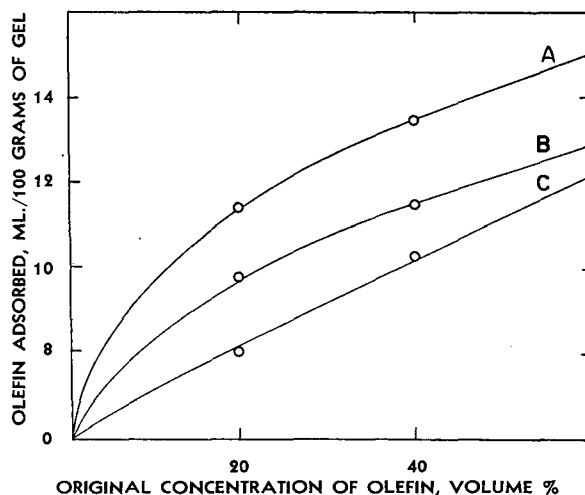

Figure 2. Adsorptive Capacity of International Silica Gel for Pure Olefins from Solutions of Pure Olefins in Iso-octane

A. Cyclohexene in iso-octane
B. Diisobutylene in iso-octane
C. trans-3-Heptene in iso-octane

The data in Figure 2 and Table IV indicate that silica gel should have a measurable capacity for selectively adsorbing certain members within a given hydrocarbon group. This property of the gel is verified in Table V, where it is shown that paraffins and olefins of low molecular weight are more strongly adsorbed than the high molecular weight compounds in the same group; naphthenes and cyclic olefins are more strongly adsorbed than the noncyclic compounds in the same group and molecular size

Table V. Adsorptive Capacity of International Gel for Saturates from Saturate Solution and for Olefins from Olefinic Solution

Vol. %	Solution Percolated	Capacity, Ml./100 G.[a]	
20	Methylcyclohexane in iso-octane	0.95	Methylcyclohexane
20	Iso-octane in tetradecane	1.75	Iso-octane
20	Cyclohexene in 1-heptene	3.6	Cyclohexene
20	1-Heptene in 1-tetradecene	4.3	1-Heptene

[a] At room temperature.

range. These conclusions hold for 20% by volume concentration of the lower molecular weight or cyclic constituent. As shown by Hirschler and Amon (4), pairs of compounds of similar adsorption characteristics may exhibit S-shaped isotherms and the order of adsorbability may be reversed at high concentrations.

Ternary Solutions. After an aromatic-olefin-paraffin solution is passed into a column containing gel in excess of the amount required to adsorb the aromatic and olefin and desorption with a polar solvent is begun, the hydrocarbons are arranged on the column as follows:
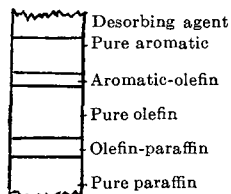
This process may be considered to occur in the following steps: The aromatic is adsorbed from the olefin-paraffin solution; after the aromatic is removed, the olefin must then be adsorbed from the paraffin. In order to calculate the quantity of gel required to separate a solution of aromatic, olefin, and paraffin, it is necessary to know the capacity of the gel for adsorbing the aromatic from the olefin-paraffin solution as well as the capacity for adsorbing the remaining olefin from the saturate. The capacity of the gel for toluene from iso-octane and from pure olefins is shown in Tables I to V and Figures 1 and 2. It would be expected that the presence of an olefinic constituent in the nonaromatic solvent would reduce the capacity of the gel for the aromatic in proportion to the olefin concentration and that the capacity of a gel for toluene from any toluene-olefin-paraffin solution could be calculated by linear interpolation of the gel capacity for toluene from the paraffin and from the olefin solutions. Determination of the capacity of Davison 28- to 200-mesh gel for toluene from toluene-cyclohexene–iso-octane solutions indicates that the olefin has an exaggerated effect and that the capacity for toluene from these solutions is lower than would be expected. The results are shown in Table VI and plotted in Figure 3.

Table VI. Adsorptive Capacity of Davison 28-200 Gel for Toluene from Toluene-Cyclohexene–Iso-octane Solutions

(Solute, 20% v. toluene in each case)

Vol. %	Solvent	Capacity, Ml./100 G.
100	Iso-octane	19.8
20	Cyclohexene in iso-octane	15.3
50	Cyclohexene in iso-octane	10.0
80	Cyclohexene in iso-octane	7.5
100	Cyclohexene	6.1

The broken line in Figure 3 represents the capacity for toluene if the effect of olefin concentration were linear; the actual data joined by the solid line show the exaggerated influence of the olefin.

From the capacity data given above it is possible to calculate the minimum quantity of gel required to adsorb the aromatics or olefins from a binary solution of the pure compounds studied. By the application of the curve shown in Figure 3, it is also possible to approximate closely the gel required to adsorb the aromatics and olefins from a ternary solution of the compounds studied. When a gasoline or refinery stock is to be separated into its hydrocarbon groups over silica gel, the precise calculation of the amount of adsorbent required involves (1) the analysis of the sample for olefins and aromatics, and (2) data concerning the capacity of the gel for the type and concentration of olefins and aromatics in the sample. Although item 1 can readily be obtained by the usual analytical methods (the silica gel method itself

can be used to advantage), item 2 requires an accurate knowledge of the major compounds present in the sample and the capacity of the gel for each of them from the appropriate solutions. For practical purposes, however, no serious error is involved in assuming that the "average olefin" behaves like diisobutylene and the "average aromatic" like toluene in iso-octane solution. Furthermore, it may be assumed that the ratio of the capacities of two gels for olefins is the same as the ratios of their capacities for toluene. In Table VII this assumption is shown to be justified. If the capacity of the gel to be used in a separation is known in terms of milliliters of toluene per 100 grams of adsorbent from a 20% by volume solution in iso-octane, the corresponding capacity for diisobutylene can be calculated by use of the data in this table.

Table VII. Calculated and Actual Capacities of Davison and International 28- to 200-Mesh Gels for Olefins

(Based on ratios of capacities for toluene)

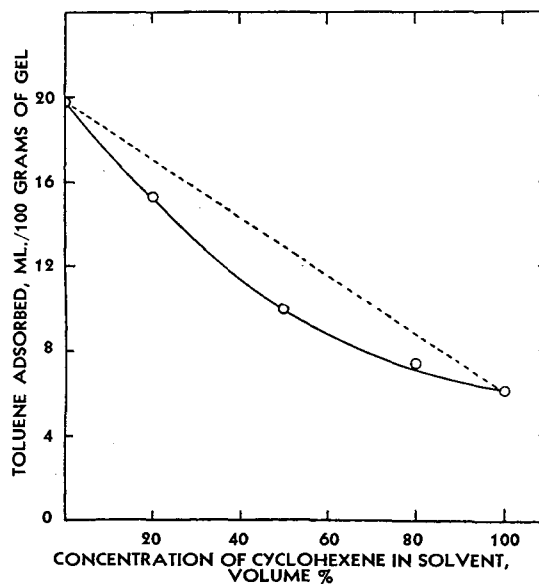| Vol. %	Solution Separated	Capacity, Ml./100 G.		International
		Davison		
20	Toluene in iso-octane	19.8		17.2
		Calcd.	Measured	
20	Diisobutylene in iso-octane	11.3	11.3	9.8
20	Cyclohexene in iso-octane	13.1	13.4	11.4

Figure 3. Adsorptive Capacity of Davison 28-200 Gel for Toluene from Toluene-Cyclohexene–Iso-octane Solutions

20% v. toluene in each case

The capacity value for the aromatics must be corrected for the olefin content of the solvent. This can be accomplished with fair accuracy by applying the same percentage deviation from linearity as was shown in Figure 3; however, where the aromatic content is above 20% by volume, the increase in aromatic capacity over the base value for a 20% solution tends to cancel out the above-mentioned deviation and both corrections may be ignored for practical purposes.

By making the above simplifying assumptions, the following expressions can be written to approximate the capacity of a silica gel for the aromatics, C_a, and olefins, C_o, in a gasoline:

$$C_a = C + 8(X_a - 0.2) - 7.5 \frac{X_o}{1 - X_a}$$

Table VIII. Effect of Temperature on Adsorptive Capacity of Silica Gel

Vol. %	Solution Percolated	Capacity of Gel, Ml./100 G.			Change in Capacity, % per ° C.[a]
		25° C.	3° C.	−40° C.	
20	Toluene in iso-octane	19.8	21.6	24.6	0.31
40	Toluene in iso-octane	22.0	23.1	25.4	0.21
20	Cyclohexene in iso-octane	13.4	..	19.6	0.49
40	Cyclohexene in iso-octane	16.0	..	22.2	0.43
20	Diisobutylene in iso-octane	11.3	..	18.6	0.60
20	Toluene in cyclohexene	6.5	..	8.6	0.38

[a] Based on capacity at −40°.

where C = gel capacity in ml. of toluene per 100 grams from a 20% by volume solution in iso-octane, X_a = volume fraction of aromatics, and X_o = volume fraction of olefins.

$$C_o = 0.5\,C + 8\left(\frac{X_o}{1-X_a} - 0.2\right)$$

The volume of gasoline, V_g, to be charged to a weight of gel, W, is calculated thus:

$$V_g = \frac{W}{\dfrac{100\,X_a}{C_a} + \dfrac{100\,X_o}{C_o}}$$

In the cases where the nonsaturate portion of the sample is predominantly olefinic or aromatic, the capacity figure for the minor constituent need not be calculated separately, inasmuch as components present in low concentrations are never recovered pure in the type of apparatus used in this work. It has been shown that no loss in separation efficiency results when an excess of gel is used; however, in fairly large scale separation it is necessary to know the approximate minimum quantity of gel necessary to effect a given separation in order to take full advantage of the adsorbent and equipment available.

TEMPERATURE COEFFICIENT. In most adsorption processes an increase in the capacity of the adsorbent is obtained by decreasing the operating temperature; all the capacities reported here have been determined at about 25° C. The effect of temperature on the adsorptive capacity of silica gel for various aromatics and olefins has been determined. These measurements were carried out in a jacketed 1 × 40 cm. column through which was circulated acetone chilled with either ice or a dry ice–acetone mixture; the outlet jacket temperatures were 3° ± 1° C. and −40° ± 1° C., respectively. Davison 28- to 200-mesh gel tempered at 100° C. for 16 hours was packed into the column.

The data in Table VIII indicate that an appreciable increase in the adsorptive capacity of silica gel can be obtained by decreasing the temperature to −40° C. The rate of change of capacity with temperature appears to be about linear in the range studied, and decreases markedly with increasing concentration in the case of the toluene–iso-octane solution and moderately in the case of the cyclohexene–iso-octane solution. In the case of solutions containing olefins, the temperature coefficient of capacity was appreciably higher than in the case of the toluene–iso-octane solution.

This increase in the capacity at reduced temperatures makes it possible to separate greater volumes of a hydrocarbon mixture over a given column of gel if cooling is employed. The volume of charge may be increased approximately 0.4% for each degree of cooling below room temperature.

EFFECT OF TEMPERING CONDITIONS. It has been generally recognized that excessive exposure of silica gel to moisture results in the loss of its capacity for adsorbing hydrocarbons. Although most commercial gel samples are shipped in sealed containers and have a high capacity on receipt, the tempering con-

ditions necessary to restore the capacity of a wet gel have been investigated briefly as a prelude to the study of regeneration. It has been found that wet silica gel can be dried to nearly optimum capacity at temperatures as low as 100° C. A sample of Davison 28- to 200-mesh gel having a capacity of 19.8 ml. per 100 grams as received was thoroughly wetted with distilled water. Small portions were placed in porcelain evaporating dishes and tempered for various periods at 110° C. The data in Table IX show that the original capacity of the gel is restored after drying only a few hours under these conditions.

It will be shown later that virtually the same capacity level is obtained at 220° C. as at 110° C.; at temperatures in excess of 300° C., however, lower than optimum capacities result.

Polymerization Activity. One of the chief difficulties encountered previously in developing the adsorption method for separating hydrocarbons was the polymerization of certain types of olefins during passage over the silica gel. Because any structural changes of the olefins caused by contact with adsorbent will lead to erroneous conclusions concerning the chemical and physical properties and engine behavior of the unsaturates originally present in the gasoline, it was necessary to study further the variables affecting this property of the gel.

Table IX. Effect of Tempering Time at 110° C. on Capacity of Water-Wetted Davison 28- to 200-Mesh Silica Gel

Time of Tempering at 110° C., Hours	Capacity, Ml./100 G.
3.5	19.1
5	19.3
7	18.9
16	19.2

The investigators at the Bureau of Standards (6) found that a highly branched olefin such as 2,4,4-trimethyl-1-pentene, one of the diisobutylene isomers, is easily polymerized over Davison 659150 gel. Cooling the gel column with ice water, increasing the flow rate of the hydrocarbon over the column, and passing a paraffin over the gel prior to passing the olefin aided in reducing the rate and extent of polymerization but did not completely solve the problem.

EFFECT OF TEMPERING CONDITIONS. From preliminary experiments carried out with gels tempered under slightly different conditions it was suspected that the conditions (temperature and duration) of tempering had a pronounced effect on the tendency of the gel to cause polymerization. A series of experiments was carried out to investigate this effect. Peroxide-free diisobutylene was passed at room temperature over 1 × 40 cm. columns of various gels which had been tempered in an oven about 5 hours at a variety of temperatures. The first 5 ml. of effluent were collected from the column in 1-ml. cuts. An increase of refractive index above that for the original diisobutylene (1.4110) indicated polymerization. In each case where polymerization occurred it was noted that the first milliliter collected was polymerized to a greater extent than the following fractions. The results of this study are shown in Table X; the refractive index of the first 1-ml. fraction is used as the criterion of the relative extent of polymerization. (Where polymerization is completely absent, the

Table X. Effect of Tempering Conditions on Tendency of Silica Gels to Polymerize Diisobutylene

Silica Gel	Tempering Temperature			
	100° C.	125° C.	150° C.	330° C.
	Refractive Index of First Ml.			
Davison 659528-2000	1.4151	1.4165	1.4200	1.4118
Davison 8595150	1.4104	...	...	...
Davison intermediate	1.4103	...	1.4104	...
International 28-200-mesh	1.4110	1.4127	1.4120	1.4275

first milliliter may have a refractive index of about 1.4104 due to the separation of a trace of saturates which occur as impurities in the olefin.) The time required for the hydrocarbon to wet the gel was approximately 30 minutes for the 28- to 200-mesh gels and about 1 hour for the finer gels.

The data in Table X show that increasing the tempering temperature has a pronounced effect on the tendency of certain gels to polymerize diisobutylene. The Davison 659528-2000 gel was appreciably more active than the International gel tempered under the same conditions. The first milliliter of effluent from the Davison gel which was heated to 330° C. had a refractive index approaching that of pure tetraisobutylene (1.4482). The fact that the Davison 8595150 and Intermediate gels caused no polymerization after being heated to 100° and to 150° C. for several hours indicates that some property of the gel, other than those affected by tempering, influences the polymerization tendency. However, the polymerization activity of certain gels can be greatly accentuated or practically eliminated by varying the heat treatment prior to use.

The effect of tempering conditions on adsorptive capacity, polymerization tendency, water loss, and surface area of the Davison gel is shown in Table XI. Adsorptive capacity was determined as described previously. Polymerization tendency was determined by passing 10 ml. of diisobutylene at room temperature over a 1.7 × 60 cm. column and eluting the hydrocarbon with methanol; it is expressed as per cent conversion to tetraisobutylene (calculated from the refractive index of the sample before and after passage over the gel). Water loss was determined by weighing the sample before and after tempering. The surface area was measured by low temperature nitrogen adsorption and application of the Brunauer, Emmett, and Teller equation.

The data in Table XI show that the adsorptive capacity remains fairly constant up to and including 220° C.; between this temperature and 700° to 900° C. the capacity falls off sharply. There seems to be no relation between adsorptive capacity and polymerization tendency. The tendency of the gel to polymerize olefins increases sharply when the water loss increases from 0.49 to 0.71% by weight, although the capacity remains essentially constant; when the water loss increases from 0.71 to 7.5% by weight, the capacity shows a sharp decrease while polymerization tendency continues to increase. The surface area and adsorptive capacities are directly related; however, there seems to be no relation between surface area and catalytic activity of the gel for polymerization of olefins. These data further show that this Davison gel can be tempered in such a way that the capacity will be high and the polymerization tendency negligible.

It might be expected that the quantity of acid adsorbed on the gel would influence the extent of polymerization. A 100-gram sample of each of the gels listed in Table X was washed with distilled water on a Büchner funnel until 100 ml. of wash water were collected; the acidities of the wash water samples were determined and found to be:

	pH
Davison 659528-2000	2.1
International	1.4
Davison 8595150	2.8
Davison intermediate	2.8

When the pH and polymerization tendencies of the Davison 659528-2000 and International gels are compared, it is seen that acid content gives no indication of a gel's ability to polymerize olefins.

It was also shown in a few experiments where varying concentrations of benzoyl peroxide and tert-butyl hydroperoxide were added to diisobutylene prior to percolation that these peroxides do not catalyze the polymerization in this process.

The ease of polymerization of other olefins was examined. It was found that the behavior of 2-methyl-2-pentene is closely comparable to that of diisobutylene. trans-3-Heptene, 1-hexene, and cyclohexene were much more difficult to polymerize than diisobutylene.

Table XI. Effect of Tempering Conditions on Various Properties of Davison 569528-2000 Silica Gel

Tempering Conditions Hours	°C.	Water Loss, Wt. %	Gel Capacity, Ml./100 G.[a]	Polymerization Tendency[b]	Surface Area, Sq. Meters/G.
Untempered[c]		0	18.8	0	780
4	100	0.14	19.0	2.4	770
22	100	0.37	19.2	7.1	780
4	220	0.49	20.2	8.2	750
23	220	0.71	19.8	32.0	790
4	700-900	7.5	12.6	69.0	280

[a] From 20% v. solution of toluene in iso-octane.
[b] % theoretically converted to tetraisobutylene.
[c] As received from manufacturer.

Table XII. Effect of Percolation Temperature on Polymerization Tendency of Davison Silica Gel

Tempering Conditions °C.	Hours	Polymerization Tendency, % Conversion to Tetraisobutylene 25° C.	3° C.	−40° C.
160	16	34	12	0
100	16	7	0	0

The easily isomerized olefin, 3-methyl-1-butene, has been percolated at room temperature over 1 × 40 cm. columns of Davison 659528-2000 gel tempered at 152° C. for 5 hours (high polymerization activity) and International gel tempered at 100° C. for 3 hours (low polymerization activity). Because the refractive indexes of 3-methyl-1-butene and 2-methyl-2-butene, the more stable isomer, differ by 229 units, any appreciable isomerization would have been indicated by a change in the refractive index. The refractive index of the effluent from the columns showed that neither of these gels altered the composition of this olefin. It has likewise been shown that neither of these gels catalyzes the isomerization of 1-pentene at room temperature.

EFFECT OF PERCOLATION TEMPERATURE. Although it is possible to temper a gel in such a way that polymerization of olefins does not occur in a 40-cm. column at room temperature, it is possible that appreciable polymerization may occur when very long columns are employed (long contact time, high ratio of gel to hydrocarbon). Since the National Bureau of Standards found that reducing the percolation temperature tended to reduce the extent of polymerization, this variable has been studied further. Experiments were carried out by passing 10 ml. of diisobutylene over 127 grams of silica gel (Davison 659528-2000 tempered at 160° C. for 16 hours) packed into a 1 × 240 cm. column. The time required for the hydrocarbons to pass down the column was approximately 5 hours; the olefin was eluted with methanol, washed with water, and dried, and the refractive index was redetermined. The extent of polymerization, expressed as per cent conversion to tetraisobutylene, was calculated from the refractive index of the effluent.

Table XII shows that with an active gel the extent of polymerization is decreased sharply as a result of reducing the percolation temperature to 3° C. and that no polymerization occurs at −40° C. The same gel tempered under mild conditions gave slight polymerization at room temperature, whereas at 3° C. the diisobutylene passed over the gel unchanged. Because the extent of polymerization is decreased and the adsorptive capacity is increased at lower percolation temperatures, cold operation of an adsorption column used for the separation of olefins seems very desirable.

REGENERATION OF ADSORBENT

In the separation of large quantities of gasolines and refinery stocks by the adsorption method it is desirable, for the sake of economy, to be able to regenerate the adsorbent. From the standpoint of the time and labor required to carry out a series of separations, regeneration in place is preferable to batch regeneration. The desirability of regeneration in place has been recognized by most investigators in this field. Regeneration may be

considered in two steps, the desorption of the hydrocarbon and the reactivation of the gel. The first step is usually accomplished by elution with methanol or ethyl alcohol as recommended by the National Bureau of Standards (6). The second step involves essentially the removal of the entrained and adsorbed eluent; however, unless the gel, charge, and eluent are absolutely dry, it is likely that desorption of traces of water is also involved to some extent. Mair and Forziati (7) have proposed either sweeping out the eluent with steam followed by inert gas at a temperature of 180° to 200° C. or simply passing inert gas while raising the temperature gradually to 180° to 200° C.
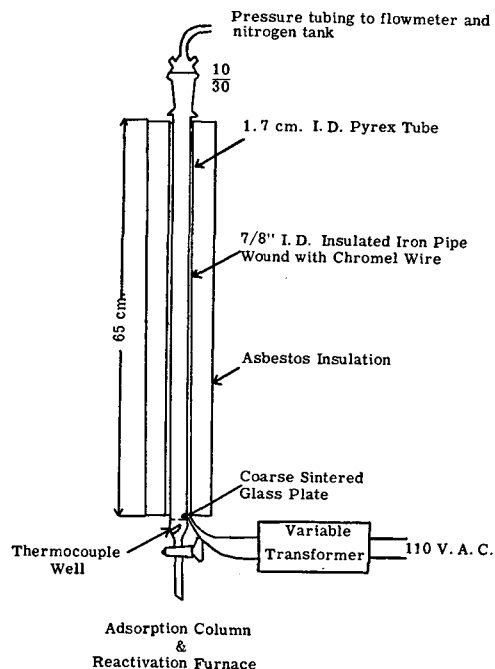

Figure 4. Apparatus Used in Regeneration of Silica Gel in Situ

Extensive data have not been presented on the effect of type and quantity of eluent, tempering time, temperature, pressure, rate of gas flow, and presence of steam on the capacity of the regenerated gel. With these variables in mind, experiments have been conducted to determine the best practical conditions for the in situ regeneration of silica gel in small glass columns.

Effect of Temperature. The diagram in Figure 4 shows the adsorption column and furnace used in the preliminary studies on regeneration.

The procedure was to pack the column with fresh gel to a depth of 60 cm., percolate a 20% by volume solution of toluene in iso-octane, collect 2-ml. fractions of filtrate until the original solution came through in order to calculate the capacity, and add c.p. methanol until pure alcohol came through. The column was then inserted in the furnace and pressure of about 2 pounds per square inch of nitrogen was applied. After the entrained alcohol ceased to drip from the column, a thermocouple was inserted in the well and the temperature of the effluent gas raised to the boiling point of the alcohol. When most of the alcohol had passed out of the column, the temperature of the effluent gas was raised to the desired value. At the conclusion of the tempering period, the heat and gas flow were cut off and the column of gel was sealed from the atmosphere while cooling.

The effect of tempering temperature on the adsorptive capacity of Davison 659528-2000 gel over a series of three regeneration cycles is shown in Table XIII. At temperatures of 120° C. and higher, maximum capacity was obtained after a 30-minute tempering period (following the initial drying of the gel) with nitrogen passing through the adsorbent column. However, at 100° C. it was necessary to attach a vacuum pump to the column outlet and extend the tempering time to 5 hours in order to obtain

maximum capacity. These data indicate that the rate of capacity decline is somewhat less at lower temperatures; however, it appears that, as the normal boiling point of the eluting agent is approached, the time required for equilibrium desorption to occur increases rapidly.

Table XIII. Effect of Tempering Temperature on Capacity of Davison 659528-2000 Gel during Three Regeneration Cycles

No. of Regeneraations	Regeneration Conditions			
	100° C., reduced pressure[a]	120° C., 50 cc. N₂/min.[b]	190° C., 50 cc. N₂/min.[b]	230° C., 50 cc. N₂/min.[b]
	Capacity, Ml. Toluene/100 G.			
0	18.9	19.6	19.8	19.9
1	18.1	17.0	16.0	17.2
2	15.8	15.9	14.1	15.0
3	15.4	14.8	11.6	12.9

[a] 5 hours required to reach optimum capacity.
[b] 30 minutes required to reach optimum capacity.

Action of Eluting Agents. If the decrease in capacity of the gel which results on regeneration is caused by a failure of the eluting agent to remove very strongly adsorbed materials from the gel, it seems likely that some desorbing agent other than methanol may prove more satisfactory. Table XIV gives the capacity of Davison 28- to 200-mesh gel after elution with two types of alcohols and various mixtures of polar solvents. Tempering of the wet gels was carried out in an oven at 100° to 110° C. for 20 hours. The results shown in Table XIV indicate:

Methanol in excess of the volume required to elute the hydrocarbon from the gel seems to have no beneficial effect on the capacity of the regenerated gel.
Absolute ethyl alcohol is definitely inferior to methanol; boiling the gel in water after elution with ethyl alcohol increases the capacity slightly.
Aqueous methanol gives results very comparable to the anhydrous alcohol; a mixture of acetic acid and methanol is harmful even when followed by pure methanol.
Washing with water after methanol elution is slightly better than washing with methanol alone.

Effect of Hydrocarbon Mixture Separated. In the experiments described regeneration of the gel was carried out after a solution of 20% by volume toluene in iso-octane had been passed over the gel. Because gasolines may contain constituents which are more difficult to desorb and are not present in the pure hydrocarbons, experiments were carried out to determine if additional steps in the regeneration process are necessary. The results are shown in Table XV. In these runs 10 ml. of a C₇ cut of a catalytically cracked gasoline, which had been stored under atmospheric conditions for a year, were passed over 25 grams of the gel. The gasoline was then eluted with 50 ml. of methanol and the gel was tempered in an oven at 100° to 110° C. for 20 hours.

Table XIV. Effect of Type and Volume of Eluting Agent on Response of Davison 28- to 200-Mesh Gel to Regeneration

(Solution percolated, 20% v. toluene in iso-octane. Original capacity, 19.8 ml. toluene/100 g.)

Eluting Agent	Volume, Ml.	Capacity after One Regeneration, Ml. Toluene/100 G.
c.p. methanol	25	19.1
	50	19.0
	200	18.6
c.p. methanol, 25 ml., followed by 2 hours' boiling in H₂O	...	19.7
Absolute ethyl alcohol	25	16.4
Followed by 2 hours' boiling in H₂O	...	17.5
10% v. H₂O in methanol	50	18.8
10% v. c.p. acetic acid in methanol	50	16.3
Followed by methanol	50 of each	16.7
c.p. methanol followed by H₂O	50 of each	19.4

The data in Table XV indicate that this gasoline has no more harmful effect on the Davison gel than do the pure hydrocarbons. This was further verified in an experiment where a straight-run kerosene was separated into saturates and aromatics by percolating 500 ml. of the material over 1000 grams of the same Davison gel. After the hydrocarbon was eluted with methanol, it was possible to regenerate the gel in an oven at 100° to 110° C. for 20 hours to a capacity of 17.8 ml. of toluene per 100 grams of gel; by in situ regeneration in a 1 × 40 cm. column at 100° C. for 4 hours in a stream of air, 18.2 ml. per 100 grams were obtained.

Response of Different Gels to Regeneration. The in situ regeneration experiments described thus far indicate that, after three regenerations under optimum conditions, the capacity of the Davison 659528-2000 gel had decreased to such an extent that further use would be impractical. In order to determine if various commercially available gels show the same behavior on regeneration, a more recent shipment of Davison 28- to 200-mesh gel (manufacturer's designation 12-08-09-01) and a recent sample of International 28- to 200-mesh gel have been compared with the Davison gel mentioned above (see Table XVI). The tempering of the first two gels was carried out in an oven at 100° C. for 16 hours, while the last mentioned gel was tempered in situ in a nitrogen stream at 100° C. for 5 hours. (It has been shown that these two procedures give closely comparable results.)

The data listed in Table XVI indicate that the Davison gel designated 12-08-09-01 is definitely superior to either of the other gels in the response to regeneration. A series of in situ regenerations has been carried out on this gel. These experiments were performed in a jacketed 1 × 40 cm. column at 100° C. for 5 hours. During the tempering period steam was passed through the jacket and a stream of dry nitrogen was passed over the gel. The results showed that the capacity of the gel had decreased from 20.3 ml. of toluene per 100 grams to 18.3 ml. per 100 grams after the second regeneration. After the third regeneration the capacity had dropped to 18.0 ml. per 100 grams; no further decrease in capacity occurred after seven regenerations. The response of this gel either to in situ regeneration in a 1 × 40 cm. column or to oven tempering indicates that it would be satisfactory for repeated use in this separation process.

Effect of Eluents at Elevated Temperature and Pressure. In situ regeneration of silica gel in large scale laboratory equipment would be expected to be much more difficult than in a small scale column, owing to the high pressure drop involved in a very long column. It is conceivable that complete desorption of the eluting agent at the pressures required to maintain reasonable space velocities of the flush gas would take place only at temperatures considerably above the normal boiling point of the liquid. Accordingly, the effect of exposing the Davison 12-08-09-01 gel to various possible eluting agents under regeneration conditions approximating large column operation has been studied.

Table XV. Effect of Catalytically Cracked Gasoline Cut on Response of Davison 12-08-09-01 Gel to Regeneration

No. of Cycles[a]	Capacity, Ml. of Toluene/100 G.
0	20.3
1	17.7
2	17.6
3	17.6

[a] A cycle consists of percolation of 10 ml. of gasoline over 25 grams of gel, regeneration, percolation of 20% v. toluene in iso-octane to determine capacity, and another regeneration.

Table XVI. Response of Three Commercial Silica Gels to Regeneration at 100° C.

No. of Regenerations	Capacity, Ml. of Toluene/100 G.		
	Davison 12-08-09-01	International	Davison 659528-2000
0	20.3	19.1	18.9
1	19.0	18.0	18.1
2	16.9	16.7	15.8
3	18.5	15.3	15.4
4	17.8	14.5	...

Table XVII. Effect of C.P. Methanol at Elevated Temperatures and Pressures on Capacity of Davison Gel

Time of Contact, Hour	Contact Temperature		
	Room Temperature	110° C.	150° C.
	Capacity after tempering, ml. of toluene/100 g.		
0	17.2[a]	...	...
16	...	14.3	8.7
24	...	13.7	...
100	...	12.3	...

[a] Sample of gel wetted with alcohol, then tempered.

Table XVIII. Effect of Eluting Agents at Elevated Temperatures on Capacity of Davison Gel

(Contact temperature, 146° ± 1° C.)

Eluting Agent	Capacity, Ml. of Toluene/100 G.
None	18.8
c.p. methanol (Mallinckrodt)	12.5
Denatured alcohol, Formula 3A	14.2
Absolute ethyl alcohol	12.2
c.p. acetone (Shell Chemical)	16.3
Freshly distilled	18.2
c.p. methyl ethyl ketone (Shell Chemical)	13.6
Anhydrous isopropyl alcohol (Shell Chemical)	11.5
Distilled water	6.7

Small metal bombs consisting of 6-inch (15-cm.) capped nipples of $^3/_4$-inch standard black iron pipe were used in these experiments. About 25 grams of fresh gel were poured into the bomb, packed tightly, and wetted with 25 ml. of solvent. The cap was then screwed on tightly and the bomb placed in a thermostated oven (±1° C.). At the end of the desired heating period the bomb was removed and allowed to cool to room temperature. The gel was then removed and tempered 5 hours at 110° C., and the capacity was determined. The results obtained with c.p. methanol at 110° and 150° C. aging temperatures are shown in Table XVII.

The results in Table XVII show that deactivation of the gel by methanol occurs at elevated temperatures and pressures likely to be encountered in large column operation. The accelerating effect of increasing the temperature or of increasing the contact time at a given temperature is clearly indicated. Because the rate of regeneration in a large column depends on the rate of removal of eluent vapor from the adsorbent, which in turn is favored by high temperatures and large pressure gradients, it is doubtful that methanol could be completely desorbed from the gel within a reasonable period under conditions that would result in a negligible capacity loss due to deactivation.

The effect of exposing Davison 12-08-09-01 gel to other possible eluting agents has been investigated in an effort to find a desorbing liquid more suitable than methanol. The procedure described for the experiments on methanol was followed, except that the bombs were heated for 16 hours at 146° ± 1° C. (Table XVIII).

The most desirable eluting agent shown in Table XVIII appears to be c.p. acetone. Its deleterious effect was reduced to practically nil by redistillation immediately before use. Although it is possible that the other organic solvents would also show improvement on redistillation, acetone appears to be the most practical eluting agent because of its additional advantages of low toxicity and high volatility.

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(Separation of Cracked Gasolines by Chromatographic Adsorption)

FACTORS AFFECTING EFFICIENCY OF SEPARATION

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The influence of the important variables affecting the efficiency of separation of complex hydrocarbon mixtures is discussed. The sharpness of separation between hydrocarbon classes in a given column increases as the particle size of the gel is reduced; for a given gel particle size the sharpness of separation of a gasoline containing aromatics plus olefins in a quantity slightly less than the calculated gel capacity is directly proportional to the length and inversely proportional to the square of the diameter of the column used—i.e., separation efficiency α L/D^2. Good separation of a catalytically cracked gasoline into saturates, olefins, and aromatics can be accomplished in a column having an L/D^2 (cm./sq. cm.) of 80 if "through-200-mesh" gel is used, or in a column having an L/D^2 (cm./sq. cm.) of 230 if 100- to 200- mesh gel is used. To obtain maximum sharpness of separation with a given column and gel, the gel should be packed into the column to the greatest possible extent; the quantity of aromatics plus olefins in the sample charged should be slightly less than the calculated gel capacity; the sample should be forced into the adsorbent column as completely as possible before the eluting agent is added; the hydrocarbon front should travel at a linear rate between 1 and 20 mm. per minute; and an eluting agent should be selected which will give a sharp interface with the hydrocarbon mixture at the percolation temperature used. Small columns made from black iron pipe are as efficient as smooth-walled glass columns and are much more easily packed with finer gels.

THE development of a satisfactory method for separating complex hydrocarbon mixtures such as cracked gasolines into pure saturate, olefin, and aromatic portions is desirable to gain a further insight into the composition and properties of various petroleum fractions. Chromatographic adsorption over silica gel is a promising physical method for effecting such a separation. The adsorptive capacity, polymerization tendency, and regeneration of various commercial silica gels have been reported (1). Another important consideration in a process of this type is the degree of separation that can be obtained. The sharpness of separation between hydrocarbon groups will determine the quantities of pure saturates, olefins, and aromatics that can be obtained over a given weight of gel; if optimum conditions are not maintained during a separation, the adsorptive capacity of the gel and the equipment available will not be utilized effectively. An understanding of the effect of column dimensions is necessary before large scale equipment can be designed.

GEL FACTORS

Most investigators in this field have noted that the sharpness of separation increases as the particle size of the silica gel decreases. In experiments in this laboratory with commercial gels of various particle size ranges it has also been noted that the fine gels give a much more efficient separation. In most cases the particle size of these commercial gels varies over a wide range. Because other studies have indicated that gels having a rather narrow particle size range would be preferable for large scale operation, the separations obtainable with fractions of various mesh sizes have been compared.

In these experiments 50% by volume toluene in iso-octane was percolated over thoroughly packed 1.7 $\times$ 100 cm. columns of the gel. In each case the quantity of solution percolated contained toluene to the extent of 100% of the gel capacity for toluene from this solution. The hydrocarbon was eluted with ethyl alcohol and collected in small fractions from the column; a hydrocarbon

material balance of 98 to 100% was obtained in each case. The degree of separation is expressed as the per cent of toluene present in the original solution which was recovered in greater than 98% purity.

Table I. Effect of Mesh Size on Degree of Separation

Type of Silica Gel	Degree of Separation, % V. Toluene Recovered in > 98% Purity
Davison 28- to 200-mesh	74
Davison 60- to 100-mesh	73
International 100- to 200-mesh	82
Davison 100- to 325-mesh	89

The data in Table I illustrate the definite advantage obtained when finer gels are employed in a separation. There are, however, limitations imposed on the use of fine gels in larger columns—for example, a pressure of more than 50 pounds per square inch is required to force a sample at a reasonable rate through an 8-foot (240-cm.) column of gel ground to pass a 200-mesh screen. Fine gels have been found much more difficult to settle completely in a tube than coarser ones. In addition, the ease of regeneration of the adsorbent in situ diminishes rapidly as the gel particle size is reduced as a result of the high pressure drops involved. In a later report it will be shown that even a gel as coarse as 100- to 200-mesh has disadvantages for large column operation. A gel containing 25 to 50% by weight through-325-mesh material can be employed in 8- to 9-foot columns for obtaining hydrocarbon analyses within an 8-hour period; pressures required do not exceed 50 pounds per square inch.

COLUMN FACTORS

Dimensions. It is well known qualitatively that the dimensions of the adsorption column exert an important effect on the degree of separation; the recovery of pure saturates, olefins, and aromatics from a given mixture increases as the column length increases and as the diameter decreases. However, no data are available from which one can predict the column dimensions

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Table II. Effect of Column Dimensions on Degree of Separation

(40% v. cyclohexene in iso-octane over Davison 28- to 200-mesh gel)

Column Length, Cm.	Column Diameter, Cm.	% Component Recovered, >98% Purity	
		Iso-octane	Cyclohexene
100	2.82	90 ± 3	49 ± 1
236	2.82	92 ± 2	68 ± 1
100	1.7	94 ± 2	75 ± 1
236	1.7	92 ± 1	86 ± 1
100	1.0	95 ± 1	89 ± 1
236	1.0	91 ± 2	94 ± 1
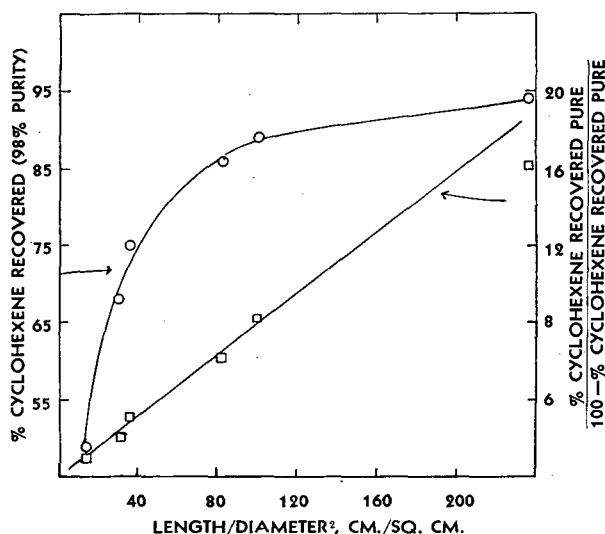
Figure 1. Effect of Column Dimensions on Degree of Separation of 40% by Volume Cyclohexene in Iso-octane over Davison 28–200 Gel

necessary for a given separation efficiency. In order to design a large scale column, some relationship between column dimensions and the degree of separation must be developed by a detailed study.

A number of separations have been performed in columns of varying dimensions. In the first set of experiments a solution of 40% by volume cyclohexene in iso-octane was separated over Davison 28-200 gel. (This solution was selected because its somewhat greater difficulty of separation, as compared to the toluene–iso-octane solution used previously, gave a wider range of values for the columns used.) In each case the volume of the solution percolated contained cyclohexene to the extent of 80% of the total gel capacity for the olefin from this solution. The rate at which the hydrocarbon front passed down the column was maintained at 1 cm. per minute by application of the proper pressure. The hydrocarbon was desorbed with methanol and collected in small fractions. The per cent of the total cyclohexene recovered in over 98% purity was determined; a hydrocarbon material balance of 97 to 99% was obtained in each case. The results of this first series of separations are shown in Table II.

The data in Table II are plotted in Figure 1; it is seen that, when the per cent cyclohexene recovered pure is plotted against column length–diameter

squared, a smooth curve results. When the ratio of length to diameter squared is plotted against the ratio of per cent cyclohexene recovered pure to 100 minus per cent cyclohexene recovered pure, a straight line results. When the recovery of pure cyclohexene is large, the precision with which the ratio of cyclohexene recovered pure to 100 minus per cent cyclohexene recovered pure can be determined decreases, even though the experimental error remains the same. The data in Table II also show that the per cent iso-octane recovered pure is not a good criterion of separation efficiency. The high recovery of iso-octane obtained in each case here, as well as in numerous separations of pure hydrocarbon mixtures and gasolines, would make it difficult to correlate recovery of saturates with column dimensions. If the straight-line relationship in Figure 1 between a factor which defines column dimensions and one which defines the degree of separation holds for gels of different particle size and for mixtures containing all three hydrocarbon classes, it will be possible to calculate the separation possible over a large scale column from data obtained on small laboratory scale columns.

A second series of separations was carried out over various size columns of the finer gel, Davison through-150-mesh. A 40% by volume solution of cyclohexene in iso-octane was separated under the conditions described previously (Table III).

The data in Table III are plotted in Figure 2. Apparently, the same relationship between column dimensions and separation efficiency holds when fine gels are employed. A comparison of the data in Tables II and III also shows the increase in separation efficiency which results when gels of fine particle size are used.

In order to determine if this relationship also holds for solutions containing three hydrocarbon classes, a solution of 30% toluene, 30% cyclohexene, and 40% iso-octane by volume was separated over various size columns of Davison through-150-mesh gel.

The data in Table IV, plotted in Figure 3, indicate that the relationship between degree of separation and L/D^2 holds for three-component as well as two-component solutions. Although the points on the cyclohexene curve fall nearer the straight line, the curve for toluene indicates that recovery of pure aromatic would also be a reliable criterion for judging column efficiency. Again, the recovery of pure iso-octane was not very sensitive to changes in column dimensions.

In the experiments described above, the percentages of pure components recovered could be determined easily and accurately by refractive index measurements because intermediate cuts contained only two pure compounds. Although it would be desirable to establish a similar relationship for gasoline and gasoline
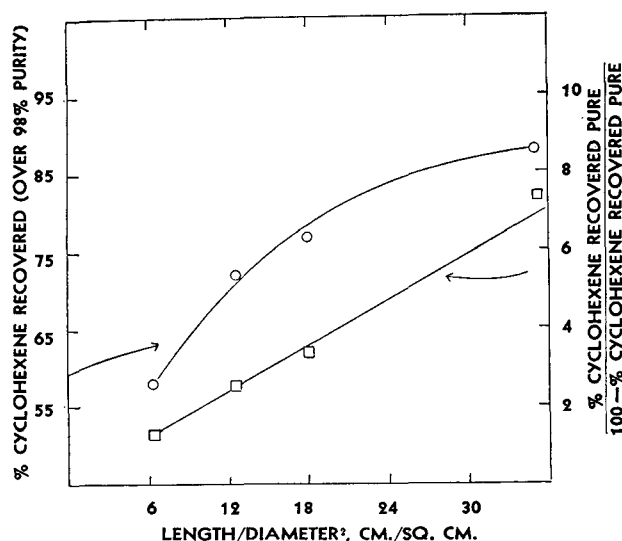
Table III. Effect of Column Dimensions on Degree of Separation

(40% v. cyclohexene in iso-octane over Davison through-150-mesh gel)

Column Length, Cm.	Column Diameter, Cm.	Length / Diameter², Cm./Sq. Cm.	% Component Recovered (>98% Purity)		% Cyclohexene Recovered Pure / 100 − % Cyclohexene Recovered Pure
			Iso-octane	Cyclohexene	
50	2.82	6.3	91 ± 1	58 ± 1	1.35 ± 0.05
100	2.82	12.6	92 ± 2	72 ± 1	2.6 ± 0.1
50	1.7	18	94 ± 1	77 ± 1	3.4 ± 0.2
100	1.7	35	95 ± 1	88 ± 1	7.4 ± 0.7

Table IV. Effect of Column Dimensions on Degree of Separation

(Three-component mixture over Davison through-150-mesh gel)

Column Length, Cm.	Column Diameter, Cm.	Length / Diameter², Cm./Sq. Cm.	% Component Recovered (>98% Purity)			% Component Recovered Pure / 100 − % Component Recovered Pure	
			I.O.[a]	C₆H₁₀	C₇H₈	C₆H₁₀	C₇H₈
236	2.2	49	96 ± 1	40 ± 1	45 ± 1	0.67 ± 0.03	0.82 ± 0.03
236	1.7	82	96 ± 1	56 ± 1	64 ± 1	1.25 ± 0.05	1.81 ± 0.04
236	1.0	236	98 ± 1	80 ± 1	82 ± 1	4.1 ± 0.2	4.6 ± 0.3

[a] Iso-octane.

fractions, the accurate determination of per cent recovery of pure saturates, olefins, and aromatics by means of bromine number and refractive index measurements is difficult. When separation efficiency is low, a large number of cuts of 85 to 98% purity are obtained and the definition of "pure" constituent becomes decidedly arbitrary; when separation efficiency is higher, fractionation of molecular species within a hydrocarbon class occurs and the base values to be used for analysis of intermediate cuts are in considerable doubt. Consequently, in the experiments described on the effect of column dimensions on the degree of separation of actual gasolines, the objectives were (1) to establish the minimum L/D^2 range necessary to separate typical gasolines into saturates, olefins, and aromatics in satisfactory yields, and (2) to determine whether fairly narrow boiling fractions are more easily separated than the full-range gasolines.

Figure 2. Effect of Column Dimensions on Degree of Separation of 40% by Volume Cyclohexene in Iso-octane over Davison through-150-Mesh Gel

A 200° to 250° F. fraction of a catalytically cracked gasoline was separated over a 1 × 230 cm. column ($L/D^2 = 230$) and a 1.7 × 230 cm. column ($L/D^2 = 80$) of Davison 100- to 200-mesh gel. The percolations were carried out at −40° C.; the charge to the columns contained olefins plus aromatics to the extent of 80 to 100% of the gel capacity. The refractive index and bromine number profiles for these separations are shown in Figures 4 and 5.

A second series of separations of the same material was carried out over a 1.7 × 230 cm. column ($L/D^2 = 80$) and a 2.2 × 230 cm. column ($L/D^2 = 48$) of International gel ground and screened to pass 200-mesh. Because this gel, after tempering at 100° C., has only a slight tendency to polymerize diisobutylene, these percolations were carried out at tap water temperature. The refractive index and bromine number profiles for these separations are shown in Figures 6 and 7.

If the olefins present in the 200° to 250° F. fraction (Figure 4) are assumed to have an average bromine number of 127 grams per 100 ml. (average of the bromine numbers of the 7- to 9-ml. fraction from the percolation), then the composition of the charge is calculated to be 30% by volume saturates, 16% by volume olefins, and 54% by volume aromatics. In the same way, from Figure 6, values of 29% by volume saturates, 17% by volume olefins, and 54% by volume aromatics are obtained. On the basis of this hydrocarbon analysis for the charge, the per cent recovery of the different hydrocarbon classes (in 95 to 100% purity) is approximately:
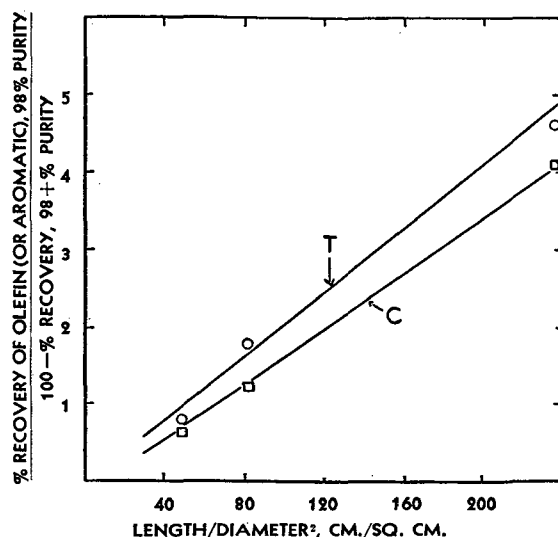

Figure 3. Effect of Column Dimensions on Degree of Separation of Three-Component Mixture over Davison through-150-Mesh Gel
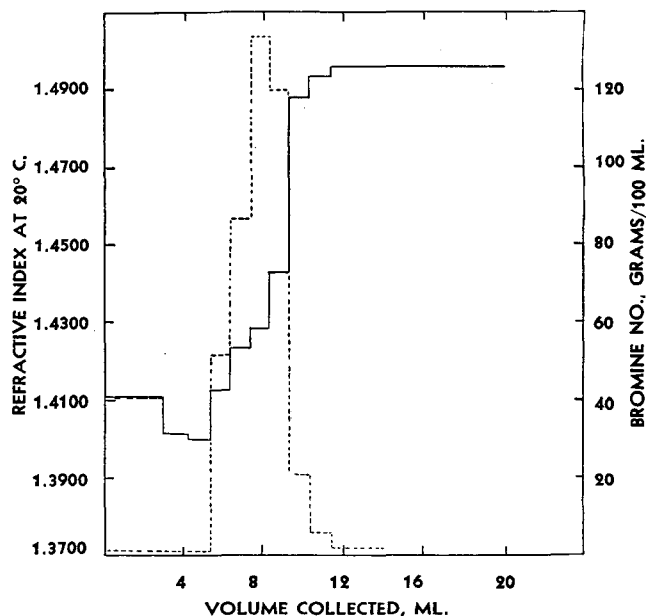
T. Toluene   *C.* Cyclohexene

Figure 4. Separation of Catalytically Cracked Gasoline Fraction (200° to 250° F.)

- - - Bromine No.   ——Refractive index
Column. 1 × 230 cm.
Gel. Davison 100- to 200-mesh (121 grams)
Charge. 20 ml.
Temperature. −40° C.

1 × 230 Cm. (100-200-Mesh Gel)	1.7 × 230 Cm. (through-200-Mesh Gel)
91% saturates	92% saturates
75% olefins	80% olefins
90% aromatics	95% aromatics

It is obvious from Figures 5 and 7 that neither the 1.7-cm. column packed with 100- to 200-mesh gel nor the 2.2-cm. column packed with through-200-mesh gel is efficient enough to give a satisfactory separation. On the basis of these data, it has been concluded that an L/D^2 of about 230 will give a satisfactory separation with 100- to 200-mesh gel; with through-200-mesh gel an L/D^2 of about 80 will give a satisfactory separation. It has been
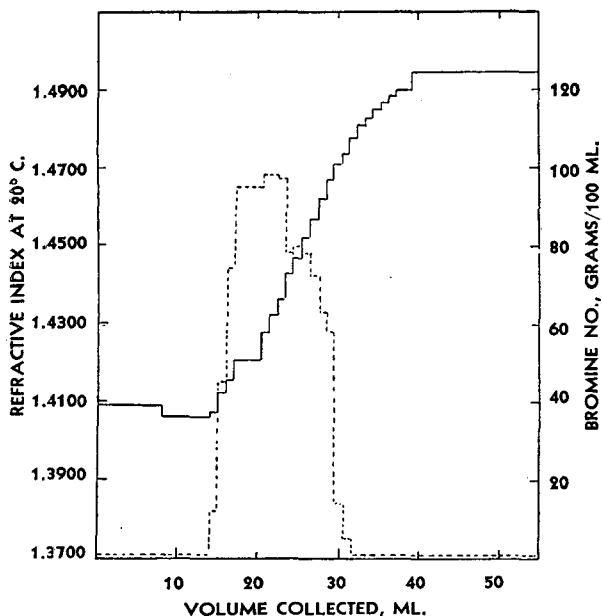
Figure 5. Separation of Catalytically Cracked Gasoline Fraction (200° to 250° F.)

- - - Bromine No.   ——Refractive index
Column.   1.7 X 230 cm.
Gel.   Davison 100- to 200-mesh (355 grams)
Charge.   60 ml.
Temperature.   —40° C.

found, however, that the through-200-mesh gel is unsatisfactory for use in a large scale column because of the excessive pressures required to maintain a satisfactory liquid flow rate and the long periods required for drying and tempering in situ.

To investigate the feasibility of separating a wide boiling range material, a partially depentanized, catalytically cracked gasoline (420° F. end point) was separated over 1 X 234 cm. and 1.7 X
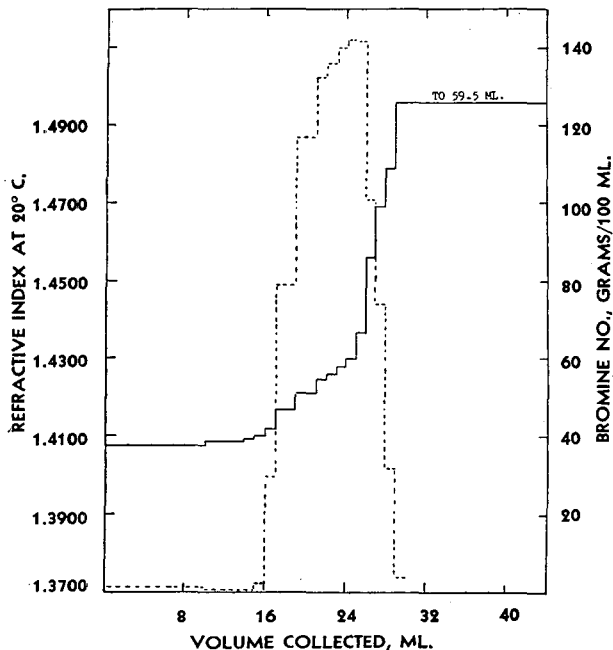

Figure 6. Separation of Catalytically Cracked Gasoline Fraction (200° to 250° F.)

- - - Bromine No.   ——Refractive index
Column.   1.7 X 230 cm.
Gel.   International through-200-mesh
Charge.   60 ml.
Temperature.   About 15° C.

234 cm. columns of Davison 100- to 200-mesh gel. These separations were carried out at −40° C. and the charge to the column contained aromatics plus olefins to the extent of 80 to 100% of the gel capacity. The refractive index and bromine number profiles for these separations are shown in Figures 8 and 9. If, in Figure 8, the average bromine number of the olefins present in the charge is assumed to be 122 grams per 100 ml. (average of the bromine numbers of the 8- to 12-ml. fractions from the percolation), the composition of the charge is approximately 45% saturates, 28% olefins, and 27% aromatics by volume. On the basis of this hydrocarbon analysis the per cent recovery of the hydrocarbon classes (98+% purity) in the 1-cm. column is approximately 93% saturates, 82% olefins, and 75% aromatics. Again it is obvious from Figure 9 that the 1.7-cm. column is too inefficient to give a satisfactory separation. Comparison of Figures 4 and 5 with 8 and 9, respectively, shows that it is as difficult to separate a relatively narrow gasoline fraction as the full range material. The conclusion that an L/D^2 of about 230 will be necessary to obtain satisfactory separations over 100- to 200-mesh gel is applicable, regardless of the boiling range of the gasoline.

Shape. The Bureau of Standards has recommended (2) that silica gel columns used for separating hydrocarbon classes have a column of small diameter sealed to a column of larger diameter, so that the hydrocarbon first passes through the large section and then through the smaller section. Presumably, the large section is intended to provide the column capacity and the small section, sometimes called the "clean-up section," the separation
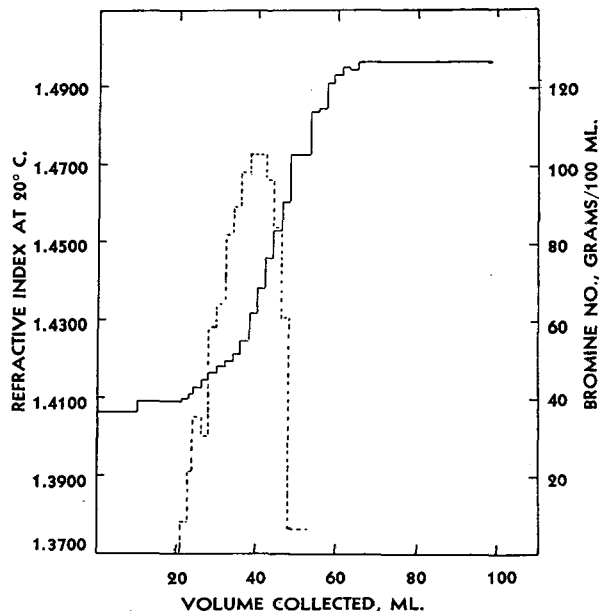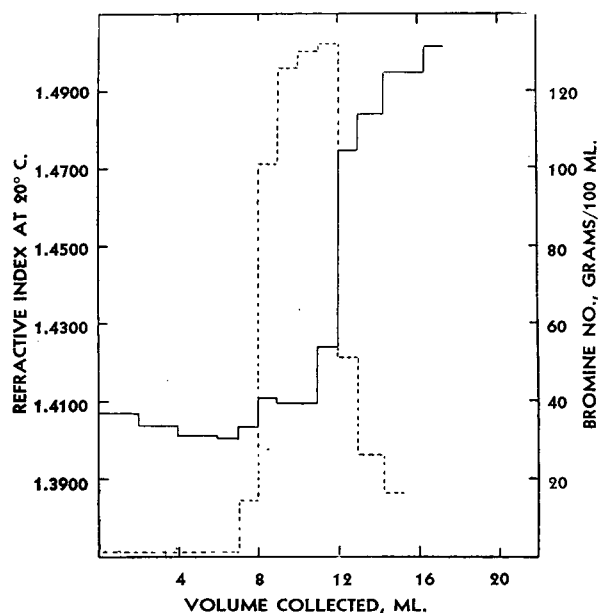

Figure 7. Separation of Catalytically Cracke l Gasoline Fraction (200° to 250° F.)

- - - Bromine No.   ——Refractive index
Column.   2.2 X 230 cm.
Gel.   International through-200-mesh
Charge.   100 ml.
Temperature.   About 15° C.

efficiency. Before a large scale column is designed it is desirable to know if a column having a clean-up section will give any better separation than one of uniform diameter and, if so, to work out a relationship between column shape and separation efficiency. For this purpose a solution of 40% by volume cyclohexene in isooctane was separated over different size and shape columns of Davison 28-200 gel. In one case 40% by volume toluene in isooctane was separated. For comparison, the same solution was separated over uniform diameter columns of the same length and

Table V. Effect of Column Shape on Degree of Separation

Column Dimensions		Equivalent Column of Uniform Diameter, Cm.	% Cyclohexene or Toluene Recovered (>98% Purity)	
Large section, cm.	Clean-up section, cm.		Nonuniform column	Uniform column

A. Solution Percolated—40% V. Cyclohexene in Iso-octane

1.7 × 61	1.0 × 61	1.4 × 122	84 ± 1	83 ± 1
1.7 × 47	1.0 × 100	1.26 × 147	88 ± 1	88 ± 1
2.2 × 48[a]	1.0 × 67[a]	1.63 × 115	77 ± 1	78 ± 1

B. Solution Percolated—40% V. Toluene in Iso-octane

2.2 × 48[a]	1.0 × 67[a]	1.63 × 115	79 ± 1	77 ± 1

[a] Column recommended by Bureau of Standards (2) for separation of aromatics and saturates.

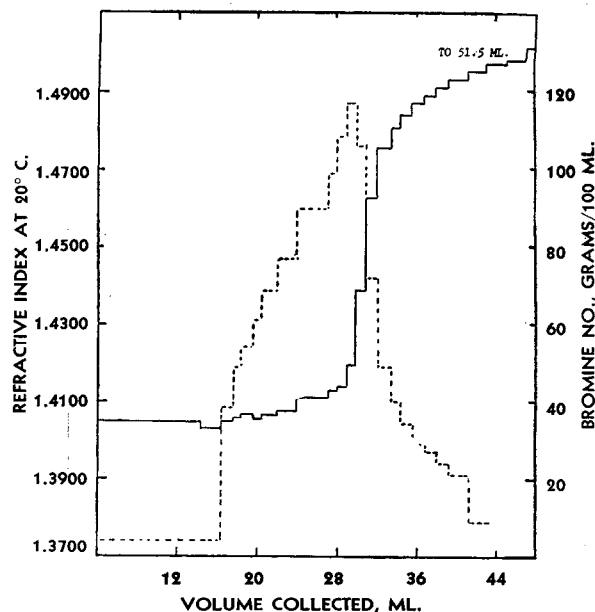Figure 8. Separation of 420 End Point Catalytically Cracked Gasoline

- - - Bromine No.   ——Refractive index
Column.   1 × 234 cm.
Gel.   Davison 100- to 200-mesh (125.5 grams)
Charge.   20 ml.
Temperature.   −40° C.

Figure 9. Separation of 420 End Point Catalytically Cracked Gasoline

- - - Bromine No.   ——Refractive index
Column.   1.7 × 234 cm.
Gel.   Davison 100- to 200-mesh (345 grams)
Charge.   59 ml.
Temperature.   −40° C.

Figure 10. Effect of Separating Varying Quantities of 20% by Volume Toluene in Iso-octane Solution
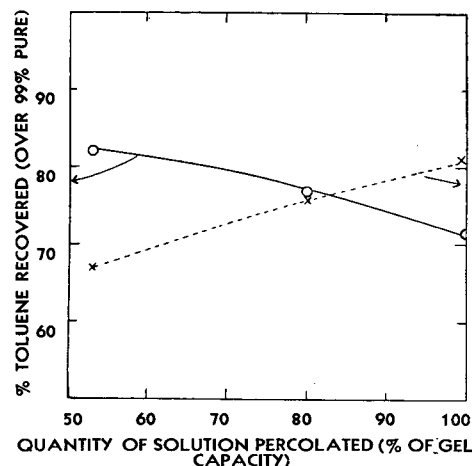
1.7 × 100-cm. columns of gel

gel capacity as the columns having the clean-up sections. The quantity of solution separated contained 80% of the gel capacity for cyclohexene; the flow of hydrocarbon down the column was maintained at 1 cm. per minute.

The results shown in Table V indicate that no advantage in separation efficiency is obtained by using a column of nonuniform diameter. This does not mean that the small section offers no advantage on the bottom of a large column; however, when compared from the standpoint of time required to carry out a separation (which is dependent on column length) and gel capacity (which determines the volume of a given solution that can be separated), the column with the clean-up section offers no advantages over the column of uniform diameter to compensate for the added difficulties of construction. .

Comparison of Iron and Glass Columns. Experiments have been conducted in small scale columns to investigate the effect of using metal columns having relatively rough inner walls in place of the smooth-walled glass ones used in previous work. A solution of 50% by volume toluene in iso-octane was separated in 1.4 × 100 cm. black iron and glass columns thoroughly packed with 28- to 200- and 100- to 325-mesh gels. The percolation rate

was kept in the range of 0.5 to 1.0 cm. per minute, where degree of separation is not influenced.

The data in Table VI show that the separation over 28- to 200-mesh gel in the iron column is much more complete than in the glass column. It was possible to pack 2 to 3% more gel in the

Table VI. Comparison of Iron and Glass Columns

Column	Silica Gel		% Toluene Recovered (>98% Purity)
	Type	Weight, g.	
Iron	Davison 28–200	114	86
Glass	Davison 28–200	111	76
Iron	Davison 100–325	117	91
Glass	Davison 100–325	115	91

iron column; this more thorough packing was also indicated by an appreciably lower flow rate under the same applied pressure. No difference in the separation could be detected in two types of columns when fine gel was used. The marked improvement in separation over the coarse gel when an iron column is used probably results from the more complete packing.

OPERATING VARIABLES

Degree of Packing. The data in Table VII show the effect of packing on sharpness of separation. A solution of 50% by volume toluene in iso-octane was separated. In runs where the gel was incompletely packed, the weight of gel necessary to pack the column thoroughly was determined; the column was then emptied and the desired quantity of gel added and settled carefully to the 100-cm. mark to ensure uniformity of packing.

The results given in Table VII show that completeness of packing is a very important factor, affecting the degree of separation in either iron or glass columns and with any of the gels used. These data indicate that it would be possible to obtain a better separation over a given column completely packed with coarse gel than over the same column incompletely packed with a finer gel. Fine gels are much more difficult to pack in small columns than coarse gels.

Table VII. Effect of Packing on Degree of Separation

Type	Column Dimensions, cm.	Gel	Completeness of Packing, %	% Toluene Recovered (>98% Purity)
Glass	1.7 × 100	International 100–200	100	82
Glass	1.7 × 100	International 100–200	97	76
Glass	1.7 × 100	International 100–200	90	68
Glass	1.7 × 100	Davison 100–325	100	89
Glass	1.7 × 100	Davison 100–325	96	81
Iron	1.4 × 100	Davison 28–200	100	86
Iron	1.4 × 100	Davison 28–200	97	82
Iron	1.4 × 100	Davison 100–325	100	91
Iron	1.4 × 100	Davison 100–325	90	82

Rate of Flow. The effect of percolation rate on degree of separation has been studied in experiments where a 40% by volume solution of toluene in iso-octane was separated over International 28- to 200-mesh gel packed into a 1.6 × 100 cm. column. When the rate at which the hydrocarbon front moved down the column was varied from 1 to 20 mm. per minute, the separation efficiency, expressed as the per cent of toluene recovered in over 98% purity, was 73 ± 2% in every case. It may be concluded that the rate of 10 mm. per minute selected for the work described previously gives the optimum separation. Experience has shown that when a percolation is stopped completely for several hours the separation efficiency is diminished, probably because of diffusion; however, it appears that as long as the hydrocarbon column is moving at a rate of at least 1 mm. per minute maximum separation efficiency is obtained.

It might be anticipated that the "waves" sent through the liquid when the pressure is adjusted to maintain the flow rate would cause some decrease in separation efficiency. Duplicate percolations at constant pressure on one hand and constant flow rate on the other show that no detectable difference in separation efficiency occurs.

Hydrocarbon-Gel Ratio. An important variable affecting the capacity of available percolation equipment is the quantity of hydrocarbon percolated over a given weight of gel. There are two important factors to consider: (1) the effect of the ratio of hydrocarbon to gel on degree of separation as defined by the per cent of components recovered in acceptable purity, and (2) the effect on the actual quantity of pure components recovered per given weight of gel. To study this variable, a 20% by volume solution of toluene in iso-octane was separated over a 1.7 × 100 cm. column of Davison 28-200 gel. The quantity of solution charged was considered to be the variable and is expressed as the

per cent of the total gel capacity which the toluene in the solution represents. The percolation rates were maintained below 10 mm. per minute.

Table VIII. Effect of Percolating Varying Quantities of Toluene

(20% v. toluene in iso-octane over 1.7 × 100 cm. column of gel)

Quantity of Solution Separated, % of Total Gel Capacity for Toluene	% Toluene Recovered (>99% Purity)	Toluene Recovered (>99% Purity), Ml./100 G. Gel
100	71	14.2
80	77	12.4
53	82	8.8

It is seen from the data in Table VIII and Figure 10 that the per cent of pure toluene increases and the volume of pure toluene recovered per unit weight of gel decreases rather sharply as the quantity of solution percolated decreases. In a separation carried out for the purpose of determining the per cent of each hydrocarbon class in the charge, the per cent of pure component recovered is of utmost importance, for the sharpness of the "break" between the hydrocarbon classes determines the accuracy of the analysis. In large scale separations, however, the volume of pure component recovered per unit weight of gel must be balanced against separation efficiency in order to take full advantage of the adsorptive capacity of the gel and of the available percolation equipment.

Effect of Degree of Penetration of Hydrocarbon before Addition of Eluting Agent. In separating hydrocarbon classes by the selective adsorption method the eluent is usually added immediately after the hydrocarbon has completely entered the gel. In large scale operation it is not always possible to avoid displacement of hydrocarbon in the dead space at the top of the column by the pressuring gas. To determine if this factor influences the degree of separation, a solution of 50% by volume toluene in iso-octane containing toluene to the extent of 100% of the gel capacity was separated in a 1.7 × 100 cm. column packed with 100- to 200-mesh gel. In these experiments the length of column wetted when the hydrocarbon had completely entered the gel was noted; the hydrocarbon was then forced varying distances down the column before alcohol was added.

Table IX. Effect of Removal of Entrained Hydrocarbon before Addition of Eluent

Length of Column Wetted after Hydrocarbon Completely Entered Gel, Cm.	% Toluene Recovered (>98% Purity)
0	73
10	77
15	80
20	80
25	82

The data in Table IX show that the degree of separation increases as the removal of mechanically entrained hydrocarbon from the gel becomes more complete. (Under the conditions used in these experiments, the wetting of 25 cm. of column after the hydrocarbon had completely entered the gel represented nearly complete removal of entrained material.) From these results it seems likely that, when the eluent is added immediately after the hydrocarbon enters the gel, considerable mixing of alcohol and entrained hydrocarbon results. The separation of this mixture of eluent and hydrocarbon charge places an added burden on the gel and poorer separation results. Forcing the entrained material as far as possible down the gel column greatly reduces the extent of mixing.

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(2) Mair, B. J., J. Research Natl. Bur. Standards, 34, 435 (1945).

Chromatographic Analysis of Gas Oils for Hydrocarbon Types

Examination of Techniques

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In analyzing mineral oils, gas oils, etc., in terms of groups of molecules of the same hydrocarbon type, it is desirable to separate the sample into fractions, each of which contains a single hydrocarbon type. Of the separation processes useful for this purpose, chromatography is outstanding. Three chromatographic methods of analysis were examined in a study of the hydrocarbon type composition of a straight-run gas oil and a catalytically cracked gas oil. The use of a weak developer to displace a saturate band and to elute several aromatic bands allows the desired separations into saturates, monocyclic aromatics, dicyclic aromatics, and tricyclic aromatics. Moreover, the fractions so recovered are suitable for further characterization by measurement of spectral and other physical properties.

IN THE study of petroleum refining processes it is frequently necessary to determine compositions of liquid hydrocarbons boiling in the gas oil and higher ranges. The approach to the analysis of these petroleum fractions has resolved itself into three lines of attack during recent years—i.e., analysis in terms of individual hydrocarbons, number of carbon atoms in rings and in alkyl chains, and molecular types.

The isolation of individual hydrocarbons by exhaustive distillation, crystallization, solvent extraction, etc., is exemplified by the work of A.P.I. Project 6 at the National Bureau of Standards (*12*). Such work must be confined to the isolation of as many pure hydrocarbons as possible from a relatively few samples.

Table I. Properties of Samples

Property	West Texas SR Gas Oil	Pilot Plant Catalytically Cracked Gas Oil
A.S.T.M. distillation		
Initial boiling point, ° C.	240	240
10% recovered at ° C.	260	254
50% recovered at ° C.	277	279
90% recovered at ° C.	302	321
End point, ° C.	329	338
Recovery, % v.	97.5	91.0
Loss, % v.	2.5	9.0
Refractive index, n_D^{20}	1.478	1.515
Density, d_4^{20}	0.858	0.896
Bromine No.	6	12
Sulfur, % w.	0.96	0.99
Molecular weight	224	208

The so-called ring analysis—i.e., an analysis in which the percentage of the total carbon atoms present in aromatic and naphthenic rings is determined—is exemplified by the methods of Deanesly and Carleton (*1*), Lipkin et al. (*6, 8*), and others. For the most part, these methods are based on simple physical properties which allow application of the methods to a large number of samples without too great an expenditure of work on each. These methods yield figures for the average composition of a sample in terms of the different kinds of atom bondings, but it is usually impossible to interpret the results in terms of the quantitative distribution of molecular types present in the sample except by assumption of the types present.

More recently, effort has been directed toward separation of groups of molecules of the same hydrocarbon type, such as paraffins, naphthenes, aromatics, etc., which allows analysis of complex petroleum fractions without assumptions of the hydrocarbon types present. Of the separation processes available today, one of the most efficient and useful is chromatography.

Work by Mair provided an adsorption method for determining the total aromatic content of gasolines (*9*), which has now been extended to higher boiling fractions (*11, 13*). Chromatographic techniques have also been reported by Lipkin et al. (*5, 7*) for measuring the paraffin, monocyclic naphthene, and dicyclic contents, etc., and the total aromatic content of the higher boiling oils.

The main interest of the chromatographic work described in this paper was the determination of the amounts of monocyclic, dicyclic, and tricyclic aromatics, in addition to the separation of the saturate hydrocarbons from the aromatic hydrocarbons. Although the present paper deals only with the analysis of gas oil samples, the techniques described also apply, with some limitations, to materials of higher boiling range.

EXPERIMENTAL

The successful application of chromatography to petroleum fractions depends largely on the use of suitable developers—i.e., liquids added to the column to increase resolution of the adsorbed sample components. Liquids which serve this purpose are divisible into two groups, depending upon their strength of adsorption in relation to the material being separated. Those developers which displace adsorbed material from the column by virtue of their greater strength of adsorption are termed displacents. In such operations the displaced material is caused to move down the column ahead of and at the same rate as the displacent. The less strongly adsorbed developers are termed eluents, because, in effect, they are used to move the adsorption bands by a washing process (*ex luere:* to wash out). When a sample consists of material of a wide range of adsorption affinities, a developer may be both an eluent and a displacent.

There are important differences in results, depending upon whether a developer of high adsorption affinity or of low affinity is used and upon the manner of use. Three techniques are compared in this paper: (1) use of a strong initial developer, (2) use of a weak initial developer to displace saturates only, and (3) use of a weak initial developer to displace a saturate band and to elute several aromatic bands.

Use of Strong Initial Developer (Total Displacement Development). In the adsorption technique of Mair et al. (*9, 11, 13*) the sample is added to a column of adsorbent, and alcohol (a strong developer) is added immediately thereafter to displace the entire sample down the column ahead of the alcohol. This technique thus falls in the category of displacement development.

The displacement technique was examined for the separation of gas oil components. For example, a sample of catalytically
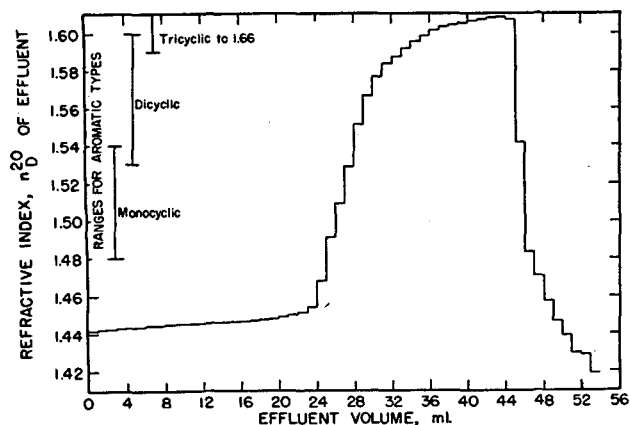
Figure 1. Displacement Development with a Strong Initial Developer, Ethyl Alcohol

50 ml. of catalytically cracked gas oil charged to 149 grams of Davison silica gel, 28- to 200-mesh, as received, in jacketed three-sectioned column. *Upper*, 1.9 cm. (diameter) × 60 cm.; *middle*, 1.2 × 60 cm.; *lower*, 0.6 × 55 cm. Temperature 50° C. Flow rate, approximately 0.5 ml. per minute

cracked gas oil (Table I) was passed over Davison 28- to 200- mesh silica gel and developed with ethyl alcohol. The refractive index of the effluent, plotted in Figure 1 as a function of the volume of effluent, reveals the overlapping between the various major hydrocarbon types. Although work here and elsewhere has shown that undoubtedly a much sharper separation can be obtained by the use of a higher temperature, a longer column, a more viscous displacent, and finer silica gel. However, some overlapping is an inherent characteristic of this method.

Use of a Weak Initial Developer to Displace Saturates Only (Selective Displacement Development). The use of a weak developer (pentane) to displace saturates, followed by a strong developer (alcohol) to displace total aromatics, is illustrated by the work of Mair and Forziati (*10*) and Lipkin *et al.* (*5*). This principle was examined, as illustrated in Figure 2, using a sample of straight-run gas oil (Table I) with methylcyclohexane (MCH) as the weak developer and ethyl alcohol as the strong developer. The results show that this procedure eliminates mixing between saturates and aromatics, as reported in the literature (*5, 10*). However, the aromatic fraction remains a complex mixture which cannot be readily characterized in terms of mono-, di-, and tricyclic aromatic content.

Although a weak developer (methylcyclohexane) was used, the saturates were displaced rather than eluted, inasmuch as they were the first components to issue from the column, which had not been previously wet with developer.

Use of Weak Initial Developer to Displace Saturates and Elute Aromatic Bands (Elution Development). In using the procedure described immediately above, when the refractive index of the effluent (Figure 2) drops to that of the weak developer (methylcyclohexane), the completion of the saturate band is indicated. If, instead of introducing ethyl alcohol to displace the aromatics, the weak initial developer is allowed to continue flowing through the column

after the saturates have been removed, other bands will be obtained. The material in these bands is eluted by the developer rather than displaced.

In carrying out the elution technique, ordinary Corning borosilicate glass pipe sections are frequently used as adsorption columns. In use they are partially filled with 28- to 200-mesh Davison silica gel, the upper, vacant portion of the pipe serving as a reservoir. (The long, jacketed columns needed for displacement developments experiments were found to be unnecessary when a weak developer was used.) In the present experiments, developer was first poured through the gel to dissipate the heat of wetting; then the sample was added. The proper size of gas oil sample was predicted from the aromatic adsorption capacity of the gel; for optimum efficiency only a slight excess of gel is recommended.

After the straight-run gas oil had been charged into the gel, developer was added continuously. When the initial developer had ceased to elute chromatographic bands, a developer of slightly higher adsorption affinity—viz., a solution of 10% toluene in methylcyclohexane—was added to obtain another band. Toluene and finally acetone were added to displace the remaining material from the adsorbent. The refractive index of the effluent was obtained on single drops of effluent at intervals of volume, the results of which are shown in Figure 3. After a particular adsorption band was collected, the oil was recovered by removing the low-boiling developer by atmospheric distillation followed by dis-
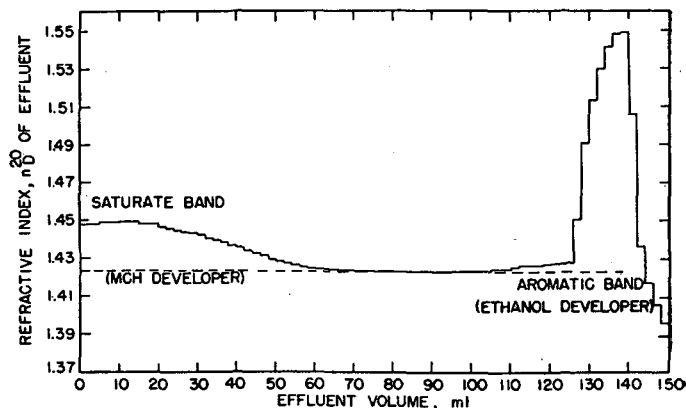

Figure 2. Displacement Development of Saturate Band Only with Methylcyclohexane

50 ml. of West Texas straight-run gas oil charged to 147 grams of Davison silica gel (not previously wet with developer), followed by 100 ml. of methylcyclohexane, and finally displaced with ethyl alcohol. Same column, temperature, and flow rate as in Figure 1

Table II. Properties of West Texas Straight-Run Gas Oil Chromatographic Bands

	Chromatographic Band					
	A	B	C	D	E	F
Process Developer	Displ. MCH[a]	Elut. MCH	Elut. MCH	Displ. 10% toluene in MCH	Displ. Toluene	Displ. Acetone
Oil recovered						
Yield, %·v.	72	11	2	9	2	4[b]
Refractive index, n_D^{20}	1.451	1.510	1.532	1.582	1.538	...
Density, d_4^{20}	0.816	0.912•	...	1.010	...	...
Refractivity intercept, $\left(n - \dfrac{d}{2}\right)$	1.043	1.054	...	1.077	...	...
Specific dispersion, $S_{F,C}$	97	147	...	230	...	...
Molecular weight[c]	238	215	...	188	...	...
Sulfur, % w.	0.0	1.0	2.7	4.8	9.7	5.0
Hydrocarbon type analysis % v.						Total
Saturates	72	...	...	...	...	...	72
Aromatics						
Monocyclic	...	11	2	...	...	...	13
Dicyclic	...	...	...	9	...	...	9
Tricyclic	...	...	...	...	...	...	0
Residue	...	...	...	...	2	4	6
							100

[a] Methylcyclohexane.
[b] Material recovered was semisolid black residue.
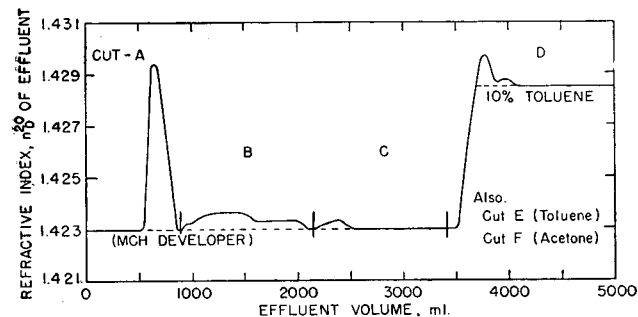[c] Molecular weight obtained from mid-boiling point and density (*14*).

Table III. Properties of Catalytically Cracked Gas Oil Chromatographic Bands

	Chromatographic Band				
	A	B	C and D	E	F
Process	Displ.	Elut.	Elut.	Elut.	Displ.
Developer	MCH[a]	MCH	MCH	10% toluene in MCH	Acetone
Oil recovered					
Yield, % v.	54	23	7	9	7[b]
Refractive index, n_D^{20}	1.447	1.560	1.581	1.645	...
Density, d_4^{20}	0.805	0.961	0.986	1.071	...
Refractivity intercept, $\left(n - \dfrac{d}{2}\right)$	1.044	1.079	1.088	1.109	...
Specific dispersion, $S_{F,C}$[c]	...	215	248	318	...
Molecular weight[c]	210	178	170	...	...
Sulfur, % w.	0.0	1.9	2.9	1.8	...
Hydrocarbon type analysis, % v.						Total
Saturates	54					54
Aromatics						
Monocyclic	...	...	...	...	...	0
Dicyclic	...	23	7	...	...	30
Tricyclic	...	...	...	9	...	9
Residue	...	...	...	...	7	7
						100

[a] Methylcyclohexane.
[b] Material recovered was semisolid black residue.
[c] Molecular weight obtained from mid-boiling point and density (14).

Figure 3. Use of Weak Initial Developer (Methylcyclohexane) to Displace Saturate Band and Elute Aromatic Bands

West Texas straight-run gas oil

51 ml. of oil charged to 272 grams of Davison silica gel, 28- to 200-mesh (previously wet with developer) in straight column 2.85 cm. (diameter) × 64 cm. Average percolation rate, 3.7 ml. per minute at room temperature

tillation at reduced pressure. The portion of the charge recovered in each band and the physical properties of these fractions are shown in Table II.

Similarly, the above chromatographic procedure was applied to a catalytically cracked gas oil (Table I). The refractive index-volume of effluent profile is shown in Figure 4. Again several bands were eluted with the initial developer. In this case, however, the second developer, 10% toluene in methylcyclohexane, eluted a band (E) rather than displaced it. This is shown by the short section of the 10% toluene plateau which was observed before band E issued from the column. The properties of the oil contained in each band are shown in Table III.

The discontinuities in the flow of sample components from the gel—i.e., the distinct bands—strongly indicated major differences in hydrocarbon types between successive bands. In these experiments, molecular weight played little part. To demonstrate this, bands of constant or closely similar adsorption affinity such as those above were subjected to precision distillation and spectroscopic examination of the cuts. Each eluted band proved to be essentially one hydrocarbon type. On the basis of such background data, the material in the chromatographic bands was assigned the hydrocarbon type indicated by physical properties, as shown in the lower portion of Tables II and III. The types of aromatics, mono-, di-, and tricyclic, refer to the number of

aromatic rings, regardless of whether they are condensed or noncondensed and regardless of the number of naphthenic rings which may be present in side chains. The compositions are in error—i.e., too high—by the amount of sulfur compounds present in each fraction.

DISCUSSION

Although development by the total displacement technique does not yield hydrocarbon types which are completely separated, the technique can be used for analysis in cases where there is a satisfactory method of characterizing each portion of the intermediate volume—i.e., the portion of the effluent in which different major hydrocarbon types exist together. For example, Gooding and Hopkins (4) have used refractivity intercept to characterize the intermediate portions of kerosenes. The validity of such proportioning depends on the assumptions that at most only two hydrocarbon types are present in each fraction and the specific average values chosen for the physical properties of the two types are correct. Because of the spread in physical property values (Table IV and Figure 1) and because synthetic products sometimes do not contain all hydrocarbon types, the use of "total displacement" development can frequently lead to such errors as the quantitatively reported presence of a component which is actually absent—for example, the absence of monocyclic aromatics is noted in the catalytically cracked gas oil.

The use of an elution development technique employing a weak initial developer presents disadvantages in the form of the larger volumes of material to be handled, the introduction of a distillation step, and the longer total time required compared to the use of a strong initial developer. However, these disadvantages are usually more than offset by the facts that suitable fractions for further characterization are in hand and that the analyses obtained on the basis of the distinct bands are not so dependent on assumptions. Thus, it is not necessary to assume which major groups are present in any fraction nor to assume a distribution of the individual compounds comprising each major group in order to arrive at an average value of a physical property for calculation purposes.
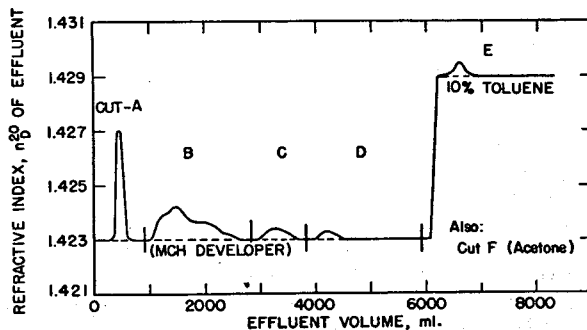
Figure 4. Use of Weak Initial Developer (Methylcyclohexane) to Displace Saturate Band and Elute Aromatic Bands

Catalytically cracked gas oil

35 ml. of oil charged to 269 grams of Davison silica gel, 28- to 200-mesh (saturated with developer) in straight column 2.85 cm. (diameter) × 56 cm. Average flow rate, 2.9 ml. per minute at room temperature

Table IV. Range of Physical Properties of Gas Oil Aromatic Types[a]

	n_D^{20}	$S_{F,C}$	$\left(n - \dfrac{d}{2}\right)$
Monocyclic	1.48–1.54	125–160	1.05–1.07
Dicyclic	1.53–1.60	160–250	1.09–1.11
Tricyclic	1.59–166[b]	300–550	>1.1

[a] From data of Doss (2) and Egloff (3).
[b] Estimated.

The monocyclic aromatics of the straight-run oil were divided into two distinct bands. The same was true of the dicyclic aromatics of the catalytically cracked material; this indicated that further type distinctions may derive from the application of this approach.

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Separation of Nitrogen Compounds by Adsorption from Shale Oil

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One of the complicating factors in elucidating the composition of distillates from Colorado shale oil is the presence of large quantities of nitrogen compounds. The content of these compounds may be as much as 50 weight % on some fractions. A procedure is described for separating shale-oil distillates into two fractions—one containing primarily hydrocarbons and the other primarily nitrogen and other heterocyclic compounds. This separation is based on adsorption and employs Florisil, a synthetic magnesium silicate, as the adsorbent. Factors investigated in selecting optimum conditions for the process are discussed. Results obtained on several shale-oil distillates are presented.

M OST of the distillate obtained from Colorado shale oil is in the boiling range above 400° F. Consequently, knowledge of the composition of this higher boiling fraction is of paramount importance in developing processes for producing engine and other distillate fuels from shale oil.

The majority of the methods (2, 6, 11) for the analysis of petroleum distillates in the higher boiling ranges estimate the carbon atoms as paraffinic, naphthenic, or aromatic. These methods are based on correlations that usually are not valid for samples containing olefinic unsaturation and nonhydrocarbon material. If the method utilizes optical properties, it is difficult, if not actually impossible to make the required determinations on dark samples. Consequently, higher boiling shale-oil distillates, which always contain large quantities of olefins and of nitrogen compounds and are dark, cannot be analyzed satisfactorily by direct application of available methods. Separation and recovery of the nitrogen compounds, therefore, would aid materially the analysis of the residual hydrocarbons as well as analysis of the nitrogen compounds themselves.

A large part of the nitrogen compounds in shale-oil naphthas and kerosenes can be removed by treatment with dilute aqueous acid (1). However, this procedure is ineffective for distillates having a 50% boiling point above approximately 525° F., although such distillates may contain 30 to 50 weight % nitrogen compounds. Adsorption had proved effective in analyzing shale-oil naphtha (3), so an attempt was made to apply the technique to the separation of nitrogen compounds from higher boiling fractions.

After preliminary tests on a number of adsorbents, Florisil was selected as the best available for the desired application. Conditions were established for a procedure that would separate a shale-oil distillate into two fractions—a light-colored one containing essentially hydrocarbons and a dark one containing principally nitrogen compounds. Results obtained by application of the procedure to several samples are presented.

APPARATUS

Adsorbent. Florisil, a synthetic magnesium silicate manufactured by the Floridin Company. Air-dried material, 30- to 60-mesh, was used.

Column. A glass tube, similar to that described by Mair and White (8), having a fritted disk or other device near the lower end for supporting the adsorbent and having a reservoir of approximately 200-ml. capacity on the top. If necessary for some applications, the column may be equipped with a heating or cooling jacket and a connection for applying pressure by means of an inert gas. In the work reported in this paper Florisil was em-

ployed only to adsorb nitrogen compounds of unknown structure from distillates obtained from crude shale oil produced in an N-T-U retort. Consequently, its activity for removing nitrogen compounds from other materials cannot be accurately estimated. Therefore, the quantity of Florisil and size of column necessary for a particular application will have to be determined empirically. For N-T-U distillates, Florisil equal to 300 times the weight of nitrogen in the sample and columns having diameters between 17 and 40 mm. and having height to diameter ratios between 12 and 150 have given comparable and satisfactory results. For smaller scale work a column having a diameter of less than 17 mm. may give more efficient separations.

Refractometer. An instrument capable of measuring the refractive index to ±0.0001.

Stripping Unit. Equipment capable of quantitatively removing pentane and methanol from the fractions. The design and size of this equipment will depend on the quantity of material being treated. In this work a batch-type stripping unit consisting of a flask and inverted Friedrichs condenser was used.

Pentane. Any mixture of saturated hydrocarbons boiling in the vicinity of 100° F. and having no high-boiling residue.

Methanol. Absolute.

PROCEDURE

A column of appropriate size is filled with Florisil and packed by tapping. An accurately weighed sample is introduced into the top of the column. It is often convenient to dilute samples that are solid at room temperature with pentane to prevent solidification in the adsorbent. When the sample has entered the Florisil, 100 ml. of pentane are added to the reservoir at the top of the column. The pentane and the portion of the sample eluted from the adsorbent are collected in a suitable receiver as they emerge from the column. Successive 100-ml. quantities of pentane are added to the reservoir and allowed to percolate through the column until the pentane issuing from the bottom of the column has a refractive index within 0.0002 of that of the pentane being introduced into the reservoir. Approximately 2000 ml. of pentane are required per 100 grams of sample for the type of material usually separated in this laboratory.

When the refractive index of the pentane-eluted fraction has reached the desired value, the receiver under the column is exchanged for a clean one, and methanol is introduced into the reservoir. Successive 100-ml. portions of methanol are added and allowed to percolate through the column until the material issuing from the column has a refractive index within 0.0002 of the value for the methanol being used. Approximately 1200 ml. of methanol per 100 grams of sample are usually required.

The pentane and methanol are stripped from their respective fractions in tared flasks. When the tared flasks have reached essentially constant weight, the quantity of material eluted by pentane and that eluted by methanol are calculated. Nitrogen is determined in each of these fractions by a modification (unpublished) of the Kjeldahl macroprocedure to check the extent of the separation of nitrogen compounds that has been achieved. The pentane-eluted material usually will be light-colored, color-stable, and practically free of nitrogen, while the methanol-eluted material will be dark and high in nitrogen.

DISCUSSION

It is theoretically possible to use as an adsorbent any solid material that will differentially adsorb the desired components from the sample and will not decompose the constituents of the sample. However, efficient application of the adsorption technique requires in addition to selection of an active adsorbent consideration of a number of additional factors, such as activation and particle size of the adsorbent. An adsorption procedure involving elution with solvents of increasing polarity and similar to one used on petroleum distillates (5, 7) was employed for the work reported in this paper. This technique is advantageous for use on high-boiling materials, particularly when it is desired to recover the separated fractions for further investigation.

Selection of an Adsorbent. The characteristics desirable in an adsorbent for separating the nitrogen compounds present in shale-oil distillates are: selective adsorption toward the nitrogen compounds; adsorption reversible enough so that desorption of the nitrogen compounds will be a simple operation; sufficient capacity so that a relatively small adsorbent-sample ratio may be used; low selective adsorption toward hydrocarbons so these may be separated from the nitrogen compounds as one fraction; and a

particle size that will give a rapid filtration rate. In practice, of course, the adsorbent selected will represent a compromise of these characteristics.

Several available adsorbents were compared as to their adsorption characteristics for the nitrogen compounds in shale-oil distillates. For a complete comparison, it would be necessary to obtain the isotherms for these compounds on the adsorbents. However, it was felt that for the work reported in this paper a comparison at a nitrogen concentration representative of that usually obtained on high-boiling shale-oil distillates would give satisfactory results. Therefore, the adsorbents were tested using a distillate having a 50% boiling point of about 725° F. and a nitrogen content of 1.78 weight %. The test method was similar to the recommended procedure, except that the adsorbent-sample ratio was reduced so that only about half the nitrogen charged to the column was adsorbed and some of the effluent contained about as high a concentration of nitrogen as the charge. The quantity of nitrogen adsorbed during the pentane elution serves as a qualitative measure of the efficiency of the adsorbent in the desired process. Results for quantity of nitrogen adsorbed and total recovery of nitrogen and sample as determined by this overloading test method are given in Table I.
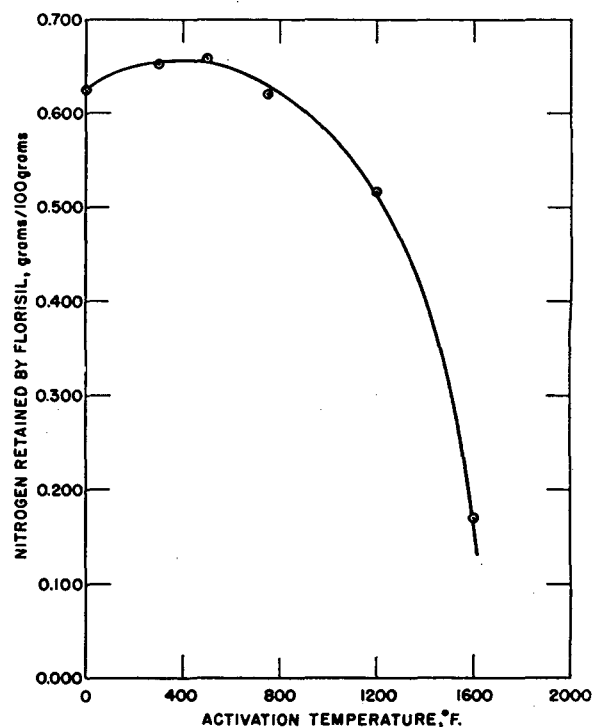

Figure 1. Effect of Activation Temperature on Adsorption of Nitrogen Compounds by Florisil

From the standpoint of the quantity of nitrogen adsorbed, color of pentane-eluted fraction, total recovery of sample and nitrogen, and rate of percolation, the Florisil was the best of the adsorbents tested. However, if these desirable characteristics are accompanied by a high selective adsorption for one or more groups of hydrocarbons, the Florisil cannot be used conveniently for separating nitrogen compounds from hydrocarbons. Investigation of this phase of the problem by a series of experiments indicated that, using Florisil, it should be possible to remove most hydrocarbons from nitrogen compounds by an elution procedure.

Preliminary work on the preceding problem showed that aromatic hydrocarbons are somewhat more strongly adsorbed by Florisil than saturates or olefins. Consequently, the separation of

Table I. Adsorption of Nitrogen Compounds by Various Adsorbents

Adsorbent	Total Material Recovered	Nitrogen Recovered	Nitrogen Retained during Pentane Elution
	%	%	G./100 g.
Silica gel	99.6	94	0.39
Alumina	98.8	93	0.41
Florex	98.9	88	0.40
Florite	a		0.37
Florisil	99.6	95	0.65
Carbon	b		

a No percolation of methanol could be obtained.
b Carbon available had such a slow percolation rate that no results were obtained.

aromatics from nitrogen compounds was studied. Because of ready availability and ease of running, some work was done using pyridine and hydrocarbons in the naphtha-boiling range. However, operating variables, particularly activation of the adsorbent, had much greater effects on the adsorption of pyridine than on that of the nitrogen compounds in higher boiling shale-oil fractions. It appeared, therefore, that results obtained using pyridine could not be considered typical.

It was found that under adsorption conditions similar to those used on shale-oil distillates nearly quantitative elution of 1-methylnaphthalene, 1, 2, 3, 4-tetrahydronaphthalene, and 1, 3, 5-triethylbenzene was obtained. A synthetic mixture was prepared which contained about 60% of a nitrogen-compound concentrate prepared from a shale-oil fraction by adsorption on Florisil and about 13% of each of the hydrocarbons mentioned in the previous sentence. Placing this mixture in a column containing Florisil and eluting with pentane permitted separation and recovery of the hydrocarbons. It was also found that anthracene and phenanthrene could be eluted from Florisil by pentane if they were dissolved in benzene before being placed on the adsorbent.

Effect of Activation Temperature. Florisil used in some of the preliminary work had been activated at 1200° F. by the manufacturer and had not received any further treatment in this laboratory. To determine the effect of activation temperature, a quantity of Florisil was obtained that had been air-dried only by the manufacturer. Samples of this material were then activated in this laboratory by heating for 4 hours at one of several temperatures between 300° and 1600° F. The activity of these heated samples was determined by the overloading test method described previously. The results obtained are shown in Figure 1. It is evident that over a considerable range the activation temperature for the Florisil has relatively little effect on the adsorption of nitrogen compounds. However, the adsorption capacity of the material decreases very rapidly if a temperature above 1200° F. is used.

Although activation of Florisil by heat increases its adsorption capacity for nitrogen compounds, the activation causes an even greater relative increase in its adsorption capacity for some non-nitrogen containing compounds in certain shale-oil fractions. Consequently, unactivated, air-dried Florisil is usually used for the separation of nitrogen compounds from shale-oil distillates by the procedure described in this paper. However, as activation apparently alters the adsorption characteristics of the Florisil, proper choice of activation conditions and eluents should make Florisil useful for a variety of separations.

Particle Size of Adsorbent. Decreasing the particle size of an adsorbent usually will increase its adsorption capacity (10), but will decrease the percolation rate. Therefore, it is advantageous to select the largest particle size that will perform the desired separation.

Florisil is furnished by the manufacturer in three particle-size grades, designated by mesh as 30 to 60, 60 to 100, and 100 up. An air-dried sample of each of these was activated for 4 hours at 500° F. and then evaluated by the overloading test method. The

results in Table II indicate that, when all conditions except particle size are constant, the capacities of the three grades of adsorbent are practically the same, but the percolation rate through the 30- to 60-mesh material is faster. Consequently, use of this material is recommended.

APPLICATION TO SHALE-OIL DISTILLATES

Four shale-oil distillates obtained from oil produced in an N-T-U retort were treated by the recommended procedure. The results are given in Table III. The average molecular weights were calculated by the method of Mills et al. (9). The content of nitrogen and sulfur compounds in each fraction was calculated assuming only one atom other than carbon and hydrogen to the molecule.

It is apparent from the results in Table III that the total recovery of sample is good; that well over 90% of the nitrogen recovered in the process is in the methanol-eluted material; and that separation of the sulfur compounds into either of the fractions is never attained. As the solvent stripping procedure employed was designed primarily for use on higher boiling fractions, the recoveries on the naphtha are poor and modifications would have to be made in the technique to adapt it for convenient use on this material.

Table II. Effect of Particle Size of Florisil on Adsorption of Nitrogen Compounds

Particle Size, Mesh	Nitrogen Retained during Pentane Elution	Approximate Time Required for Pentane Elution
	100 g.	Hours
30–60	0.66	2.5
60–100	0.65	3.25
100 up	0.66	4.0

Considering the large quantity of nitrogen compounds in the methanol-eluted fraction on the higher boiling materials and that this fraction contains substantial quantities of sulfur compounds and probably most of the oxygen compounds, it would seem that there are few if any hydrocarbons in the fraction.
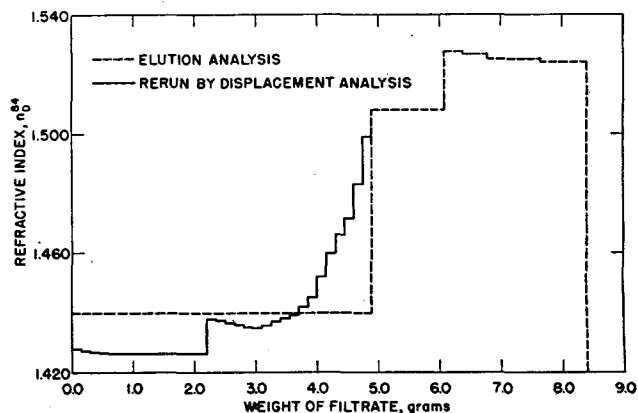
Figure 2. Adsorption Analysis of Pentane-Eluted Fraction from N-T-U Heavy Gas Oil

Although the complexity of the original sample makes a direct analysis extremely difficult, the pentane-eluted fraction contains mostly hydrocarbons, so an estimate of its composition may be obtained by available methods. Results of analysis of the pentane-eluted fraction from the heavy gas-oil sample are shown in Figure 2. The aromatics were obtained by the elution technique of Lipkin et al. (5). By this method any molecule containing one or

Table III. Separation of Nitrogen Compounds from Four Shale-Oil Distillates by Use of Florisil

	Av. Mol. Wt.	Material Recovered, in Fraction Wt. %	Nitrogen Wt. %	Nitrogen Compounds Wt. %	Relative Quantity of Recovered Nitrogen in Fraction %	Sulfur Wt. %	Sulfur Compounds Wt. %	Relative Quantity of Recovered Sulfur in Fraction %
			N-T-U[a] Heavy Gas Oil, Boiling above 625° F.					
Original sample	320		1.78	40.8		0.65	6.5	..
Fractions								
Pentane eluted		55.5	0.11	2.5	3.7	0.63	6.3	55.9
Methanol eluted		41.3	3.73	85.4	96.3	0.67	6.7	44.1
			N-T-U Light Gas Oil, Boiling Range 570–750° F					
Original sample	280		1.82	36.4		0.71	6.2	..
Fractions								
Pentane eluted		62.6	0.13	2.6	4.7	0.81	7.1	71.0
Methanol eluted		37.0	4.34	86.8	95.3	0.56	4.9	29.0
			N-T-U Kerosene, Boiling Range 400–585° F.					
Original sample	200		1.41	20.2		0.74	4.7	..
Fractions								
Pentane eluted		76.1	0.11	1.6	6.4	0.76	4.8	86.5
Methanol eluted		23.5	5.08	72.6	93.6	0.38	2.4	13.5
			N-T-U Naphtha, Boiling Range 155–415° F.					
Original sample	140		1.21	12.1		1.15	5.0	..
Fractions								
Pentane eluted		75.0	0.0	0.0	0.0	1.08	4.7	76.4
Methanol eluted		18.0	4.04	40.4	100	1.39	6.0	23.9

[a] An internally fired retort employed by the Bureau of Mines in experimental operations at the Oil-Shale Demonstration Plant, Rifle, Colo.

more benzene rings is classified as an aromatic. The paraffin-naphthene-olefin fraction obtained by Lipkin's method was rerun by a displacement technique developed in this laboratory (4). The displacement technique was not applied directly to the fraction because a suitable desorbent for the aromatics in this boiling range was not available. The results indicate that the composition of the hydrocarbon fraction is approximately 26% paraffins and naphthenes, 30% olefins, and 44% aromatics and sulfur compounds.

SUMMARY

Shale-oil distillates in the boiling range above 400° F. contain large amounts of nitrogen compounds, which complicate efforts to determine the composition of these distillates. Adsorption was selected as a technique which might permit the separation of these distillates into less complex fractions more suitable for subsequent analysis.

A procedure is described for separating shale-oil distillates into two fractions. One of these fractions consists predominantly of hydrocarbons, whereas the other contains predominantly nitrogen compounds. The separation is based on selective adsorption of the nitrogen compounds by Florisil, a synthetic magnesium silicate.

Results obtained on four shale-oil distillates by the recommended procedure indicate that approximately 95% of the nitrogen will be concentrated in one fraction and that this fraction will consist predominantly of nonhydrocarbons. The other fraction obtained will be a light-colored, color-stable material consisting predominantly of a mixture of saturated, olefinic, and aromatic hydrocarbons.

ACKNOWLEDGMENT

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Adsorption Analysis by Displacement Techniques

Applied to Shale-Oil Distillates

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Several applications of the displacement technique for adsorption analysis are described: the analysis of small samples boiling from 200° to 325° C. and containing olefins and nonhydrocarbon materials; a dilution procedure that aids in the analysis of samples for which the adsorptogram shows a poor separation between adjacent groups of compounds; and a procedure for the separate determination of paraffins and cycloparaffins using a combination of refractive index and adsorption techniques.

TWO methods of adsorption analysis have been developed for use on hydrocarbon mixtures—the displacement technique (*2, 4–6, 8, 11, 13, 14, 18*) and the elution technique (*4, 7–9, 12*). The former has been applied mostly to naphthas while the latter has been used on higher boiling materials. The versatility of the displacement technique seems to warrant its more extensive use on higher boiling samples.

ANALYSIS OF HIGHER BOILING FRACTIONS

Application of the displacement technique to higher boiling straight-run petroleum distillates has been described (*6, 13, 14*). However, the analysis of distillates containing substantial quantities of olefins and nonhydrocarbon material presents problems not studied extensively by these investigators. It was also desired to apply the method to small samples which accentuate the problems of sample losses and of a sharp separation between sample and desorbent.

Procedure. The method is based on one (*5*) published by this laboratory for the analysis of shale-oil naphthas.
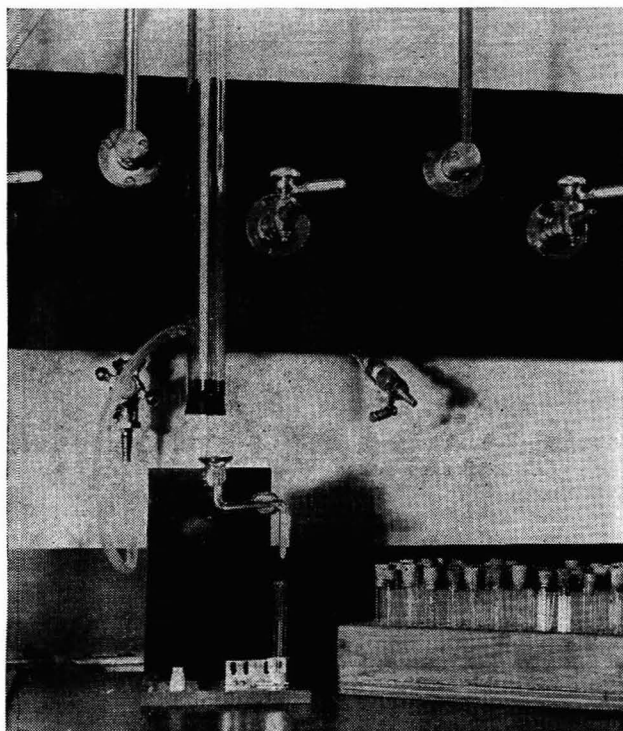

Figure 1. Fraction-Collecting Equipment

The following changes were made in the published procedure: 1-Octanol or cyclohexanol is used as the desorbent; water at 70° ± 2° C. is circulated in the jacket of the column; effluent from the column is collected volumetrically by means of the tip shown in Figures 1 and 2; and results are calculated on the basis of the volume of material recovered in the analysis.

The collection tip should be clamped securely in such a position that it is level along line *AB* (Figure 2) and the end of the column touches the funnel portion of the tip some distance from the capillary opening. The tip should be calibrated for the volume delivered in this position.
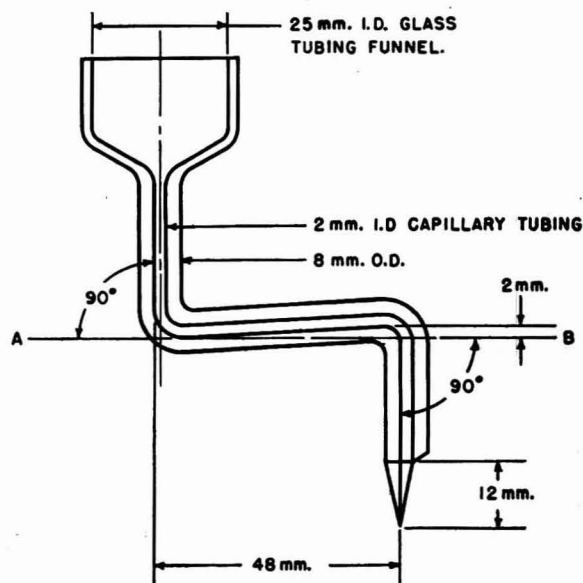

Figure 2. Tip for Collecting Fractions

Use of the collection tip permits the determination of the sample loss during an analysis. Part of this loss is a normal handling loss (usually 2 to 4%) which should be determined for hydrocarbons under the conditions being used. The remaining loss is due to nitrogen, sulfur, and oxygen compounds which may be classed with the aromatic group. Results of an analysis are calculated as follows: The volume of material in each plateau on the adsorptogram is divided by the volume of sample used and the result is multiplied by 100; the handling loss in per cent is apportioned to the various groups in proportion to their concentration in the sample; the remaining loss in per cent is assigned to the aromatic group.

Basis of Method. Successful application of the displacement technique requires a desorbent that will quantitatively remove the sample from the adsorbent. The characteristics desirable in a

Table I.   Quantity Adsorbed by Silica Gel and Viscosity of a Number of Materials

Compound	Quantity Adsorbed, Ml./100 G. Gel	Viscosity, Cs. at 70° C.
Cyclohexanol	25.7	6.1
1-Heptadecanol	25.7	6.3
1-Hexanol	27.5	1.8
2-Ethylhexanol	27.5	2.1
1-Octanol	29.0	2.6
2-Propanol	29.9	0.6
2-Methyl-2,4-pentanediol	33.4	4.7
Triethylbenzene	16.2	0.5
Tetrahydronaphthalene	19.6	1.5
1-Methylnaphthalene	23.0	1.3
Aromatic portion from shale oil (boiling range 200–325° C.)	....	2.2
Isoquinoline	33.0	1.6

desorbent are: a strength of adsorption greater than any component in the sample, a viscosity higher than that of any component of the sample, complete miscibility with the aromatic portion of the sample, and a refractive index sufficiently different from the aromatic portion so that the final break on the adsorptogram may be determined satisfactorily. Some information on the last three characteristics may be obtained from the literature or determined by recognized procedures, but there is no generally accepted method for determining adsorptive strength. A frontal analysis method (4, 12) was used to obtain an indication as to the strength of adsorption. The test mixture of 75 volume % of hexadecane and 25 volume % of the liquid to be tested was in the range where the concentration has relatively little effect on the quantity of material adsorbed. The adsorption relative to hexadecane and the viscosities at 70° C. for several desorbents are given in Table I, which also includes data for the types of aromatics probably present in the 200° to 325° C. fraction, an aromatic portion isolated from a shale-oil distillate in this boiling range, and isoquinoline.

Considered only on the basis of quantity adsorbed, all the alcohols listed should be good desorbents for the hydrocarbons tested. Although four of the desorbents are more viscous than the aromatic portion of the shale-oil distillate, only cyclohexanol and 1-octanol were used successfully for analyzing shale-oil fractions. The 1-heptadecanol and 2-methyl-2,4-pentanediol gave poor adsorptograms, showing a high loss in the aromatic plateau. This may be due to poor miscibility with some of the aromatics present in shale-oil distillates. It may be concluded that although these criteria aid in the selection of a desorbent, empirical testing is the final proof of its suitability.

The results in Table I indicate that it should be extremely difficult to desorb isoquinoline. This is confirmed in practice, as none of the desorbents available will satisfactorily remove basic nitrogen compounds from silica gel. Consequently, if these compounds are present in the sample, they are lost in the analysis.

Reducing the time required for an analysis by raising the temperature at which it is conducted is desirable. Analyses made by the same procedure on the same samples at room temperature and at 70° C. showed no significant differences. Consequently, the latter temperature was adopted for all work on the 200° to 325° C. fraction. It was found necessary to maintain relatively close control of the temperature of operation in order to prevent remixing of the plateaus.

Collection of effluent from the column on the basis of an equal number of drops per fraction as proposed pre-

viously (5) does not give an accurate measure of the volume of material in the fraction. This is a disadvantage for all samples and is particularly unsatisfactory for higher boiling shale-oil distillates where the loss of sample is relatively large and apt to be preferential to certain classes of compounds. The collection tip shown in Figures 1 and 2 was designed somewhat similar to one suggested by O'Connor (15). The results in Table II show that the tip delivers an essentially constant volume for various classes of hydrocarbons over a wide molecular weight range. Use of the tip improves the accuracy of analyses by providing a means of determining the volume of sample recovered in the analysis.

Table II.   Volumes of Various Compounds Delivered by Collection Tip

Compound	Average Volume per Delivery, Ml.	No. of Deliveries Averaged	Maximum Deviation of Single Delivery from Average, Ml.
Heptane	0.1053	20	0.0001
Dodecane	0.1058	20	0.0002
1-Decene	0.1059	20	0.0001
Toluene	0.1055	15	0.0003
Av.	0.1056	75	0.0004
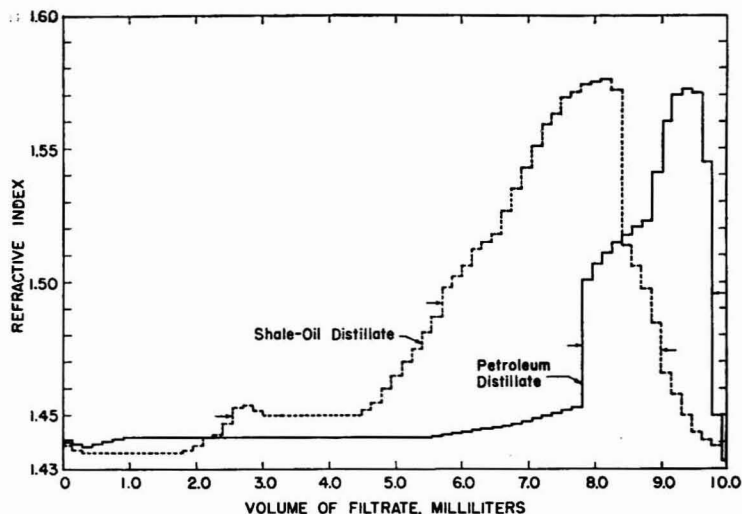
Figure 3.   Adsorptograms of Distillates in 200° to 325° C. Boiling Range
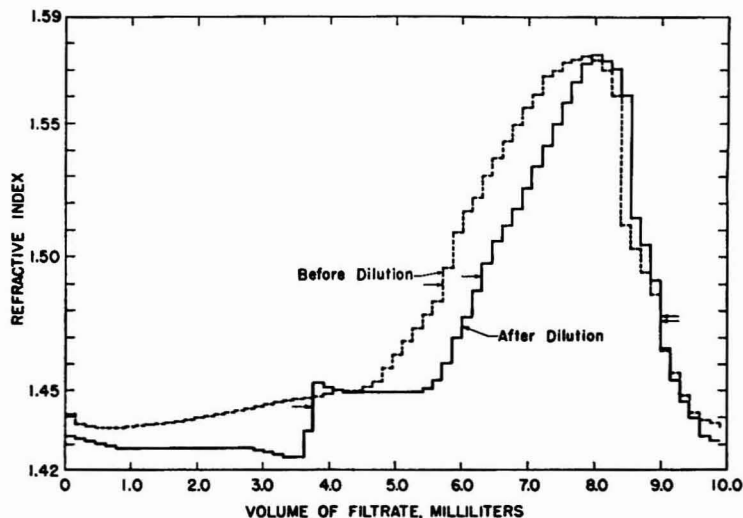
Figure 4.   Effect of Dilution on Shale-Oil Distillate in 200° to 325° C. Boiling Range

The problems of adequate adsorbent-sample ratio and of sample loss are closely interrelated. The capacity of the silica gel decreases with increase in average molecular weight of the sample and with increase in temperature of the silica gel. Increasing the amount of gel will compensate for the above factors but simultaneously will result in an increase in sample loss. The difficulty of desorbing the sulfur and nitrogen compounds in shale-oil distillates tends to accentuate the problems of sample loss. Analytical losses using various quantities of silica gel were determined on one petroleum and three shale-oil distillates in the boiling range 200° to 325° C. The results are given in Table III. The shale-oil samples had the following characteristics: No. 4 high in both sulfur and nitrogen, No. 12 high in sulfur but low in nitrogen, and No. 84 low in both.

A large proportion of the nitrogen was lost on passage through 50 grams of gel, whereas only a relatively small loss of sulfur occurred even when 100 grams of gel were used. The volume loss is greater on samples containing nitrogen but increases for all samples with the amount of gel used. Consequently, it is advisable to use the minimum amount of gel that will accomplish the desired separation. On all samples analyzed thus far, 50 grams of adsorbent have given satisfactory results on a 10-ml. sample. In no case has an analysis which gave relatively poor breaks using 50 grams of gel been improved by the use of additional quantities.

Results. Adsorptograms obtained on shale-oil and petroleum distillates are shown in Figure 3. The aromatic plateau contains any hydrocarbon having at least one benzene ring in the molecule, sulfur compounds, and those nitrogen compounds which are not so strongly adsorbed as to be lost in the analysis.

The breaks between various plateaus on adsorptograms for petroleum distillates are generally sharp, showing a reproducibility for the various groups of about 2%. The separation within the aromatic group of monocyclic and dicyclic compounds may be sufficiently good to permit individual estimation of these classes (6).

The more complex shale-oil distillates give rather sloping breaks between the various groups, so that the reproducibility is only about 5% on this type of material.

Because of limited availability of pure compounds in this boiling range, the composition of synthetic samples is simple in comparison to shale-oil distillates, so results obtained on the two types of sample probably are not directly comparable. Previous experience in this laboratory has indicated that except for adsorption, one of the more satisfactory methods for the deter-

mination of total olefins and aromatics on distillates in this boiling range is by absorption in sulfuric acid–phosphorus pentoxide reagent.

A comparison of results by acid absorption and by adsorption on silica gel is given in Table IV. The samples are the same as those used for the determination of sample losses. The excellent agreement of the results in the table and the reproducibility discussed above indicate that the displacement technique provides an adequate method for the analysis of samples in the 200° to 325° C. boiling range.
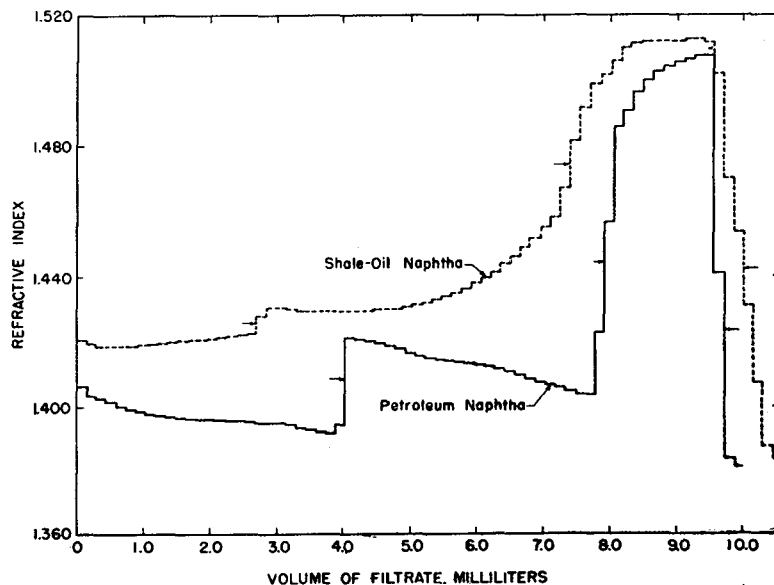

Figure 5. Adsorptograms Illustrating Small Amount of Separation Obtained between Paraffins and Cycloparaffins

Table IV. Comparison of Results by Silica Gel Adsorption and Sulfuric Acid–Phosphorus Pentoxide Methods

| | Paraffins and Cycloparaffins, Volume % | |
Sample No.	By silica gel	By acid absorption
4	28	28
12	33	35
84	40	40
159	80	80

DILUTION TECHNIQUE FOR IMPROVING ADSORPTOGRAMS

Analysis of a sample which contains paraffins, cycloparaffins, olefins, and aromatics usually gives an adsorptogram similar to those used as illustrations in the previous discussion. However, occasionally, such a sample will give an adsorptogram with only one plateau preceding the aromatic plateau (sample before dilution, Figure 4). This result may be caused by one or more of several factors. Among these are: a paraffin-cycloparaffin plateau containing sufficient cycloparaffins so that its refractive index is approximately equal to that of the olefin plateau and no break between them is apparent; and differences in viscosity between the groups which may cause sufficient mixing to obscure the break. Dilution of the sample with a suitable paraffin will correct the difficulty.

Procedure. Ten milliliters of sample are diluted with 2 ml. of paraffin (heptane for naphthas and decane for higher boiling fractions are satisfactory). Ten milliliters of the thoroughly mixed sample are then analyzed by the regular procedure. From the adsorptogram obtained the composition of the mixture analyzed is calculated in the usual manner. These results are converted to the basis of the original sample by correcting for the amount of paraffin added.

Table III. Loss on Different Quantities of Gel

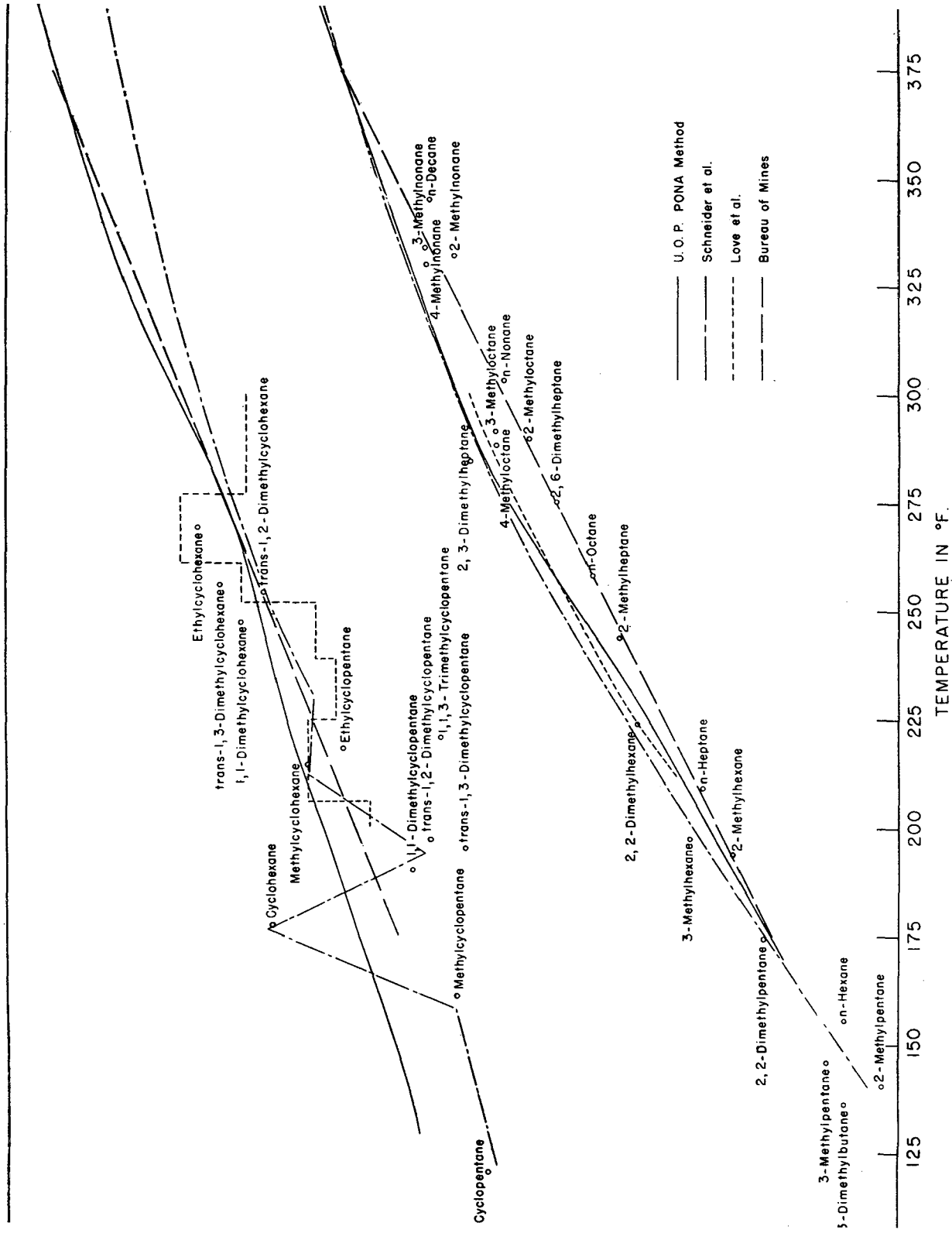| Sample No.	Quantity of Silica Gel, G.	Loss, Ml.	Nitrogen, Weight %	Sulfur, Weight %
4	...	...	0.55	0.81
	50	1.0	0.14	0.72
	75	2.0	0.05	0.75
	100	2.3	0.05	0.75
12	...	...	0.12	0.62
	50	0.5	0.04	0.58
	75	1.1	..	..
	100	1.6	..	..
84	...	...	0.13	0.05
	50	0.4	0.05	0.04
	75	0.7	..	..
	100	1.0	..	..
159	...	...	..	0.54
	50	0.2	..	..
	75	0.8	..	..
	100	1.2	..	0.51

Figure 6. Refractive Index Data for Paraffins and Cycloparaffins

Results. The adsorptograms obtained on a sample before and after dilution are shown in Figure 4. The improvement in the analysis is apparent. As the analysis is actually performed on only a little over 8 ml. of the original sample, the accuracy is correspondingly lower than when it is possible to use an undiluted sample.

Other Applications of Dilution Technique. The dilution technique is described for improving the saturate-olefin break, as difficulty is most often encountered at this point because of the relatively small difference in refractive index between these plateaus. However, the technique using an olefin or an aromatic as the diluent will be advantageous in certain instances.

DETERMINATION OF PARAFFINS AND CYCLOPARAFFINS

An adsorption method (5) based on the displacement technique has been developed in this laboratory for analyzing small samples of shale-oil or cracked-petroleum naphthas. Unfortunately, in this type of material, differences in adsorbability of paraffins and cycloparaffins are not sufficient to permit their separation directly by adsorption. This is illustrated in Figure 5, in which the first plateau of each adsorptogram consists of paraffins and cycloparaffins. Adsorption must, therefore, be supplemented by some other method in order to determine these two classes of compounds separately.

Basis of Method. The method described in this paper depends on refractive index and boiling point and is similar to those proposed by previous investigators (10, 17, 19). It differs from these in that the refractive index of the paraffin-cycloparaffin group is determined from the adsorptogram and simplified equations are used for the paraffin and cycloparaffin base lines. These lines, together with those previously proposed by others, are shown in Figure 6, which also includes the paraffins and cycloparaffins identified from mid-continent crude oil (16). Although curves give the best approximation, it was felt that over the boiling range 176° to 347° F. (80° to 175° C.) sufficient accuracy could be obtained using more conveniently handled straight lines whose equations are:

$$\text{Paraffin line.} \quad n_D^{20} = 0.000192\,t + 1.348$$

$$\text{Cycloparaffin line.} \quad n_D^{20} = 0.000155\,t + 1.388$$

where t is the temperature in degrees Fahrenheit.

The paraffin line is lower—that is, nearer the normal compounds—than would be indicated by an average of values for the isomers. This location was chosen because the paraffins in shale-oil naphthas are predominantly the normal compounds. The cycloparaffin line was placed at the average of the available data.

Procedure. The mid-point of the paraffin-cycloparaffin plateau is taken as the average refractive index of the group. Results on a large number of samples indicate that the mid-point will not differ from the arithmetic average of the fractions by more than ±0.0010. Furthermore, as the break between the paraffin-cycloparaffin plateau and the olefin plateau is not infinitely sharp, it is difficult to exclude completely the effect of olefins on the arithmetic average.

Average values for the refractive indexes of the paraffins and of the cycloparaffins in the sample are calculated from the equations given previously, using the 50% evaporated point of an A.S.T.M. distillation (1) on the sample for t. The paraffin and cycloparaffin contents are then calculated by the following equations:

$$\text{Paraffins.} \quad \% = \frac{S(N_{cp} - N_s)}{N_{cp} - N_p}$$

$$\text{Cycloparaffins.} \quad \% = \frac{S(N_s - N_p)}{N_{cp} - N_p}$$

where S = per cent of paraffins and cycloparaffins in sample
N_s = refractive index of mid-point of paraffin-cycloparaffin group from adsorptogram

Table V. Comparison of Results by Proposed and Refractivity Intercept Methods

	Paraffins, Volume %		Cycloparaffins, Volume %	
Sample No.	By proposed method	By refractivity intercept	By proposed method	By refractivity intercept
Shale-Oil Naphthas				
51	16	23	11	6
58	27	27	6	8
60	35	36	2	0
61	16	15	4	5
70	25	21	7	13
71	26	28	7	4
Petroleum Naphthas				
6	71	66	22	24
7	34	29	4	10
10	62	64	11	8
11	64	61	13	13
17	70	77	25	18
18	69	70	26	24
19	31	33	7	9
20	37	35	9	10
33	68	71	17	15
36	36	36	15	18
38	52	53	15	14
39	30	34	0	0

N_{cp} = refractive index of cycloparaffins
N_p = refractive index of paraffins

Results. Results obtained by the method described are compared in Table V with those obtained on the same samples by a method (3) based on determinations of refractivity intercept and density. These latter determinations are made on the paraffin-cycloparaffin raffinate from a naphtha that has been extracted with sulfuric acid–phosphorus pentoxide reagent and it is stated that duplicate determinations usually will not differ from the average by more than ±5. Duplicate determinations by the method described in this paper will have an absolute variation from the average of not more than ±3%. Inspection of the data in Table V indicates that results by the two methods check within the limits claimed for the individual methods. Consequently, it may be concluded that the methods give results of comparable accuracy.

SUMMARY

A displacement development technique is described for the determination of saturates, olefins, and aromatics on small samples in the boiling range from 200° to 325° C. Variables affecting this method of analysis are discussed.

A dilution procedure is described which is primarily helpful in the analysis of samples that do not show a satisfactory olefin plateau by the displacement technique.

A method is described for the determination of paraffins and cycloparaffins in hydrocarbon mixtures in the naphtha-boiling range. The method utilizes adsorption to separate the saturates from the sample and boiling point and refractive index to determine the percentage of paraffins and cycloparaffins. The reproducibility of the method is approximately ±3% and its accuracy compares favorably with other available methods.

Bureau of Mines, United States Department of the Interior, and the University of Wyoming.

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Evaluating Petroleum Residua and Lubricating Oil Distillates

Adsorption Method

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A laboratory method for fractionating petroleum residua and lubricating oil distillates is described which employs adsorption fractionation of a 200-gram sample. By blending fractions, oils are obtained covering the entire range of composition from very low to very high viscosity index. Property-yield relationships are obtained for this range, including gravity, viscosities, viscosity index, per cent sulfur, micro solid point, and refractive index. Data are presented for three petroleum residua from different types of crude oil, one solvent extract, and one lubricating oil distillate. Yields of treated oils of any viscosity index may be accurately estimated.

THE laboratory separation of crude oil into its components and the evaluation of these fractions for various uses are problems that have received the attention of chemists and engineers in the petroleum industry since its inception. The discovery of new oil fields, the changes in existing fields, and the decline of old fields necessitate many evaluations of crude oils, especially as sources of lubricating oil. In the case of crude oil from a new field, for example, it is essential to have accurate data in order to estimate properly the probable value of the field. Reliable procedures for evaluating the light fractions of crude oil are available, but up to now a suitable method for the quantitative determination of the viscosity index–yield relationship in the lubricating oil range has not been reported.

Laboratory methods for evaluating crude oils with respect to the production of lubricating oils by acid treatment of distillates have been satisfactory, as commercial operation can be duplicated in the laboratory fairly well by actually distilling and acid treating on a small scale. When distillates are treated with single selective solvents, such as phenol and furfural, however, laboratory data on yield and quality are not equal to those obtained in commercial practice unless elaborate treating equipment, similar to that employed commercially, is used in the laboratory evaluation. Laboratory single-stage or multiple-stage treatment is possible, but the results obtained do not equal the results obtained from the more efficient multiple-stage countercurrent commercial operation. Kalichevsky (4) described a laboratory evaluation method employing a single application of solvent in

which the results are correlated with those obtained through more efficient, multiple-stage commercial treatment. However, in any single-stage treatment only one point on the viscosity index–yield curve is obtained. When such correlating information on a new crude was lacking in the past, evaluations have consisted generally of single-stage treatment and a comparison of the results with those of similar fractions of a known crude oil.

A more accurate evaluation requires extensive pilot plant treatment of the residuum or distillate at large expense. This is particularly true for the double solvent (Duosol) treatment of residua, as laboratory reproduction of double solvent treating is very difficult and the cost of pilot plant operation is prohibitive for all but the most important evaluations. Including operating and laboratory costs, the total expense of operating a typical pilot plant is in the order of $200 to $300 a day; the evaluation of one crude may require 2 weeks of operation at a cost of several thousand dollars. It is true, however, that sufficient treated oil may thereby be made for service tests, a result that cannot be obtained in small scale laboratory work.

The objective of the work reported here was to develop a laboratory method for establishing the viscosity index–yield relationship for lubricating oil from residua and lubricating oil distillates, and to learn some of the properties of the oil and wax which could be made from these stocks. The principal requirements were that a small quantity of stock be used, and that the analysis be completed within a relatively short time and at reasonable cost. Earlier work of Mair and associates (7, 8), Willingham (11), and

Allibone (1) showed that fractionation by adsorption could be used to obtain separation of petroleum fractions of high molecular weight. Hibbard (2) and Lipkin (6) used adsorption methods for separation of oils in the lubricating oil range. It was necessary for the present purpose to include deasphalting and dewaxing steps and to devise a means of obtaining a continuous relationship between properties (particularly viscosity index) and yield over the entire range of molecular types of the lubricating oil fraction.
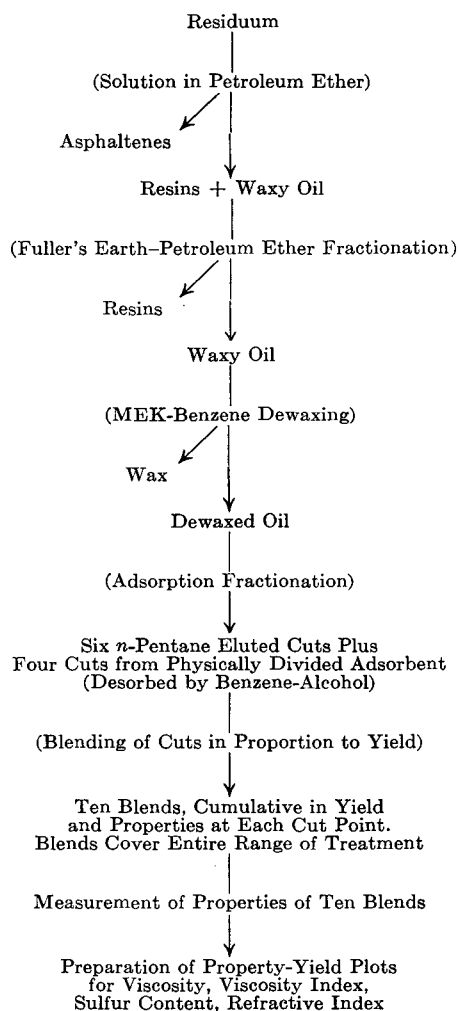
Residuum
|
(Solution in Petroleum Ether)
|
Asphaltenes
|
Resins + Waxy Oil
|
(Fuller's Earth–Petroleum Ether Fractionation)
|
Resins
|
Waxy Oil
|
(MEK-Benzene Dewaxing)
|
Wax
|
Dewaxed Oil
|
(Adsorption Fractionation)
|
Six n-Pentane Eluted Cuts Plus
Four Cuts from Physically Divided Adsorbent
(Desorbed by Benzene-Alcohol)
|
(Blending of Cuts in Proportion to Yield)
|
Ten Blends, Cumulative in Yield
and Properties at Each Cut Point.
Blends Cover Entire Range of Treatment
|
Measurement of Properties of Ten Blends
|
Preparation of Property-Yield Plots
for Viscosity, Viscosity Index,
Sulfur Content, Refractive Index

Figure 1. Scheme of Adsorption Analysis

The method developed comprises the following main steps (shown schematically in Figure 1) as applied to an asphaltic residuum or extract:

a. Precipitation of asphaltenes from a suitable residuum by petroleum ether.

b. Adsorption of resins, oil, and wax by granular fuller's earth.

c. Extraction of oil and wax from fuller's earth using petroleum ether.

d. Extraction of the resins from the fuller's earth by benzene–ethyl alcohol (50/50).

e. Dewaxing of the waxy oil employing methyl ethyl ketone–benzene.

f. Fractionation of the dewaxed oil on the basis of molecular type by a flowing chromatographic procedure employing n-pentane.

g. Mechanical separation of the adsorbent column into sections and extraction of the aromatic fractions from the adsorbent sections using benzene–ethyl alcohol.

h. Reblending of cuts obtained from f and g in proportion to

yield, thus obtaining oils cumulative in yields and properties up to the cut point.

i. Measurement of properties of the oils including the viscosity at 100° and 210° F., density, refractive index, sulfur content, and micro solid point (pour point).

j. Calculation of viscosity indexes and correction of yields to volume per cent yields of zero pour point oil from 460° F. flash residuum. In calculating yields, the slack wax is arbitrarily defined as containing 20% of zero pour point oil.

PROCEDURE

Charging Stock. The residuum chosen from a given crude for analysis is that which would be used as charging stock for lubricating oil manufacture—i.e., a residuum containing all the usable lubricating oil fractions. A residuum of 460° F. flash point (Cleveland open cup) is generally suitable for the production of lubricating oils covering the viscosity range normally used. Fortunately, the "residuum after 40 viscosity gas oil" obtained in the Method D crude analysis described by Mithoff, MacPherson and Sipos (10) is usually in this flash range, and the residuum from such analysis is therefore a convenient starting material for the adsorption analysis. The yield and properties of the residuum from the Method D analysis have already been accurately determined in the course of that analysis; and as this method is used in these laboratories on nearly all new crude oils, it is a particularly good source of residuum.

If the residuum available differs from 460° F. flash point, the yield data are subsequently corrected, assuming that the distillate to be added or subtracted to obtain 460° F. flash point will give yields of treated oil equal to those obtained from deasphalted residuum.

Any other type of stock containing lubricating oil fractions, such as solvent extracts or distillates, may be analyzed by suitable variation in the procedure.

Deasphalting Steps. The deasphalting steps are carried out prior to dewaxing because dewaxing in the presence of large quantities of asphalt results in a difficult dewaxing operation, poor yields, and a poor quality of dewaxed oil. The deasphalting method used is similar to the methods first employed by Marcusson (9) for the separation of the constituents of asphalts.

1. Two 100-gram samples of the residuum are each warmed with 2 liters of petroleum ether and allowed to stand for 16 hours at 75° F. The undissolved asphaltenes are removed by filtration, washed, dried, and weighed.

2. The filtrates from step 1 are distilled until the petroleum ether content is reduced to 25 to 50%. Each reduced filtrate is poured on top of fuller's earth (30- to 60-mesh) in two Soxhlet extraction apparatus containing 550 grams of fuller's earth. After standing overnight, petroleum ether is cycled in the Soxhlets for 8 hours and the oil and wax fractions are thereby removed from the fuller's earth. The petroleum ether solutions of oil and wax are reduced on a steam plate, and stripped with nitrogen.

3. The resins adsorbed by the fuller's earth are removed by cycling a 50/50 solution of benzene–ethyl alcohol in the Soxhlets for 8 hours. The resin solutions are then reduced on a steam plate and the resins are weighed.

Dewaxing. The waxy oil samples from step c are combined and dewaxed at −15° F. using methyl ethyl ketone–benzene solvent. The laboratory method is designed to correlate with commercial dewaxing results, the object being the removal of zero pour point oil with small loss of oil in the wax cake. The pour point is estimated by the measurement of the "micro solid point," obtained in a method similar to that described by Levin, Morrison, and Reed (5) by measuring the temperature at which a small wire frozen to the bulb of a thermometer held in a horizontal position first moves as the oil warms. In the yield calculation subsequently made, the dewaxing yield is corrected to a standard value for oil content of slack wax (in the present work, 20% zero pour oil in the wax cake).

Adsorption Fractionation Step. The final adsorption fractionation step employs silica gel (Davison No. 659528-2000, 28–200

mesh) or Thermofor catalytic cracking catalyst ground to the above mesh size. The apparatus used is shown diagrammatically in Figure 2.

A glass column 1.5 inches (3.75 cm.) in inside diameter and 7 feet high is used. The lower end of the column is tapered to a 0.25-inch outlet fitted with a stopcock. The upper end is closed by a four-hole rubber stopper provided with connections for a charging vessel, nitrogen line, manometer, and pressure-control valve. A rubber-stoppered 500-ml. balloon flask with a small outlet at the bottom is used as the charging vessel. This is connected by rubber tubing to a 0.25-inch glass tube which extends through the rubber stopper to a depth of 5 inches in the column. The end of the glass tube is tapered to facilitate automatic feeding to the column. All other connections to the column consist of rubber tubing attached to glass tubes extending through the stopper into the column to a depth of 1 inch. All connections except that to the pressure-control valve (Victor 0.25-inch ball seat valve) and the charging vessel are provided with pinch-clamps to allow for selective closing of the various lines.

As the eluant emerges from the bottom of the column, it enters a continuous stripping apparatus where partial evaporation of the solvent occurs. The apparatus, which is merely a steam-jacketed glass tube with funnel-shaped top, serves to evaporate about 95% of the pentane used as diluent. Emerging from the steam-heated stripper, the eluant is gathered in calibrated 10-ml. test tubes held in a water bath which is heated by steam to facilitate further removal of the n-pentane diluent.
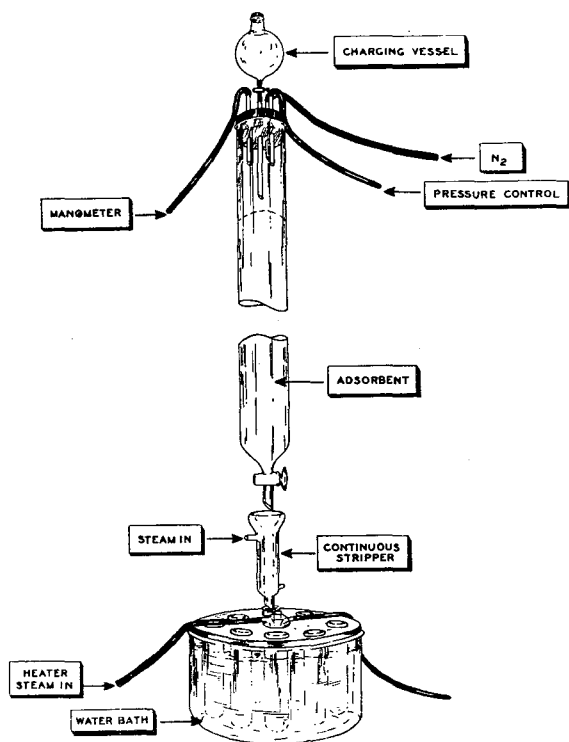

Figure 2. Apparatus Used in Adsorption Fractionation Step

Operating Procedure. 1. The fractionating column is closed at the bottom with a small wad of cotton and filled with the absorbent to within 6 inches of the top. To assure complete and uniform packing of the adsorbent, the column is vibrated while being filled, by an Oster Massaget scalp vibrator attached to the operator's hand; the operator grasps the column at the rising level of the adsorbent.

2. The adsorbent column is prewetted with n-pentane by adding 1500 ml. through the charging vessel.

3. One hundred grams of the dewaxed oil from step e are dissolved in 300 ml. of n-pentane and transferred to the charging vessel. The solution in the charging vessel is allowed to flow slowly onto the adsorbent, and a liquid head of 1 inch is established as determined by the distance between the end of the tube and the top of the adsorbent column. Feeding is then automatic as the level of liquid inside the column drops below the end of the feed tube. Successive portions of n-pentane are added to the

charge vessel until 2800 ml. of n-pentane have been used. After essentially all of the n-pentane has drained from the column (about 4 hours after starting), nitrogen is passed through until the adsorbent is dry.

During this operation, cuts are taken in calibrated test tubes at the lower end of the steam-heated stripper. The volume of each cut depends upon the number of fractions desired for a particular analysis. Six eluant cuts are generally obtained, although the number may vary, depending upon the stock.
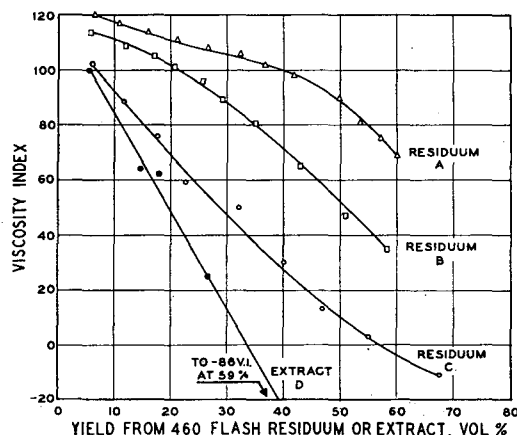

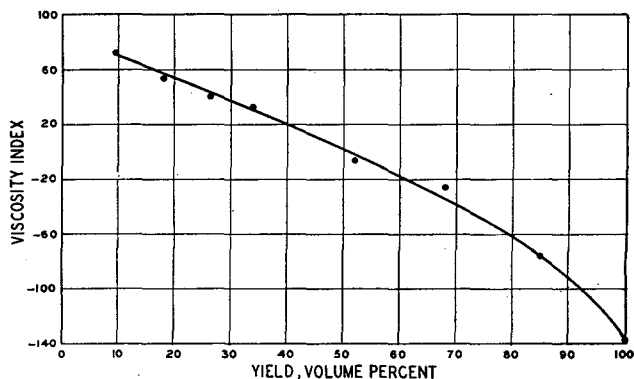Figure 3. Viscosity Index–Yield Relationship

Figure 4. Viscosity Index–Yield Relationship

Wax-free distillate of 83 S.s.u. at 210° F. and −140 V.I.

4. The adsorbent in the column, containing the more aromatic material, is normally divided into five equal parts, and four cuts are taken, the lower cut comprising the lower two fifths of the column. The number of cuts may be varied for different stocks. Care is taken to obtain a sharp mechanical separation by using a brass rod with small shovel head to rake the adsorbent from the column. Each of the four samples of adsorbent is mixed with fuller's earth in order to reduce its density and is transferred to a Soxhlet extraction apparatus. The adsorbed oils are then extracted by cycling a 50/50 mixture of benzene–ethyl alcohol in the Soxhlets for 8 hours.

5. Solutions from 3 and 4, containing the fractionated oils in n-pentane or benzene-alcohol solution, are first stripped on a steam plate and then finished in a heated vacuum desiccator at not over 150° F. and 1-mm. pressure.

6. The stripped cuts from 5 are weighed, placed in 100-ml. volumetric flasks, and diluted with benzene to a total volume of 100 ml. These solutions are placed in burets and blended together volumetrically in proportion to the yield of each cut from the adsorption separation, so that at each cut point there is a sample representing the cumulative product at that point.

7. The benzene solvent is again stripped, as above, first on the steam plate and then in the vacuum desiccator, and the properties of the blended cuts are determined.

8. The viscosity index is calculated from the measured viscosities.

9. The viscosity index is plotted against volume per cent yield, which is calculated from weight per cent yields by employing the densities. When necessary, correction is made for the deviation of the micro solid point from zero pour point for each blend. In

making the latter correction, zero pour point is taken as equivalent to $+8°$ F. micro solid point, and 1 weight % of "average" wax (oil-free) will raise the micro solid point $6°$ F. This correction is generally very small, and in view of the precision of the entire analysis it can be neglected. Yield correction by this method cannot be used for low viscosity index oils, where high micro solid point is due to high viscosity instead of to the presence of wax.

RESULTS

Typical data from the deasphalting and dewaxing steps obtained for three residua and one asphaltic extract are shown in Table I. The asphaltic extract was obtained by the Duosol treatment of residuum B. Data from the adsorption fractionation step for residuum A are presented in Table II. The viscosity index-yield relationships for the four stocks are plotted in Figure

3. In Figure 4 the viscosity index-yield relationship for a wax-free lubricating oil distillate is shown. In this case, only the adsorption fractionation step was employed.

DISCUSSION

In developing the above procedure, a number of modifications were tried. The use of a 200-gram sample of oil charged to the adsorbent column gave substantially less separation than the 100-gram sample, and therefore the charge of smaller size was chosen.

Initially, the adsorbent was not prewetted before percolation of the n-pentane–oil mixture, and considerable heat was evolved at the forefront of the descending column of liquid. When the adsorbent is prewetted with n-pentane, the oil being treated must replace n-pentane previously adsorbed, and the heat evolved is the difference between the heat of adsorption of n-pentane and that of the oil. This difference is much less than the heat of adsorption of the oil alone, or of the n-pentane alone, with dry adsorbent. The adsorbing power of the adsorbent increases with decreasing temperature. Less internal mixing of materials due to thermal gradients will occur if temperature differences within the column are maintained as low as possible. The finally established practice of prewetting with n-pentane left the adsorbent at equilibrium with n-pentane at room temperature. The high temperatures obtained within the column by wetting dry adsorbent are shown by the following experiment. A thermocouple was placed in the center of a tube 1 inch in diameter, 4 inches below the top surface of the silica gel adsorbent, the column of gel being 10 inches long. Solvents were percolated through the column under a head of about 0.5 inch of solvent. The following maximum temperatures were obtained (where the temperature shown is above the normal boiling point of the solvent, the maximum temperature was obtained in the vapor preceding the advancing liquid front):

Solvent	Temperature, Maximum, ° F.
Methanol	295
Ethyl alcohol	268
Ethyl ether	290
Water	212
Benzene	167
n-Pentane	160
Carbon tetrachloride	134
Cyclohexane	125

Although it would be possible to control the temperature by circulating a liquid of controlled temperature in a jacket about the column, the percolation rate would have to be very low because of poor heat transfer to the center of the column. The prewetting method was found to be more practical for the purpose of the analysis described here.

Table I. Data from Deasphalting and Dewaxing Steps for Three Residua and One Asphaltic Extract

	Residuum			
	A	B	C	D
		Crude Source		
	Mid-continent	California-waxy	California-naphthenic	Duosol extract of B
Yield from residuum, wt. %				
Asphaltenes	0.8	2.7	5.6	5.0
Resins	17.8	26.5	27.2	33.7
Waxy oil	81.4	70.8	67.3	61.3
Dewaxed oil (assuming no oil in wax)	63.6	60.6	65.9	58.3
Wax	17.8	10.2	1.3	3.0
Dewaxed oil (assuming 20% oil in wax)	59.1	58.0	65.6	57.6
Slack wax	22.3	12.8	1.6	3.7
Solidification point of wax, ° F.	134	132	128	138
Oil content of wax, %	9.6	5.1	6.5	5.0
Dewaxed oil, properties				
Gravity, ° A.P.I.	23.6	18.4	15.7	10.3
Viscosity at 100° F., S.s.u.	979	2155	6976	41000
Viscosity at 130° F., S.s.u.	379	678	1675	6600
Viscosity at 210° F., S.s.u.	77.4	100	158	323
Viscosity index	+69	+36	−11	−86
Micro solid point, ° F.	−2	−5	28	45
Refractive index, n_D^{68}	1.5034	1.5257	1.5310	1.56
Sulfur, %	0.25	0.71	1.13	0.90
Residuum, properties				
Yield from crude, vol. %	27.0	33.1	52.3	62[a]
Gravity, ° A.P.I.	21.2	15.1	11.6	6.9
Flash, COC, ° F.	460	460	460	460
Viscosity at 210° F., S.s.u.	114	225	809	1904
Conradson carbon	5.3	8.0	11.6	11.5
Sulfur, %	0.38	0.70	1.27	0.90
Wax (distillable), %	9.3	5.3	0.27	...
Pour point, ° F.	105	100	65	90
Estimated yield 460° F.				
Flash residuum	27.0	33.1	52.3	...
Crude gravity, ° A.P.I.	41.5	32.8	21.5	...

[a] Duosol treating yield from residuum B.

Table II. Data from Adsorption Fractionation Step, Residuum A

										Cumulative Blend Data
Cut No.	Eluant	Weight Oil, G.	Total Oil Weight, G.	Specific gravity, 60/60	Viscosity at 100° F., S.s.u.	Viscosity at 210° F., S.s.u.	Viscosity index	Micro solid point, ° F.	Refractive index, n_D^{68}	Sulfur, wt. %	Yield from adsorption fractionation step, vol. %	Yield from residuum, vol. %
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1	n-Pentane	8.70	8.70	0.8564	338	58.8	120	+8	1.4705	0.01	9.3	5.6
2	n-Pentane	8.44	17.14	0.8596	322	56.6	117	+9	1.4715	0.01	18.2	10.9
3	n-Pentane	8.17	25.31	0.8618	326	56.6	114	+8	1.4728	0.02	26.8	16.1
4	n-Pentane	8.22	33.53	0.8644	333	56.5	111	+7	1.4738	0.03	35.4	21.2
5	n-Pentane	8.62	42.15	0.8671	345	56.7	108	+7	1.4748	0.05	44.3	26.6
6	n-Pentane	9.23	51.38	0.8701	359	57.3	106	+5	1.4759	0.07	53.8	32.3
7	n-Pentane	7.00	58.38	0.8734	384	57.8	101	+4	1.4771	0.09	61.0	36.6
8	n-Pentane	8.55	66.93	0.8785	450	60.9	98	+4	1.4799	0.12	69.5	41.7
9(X_1)	(Benzene–ethyl alcohol in Soxhlet)	14.20	81.13	0.8890	554	64.5	90	−1	1.4871	0.17	83.3	50.0
10(X_2)	(Benzene–ethyl alcohol in Soxhlet)	6.58	87.71	0.8977	676	68.3	81	−1	1.4928	0.20	89.1	53.5
11(X_3)	(Benzene–ethyl alcohol in Soxhlet)	6.94	94.65	0.9068	806	72.4	75	0	1.4989	0.23	95.2	57.1
12(X_4)	(Benzene–ethyl alcohol in Soxhlet)	5.32	99.97	0.9124	990	78.0	69	0	1.5034	0.25	100.0	60.0

The steam-heated stripper was devised when it was found impractical to estimate the amount of oil in unstripped eluant cuts, at the time the cuts were taken. By using the stripper, it was possible to fix the size of each oil cut within narrow limits.

It was first attempted to elute the low viscosity index adsorbed constituents by following the n-pentane wash with more polar percolants of increasing desorbing power. Ethyl ether, benzene, and ethyl alcohol were used successively in that order, but the method proved unsatisfactory, apparently because of remixing of fractionated material within the column. In an attempt to improve the separation, several n-pentane–ethyl alcohol washes of increasing alcohol strength were used, starting with a mixture of 98% n-pentane and 2% alcohol. This method also proved unsatisfactory for the same reason as before. Finally, the method described, taking adsorbent cuts mechanically and extracting each cut in a Soxhlet, was used. This was found to be satisfactory with regard to recovery without remixing of fractionated material, although it is a more time-consuming operation.
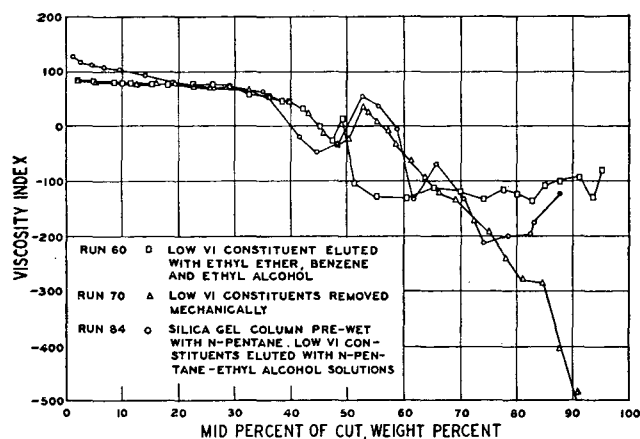

Figure 5.   Adsorption Fractionation of Reference Pale Oil

The effect of the above variables on the efficiency of separation is shown in Figure 5. Three runs were made employing a reference pale oil of 85 S.s.u. at 210° F. and −2 viscosity index prepared by blending acid-treated pale neutral oils, and a large number of cuts were taken. In run 60, following the n-pentane wash, the low viscosity index constituents were eluted successively with ethyl ether, benzene, and ethyl alcohol. All the material between 50 and 100% yield was found to be between −80 and −135 V.I., and reversals of viscosity index with increasing yield occurred. However, in run 70 the column was mechanically separated into 15 parts following the n-pentane wash, and the adsorbed oils were recovered in Soxhlets. In this case, the recovered oils were between −36 and −506 V.I., and the results could be plotted on a fairly smooth continuous curve. In run 84, prewetting of the adsorbent with n-pentane, as described above, raised the viscosity index of the initial cut from 85 to 127, and all the percolate up to 19% yield was of higher viscosity index than for the previous runs. The desorbent used in this run, n-pentane plus increasing amounts of ethyl alcohol, effected better recovery of low viscosity index constituents than did the combination used in run 60, but considerable mixing of fractionated materials still occurred.

Silica gel was used in the first series of experiments employing this method. It was found that total yields from the adsorption fractionation step were erratic, particularly with high-sulfur, high-asphalt-content residua. This difficulty was overcome by the use of Thermofor catalytic cracking catalyst, ground and screened to 28 to 200 mesh. Total yields of 99 + % are obtained with the latter. The larger average pore size of the Thermofor catalytic

cracking catalyst apparently accounts for the better recovery. Viscosity index was used as the distinguishing property of fractionated oils because commercially it is of primary importance as a control in manufacture of lubricating oil. If a large number of cuts is taken and the viscosity index of each cut is plotted against yield (mid per cent point), two reversals of slope occur,
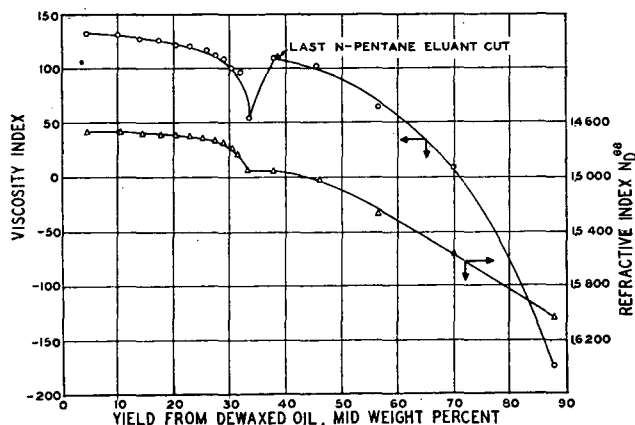

Figure 6.   Results of Adsorption Fractionation Step

the last one or two eluant cuts being higher in viscosity index than the preceding cut. Figure 6 shows such a relationship as well as the relationship between refractive index and yield for the same cuts. The refractive index–yield curve has a flat portion at the region of reversal of viscosity index. However, the discontinuity for the refractive index curve is markedly less than for the viscosity index curve. Oils of the same viscosity index but differing appreciably in refractive index are obtainable in the case cited—for example, three oils of +90 V.I. can be obtained whose refractive indexes would be 1.4880, 1.4950, and 1.5140. Increase in molecular weight accounts for only part of these differences in refractive index. Refractive index, therefore, is a better measure of that quality which determines adsorbability and hence separation by adsorption fractionation. All this is evidence of the well-known fact that viscosity index is not a simple function of polarity, aromaticity, or molecular type.
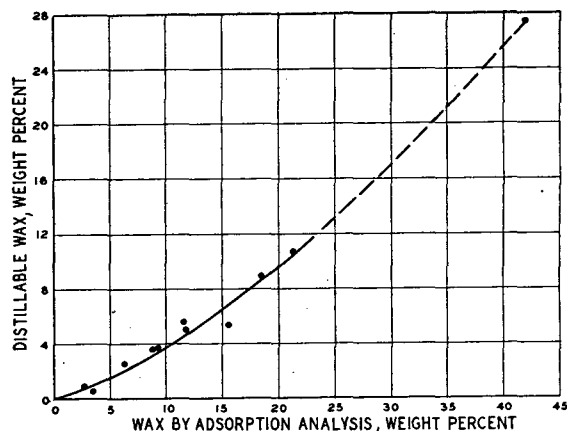

Figure 7.   Wax Content of Residua

One of the major advantages of the analysis is the accurate establishment of the wax content of a residuum. Some commonly used methods, involving the measurement of distillable wax, give results far from the correct value because the destructive distillation of the residuum causes cracking of high boiling

wax fraction. Figure 7 compares the wax content as determined in the adsorption analysis with that obtained by a distillation method (3). Comparative values from Figure 7 are as follows:.

Wax Content (Adsorption Analysis), Weight %	Distillable Wax, Weight %	Distillable Wax ÷ Wax Content (Adsorption Analysis), %
2	0.6	30
5	1.7	34
10	3.9	39
15	6.4	43
20	9.4	47
25	12.8	51
40	26	65

By the use of Figure 7, wax content for unknown crude oils may be estimated approximately from methods measuring distillable wax.

The repeatability of the final viscosity index–yield curve is of importance in assessing the value of the method. The method does require very careful workmanship in carrying a 200-gram sample of residuum through the above steps. The repeatability is estimated to be about .±5% of the indicated yield at a given viscosity index, as shown by several check analyses.

The yields obtained by the adsorption method of analysis are greater than those obtained from commercial methods of manufacture of lubricating oils, especially in the high viscosity index range. Good relationships with commercial yields have been established, however, and the method has been found very useful because in a single analysis the entire viscosity index range of lubricating oil obtainable by commercial treatment is covered. It is planned in a later paper to show the relationship with com- mercial yields and the methods of using the data for plant design purposes.

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[End of Adsorption Symposium]

Analysis of Natural Gas

Comparison of Two Chemical Methods

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Two volumetric methods of absorption-combustion are compared by studying the results of the analysis of a standard sample of the natural gas type. One depends upon the measurement of contraction on burning and carbon dioxide produced; the other adds to these the measurement of oxygen consumed. The latter method, not in general use, is shown to be the more accurate. The analyses were performed by laboratories cooperating with Subcommittee VII of Committee D-3 of the American Society for Testing Materials.

THIS is the seventh in a series of reports (3–9) dealing with the cooperative analysis of standard samples of fuel gases. (These samples are not to be confused with the regular standard samples offered for sale by the National Bureau of Standards. They are prepared by the bureau especially for these analyses, and are issued free to laboratories cooperating with Committee D 3-VII of the American Society for Testing Materials.) These analyses are designed to furnish basic information for the development of tentative standard methods for the analysis of fuel gases, a task assigned to Subcommittee VII, Committee D 3, American Society for Testing Materials. The plan for this development has been outlined in two previous reports (5, 6).

The preparation of the standard sample used in this series of analyses, designated as A.S.T.M. D 3-VII-4, has previously been described (6); the sample was designated in the reference cited as A.S.T.M. D 3-VII-2. The No. 2 and No. 4 samples were identical. The instructions issued with respect to transfer of sample from cylinder to analytical apparatus have also been given (6). Accordingly, these matters are not discussed here.

In the work previously reported (6), the majority of the laboratories used the conventional method of analysis by combustion, which takes account only of the amount of contraction on burning and the amount of carbon dioxide produced (Method A); but a few laboratories used a combustion method (long in use at the National Bureau of Standards) which also takes into account oxygen consumed (Method B). The results from the latter group did not vary markedly, as did those from the former. However, relatively few laboratories used Method B, and a somewhat more complete study was accordingly planned to decide whether the virtue of consistency is really a characteristic of the more complete Method B. Twelve laboratories cooperated in this study. Seven contributed ten analyses each by

Method A and by Method B; the other five added enough analyses to make a total of 100 for each method.

OUTLINE OF THE TWO METHODS

The two methods were outlined in a set of instructions issued to the cooperating laboratories.

Method A. 0. Equilibrate all reagents.
1. Determine carbon dioxide by absorption in an aqueous solution of potassium hydroxide.
2. Determine oxygen by absorption in alkaline pyrogallol. For the sake of uniformity, use a solution prepared as follows:

To each 100 ml. of a clear, decanted solution of potassium hydroxide which was saturated at 20° C., add 17 grams of reagent pyrogallol dissolved in 7 or 8 ml. of warm water. If the pyrogallol solution regularly used is saturated with respect to potassium hydroxide and contains nearly the same proportion of pyrogallol, it will not be necessary to prepare another. If any fresh solution is prepared, absorb about 500 ml. of oxygen from air before using the solution for the analysis of this sample. If a chromous solution is preferred, make ten analyses with this in addition to the ten made with the pyrogallol solution. [A recent experimental study of the behavior of pyrogallol solutions by Kilday is being published soon (1). An improved formula for a pyrogallol solution will be given.]
3. Burn the residue (or portion thereof) from the absorption analysis over hot platinum in the presence of excess oxygen, and note the rate at which the sample is transferred to the combustion pipet during the first passage. Measure the contraction (TC) after burning, and the carbon dioxide produced (CO₂) by the combustion. Compute methane and ethane according to the stoichiometric relations:

$$CH_4 = \frac{1}{3}(4TC - 5CO_2)$$

$$C_2H_6 = \frac{1}{3}(4CO_2 - 2TC)$$

Method B. 0. Connect to the manifold two pipets filled with the saturated solution of potassium hydroxide, and two pipets filled with the pyrogallol solution. Use one pair to absorb carbon dioxide and oxygen from the original sample, and equilibrate accordingly. Use the other pair to absorb the carbon dioxide produced by combustion and the excess oxygen after combustion, and equilibrate with the mixtures entering each. If the manifold will not accommodate these pipets, use one pair, making ten analyses for carbon dioxide and oxygen in the sample. Then equilibrate these for the combustion analyses to follow.
1. Determine carbon dioxide by absorption in saturated aqueous potassium hydroxide.
2. Determine oxygen by absorption in the pyrogallol solution previously noted.

Make ten analyses according to (1) and (2) above. Then make ten combustion analyses as follows:
3. After flushing the manifold with nitrogen, measure about 40 ml. of nitrogen and transfer to the second potassium hydroxide pipet—i.e., the one used for absorption of carbon dioxide produced by the combustion.
4. Measure about 95 ml. of oxygen, the purity of which is known, and transfer to the combustion pipet.
5. Measure about 33 ml. of sample, taking a fresh portion—not the residue after the absorption of carbon dioxide and oxygen. Transfer this over the hot platinum in the combustion pipet at a rate not exceeding 1.5 ml. per minute for the first complete passage. At the end of the first passage into the combustion pipet, take into the buret the gas in the arm of the manometer connected to the manifold; and transfer this in turn to the combustion pipet. Succeeding passages may be made at greater rates, say 10 ml. per minute. (If the manometer is connected to the buret instead of the manifold, do as well as possible without upsetting it.)
6. Measure the contraction after combustion. (Allow no more than 0.1 ml. of water to collect in the combustion pipet at any time.)
7. Determine carbon dioxide produced by absorption in the second potassium hydroxide pipet. Correct this by subtracting the average value obtained from the ten independent analyses for carbon dioxide in the original sample. (Because the measured nitrogen is added at this point, allow for it.)
8. Determine the excess oxygen by absorption in the second pyrogallol pipet. Compute the oxygen consumed by subtracting the excess oxygen from the oxygen originally taken (corrected for known purity) plus the oxygen originally in the sample.
9. Subtract both the nitrogen added at the beginning of the analysis, and the nitrogen added as an impurity of the oxygen,

from the residue, and report the remainder as "N₂" or inert in the sample.
10. Compute methane and ethane as follows:

$$CH_4 = \frac{1}{3}[7(TC + CO_2) - 9O_2]$$

$$C_2H_6 = \frac{1}{3}[6O_2 - 4(TC + CO_2)]$$

Although the chief difference between the two methods is the measurement of oxygen consumed and the method of calculation made possible by this additional datum, there are other important differences, and some advantages are gained.

The saturated solution of potassium hydroxide is the most obliging on the list of gas analysis reagents with respect to freedom from exchange of gases between the solution itself and the gas mixture in contact with it, and errors caused by physical solution are considerably reduced.

Errors from sorption and desorption are further minimized by the use of the separate pairs of pipets whose reagents are properly equilibrated with respect to the mixtures they encounter.

The fresh sample for combustion ensures one that has undergone no change of composition by previous reaction or physical absorption. The combustion characteristics of the sample are thus measured directly.

A direct measure of the unreacted inert is an over-all check on the analysis and preferable to computing nitrogen as 100% minus the sum of the percentages of other components as calculated.
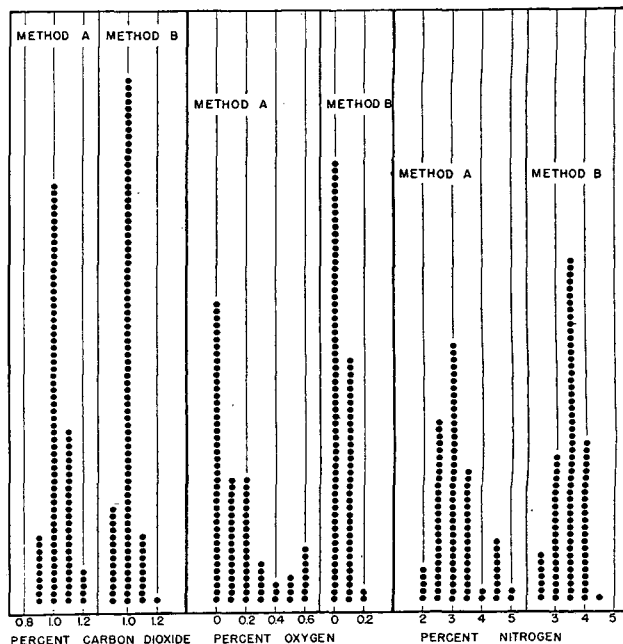

Figure 1.   Frequency Distribution Plot of Carbon Dioxide, Oxygen, and Nitrogen

In addition, it has been repeatedly shown (9) that in the combustion analysis the contraction is always too high and the carbon dioxide produced is always too low. This is caused by the solution of carbon dioxide in rubber and water present in the analytical apparatus and by the deviation of carbon dioxide from ideality. The net effect is significant, causing the calculated methane to be always too high and the ethane too low. These combined errors are eliminated by using the contraction after burning plus carbon dioxide as one term of the stoichiometric equations and solving with oxygen consumed as the other.

Aside from the additional time required, Method B has the disadvantage that, in calculating, the observed volumes are multiplied by factors as great as 2 or 3, whereas the calculation for
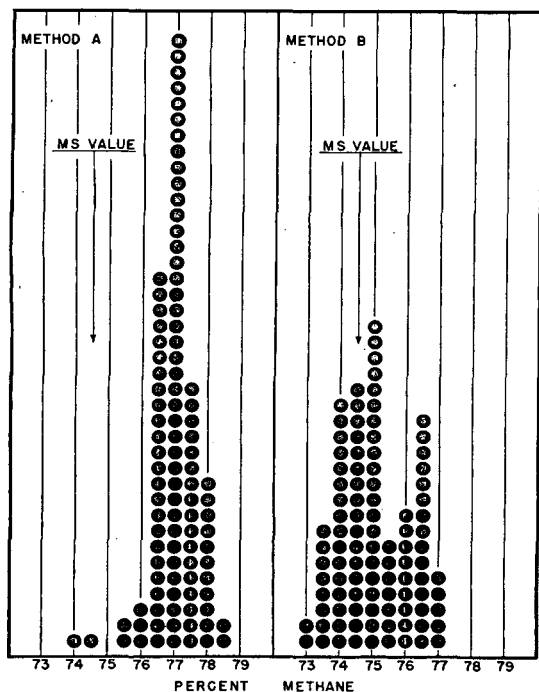
Figure 2. Frequency Distribution Plot of Methane

Method A employs 1.67 as the maximum factor. The determination of oxygen consumed depends upon the measurement of the oxygen taken for combustion, the previous analysis of this oxygen for purity, the oxygen in the sample, and the measurement of the residual oxygen. Possibly these considerations have made the method appear unattractive. At any rate, it has not been extensively employed.

ANALYTICAL DATA

The analytical data are presented in a series of frequency distribution plots as in previous reports of this series. These plots have the virtue of showing at a glance what otherwise would require considerable study of the tabulated data. Each circle of a plot represents a single determination of the substance named in the legend. The abscissas are values derived from the analyses; and these values are plotted equidistant on the ordinates, and so indicate the frequency with which they occur. For example, in the plot showing the determination of carbon dioxide (Figure 1, left section) it is seen that by Method A, 10 values of 0.9% were reported, together with 60 determinations of 1.0%, 25 of 1.1%, and 5 of 1.2%.

Determination of Carbon Dioxide. Continuing the study of this plot, it is seen that Method B gives somewhat greater reproducibility and accuracy in reporting correctly the 1.0% carbon dioxide of this sample (3–9). This may be expected when a reagent is equilibrated specifically with the sample to be analyzed. In the case of Method A, where the single solution of potassium hydroxide served for the removal of carbon dioxide from both sample and products of combustion, the reagent could be expected alternately to yield oxygen and nitrogen to the sample during absorption of carbon dioxide therefrom, and to yield various components of the sample itself to the products of combustion during absorption of carbon dioxide from these products. Also, the solution would absorb components of the sample other than carbon dioxide with each analysis, inasmuch as an absorption of carbon dioxide from the products of combustion interposed between each absorption of carbon dioxide from the sample would never allow the solution to become properly equilibrated with

respect to the original sample. If the sample as a whole were more soluble in the solution than were the products of combustion, the net error would be too large an amount of carbon dioxide indicated, which is the tendency shown here.

Determination of Oxygen. Again continuing the study of this plot (Figure 1, mid-section) it is seen that Method B gives greater reproducibility and greater accuracy in the determination of oxygen, approaching but not equaling the excellent performance of the mass spectrometer with this same sample (3). There was no oxygen in this sample, and Method B indicates this fact more nearly than does Method A. Again this may be expected when a reagent is equilibrated specifically with the sample with which it is to react. In the case of Method A, the solution of potassium pyrogallol was alternately used for removal of oxygen from the original sample and from the products of combustion of this sample. Thus, as in the determination of carbon dioxide, the reagent would never become properly equilibrated with respect to the sample itself, because passage of the products of combustion into the solution would displace dissolved portions of the sample and thus cause the physical absorption of more of the sample during each determination of oxygen originally present. This particular determination has caused a good deal of trouble in the analysis of fuel gases.
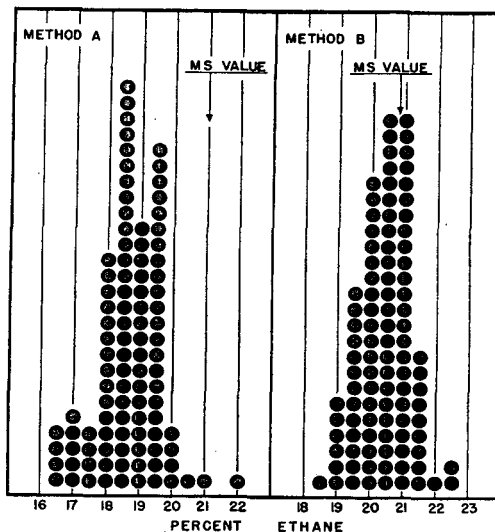

Figure 3. Frequency Distribution Plot of Ethane

Determination of Nitrogen. No matter what chemical approach is used for the analysis, in the absence of errors nitrogen should be the same, but this is not the case. Method A calculates nitrogen as 100 minus the sum of everything determined. Method B measures the nitrogen as unreacted residue at the end of the analysis. The frequency distribution plot (Figure 1, right section) shows a greater reproducibility for Method B, and better agreement with the most probable value of 3.45. The highest frequency for Method B, 3.5, agrees also with the mean and the median, 3.5. The highest frequency, mean, and median for Method A are all 3.0.

Determination of Methane. The frequency distribution plot for methane (Figure 2) shows the highest frequency at 77.0% by Method A. The mean and median are both 77.0%, in agreement with the highest frequency. Method B yields a highest frequency, mean, and median of 75.0%. The spread is about the same for both methods: 4.5% for Method A and 4.0% for Method B. Method A appears to give the greater reproducibility, although it will be shown later that Method B yields the greater accuracy. The secondary high frequency appearing at 76.5% (Method B) is explained by results from a single labora-
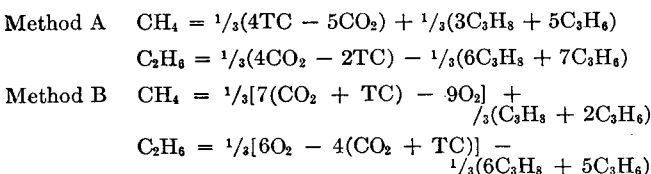
tory whose determinations were unusually reproducible, 8 out of 10 being 76.5. The most probable values for methane are:

By Method A   77.0%
By Method B   75.0%

Determination of Ethane. The frequency distribution plot for ethane (Figure 3) shows the highest frequency at 18.5% for Method A and 20.5 to 21% for Method B. The mean for Method A is 18.7%; the median is 18.5. The mean for Method B is 20.6%; the median is 20.5. The spread is 5.5% for Method A and 4% for Method B. Reproducibility is essentially the same, but the accuracy of Method B will be shown to be greater. The most probable values for ethane appear to be:

By Method A   18.5%
By Method B   20.5%

Accuracy of Determination of Methane and Ethane. It is well known that a combustion analysis does not disclose the true composition of a mixture containing more than two hydrocarbons of a related series. Propane and propylene, indicated by the mass spectrometer, were present in this sample in the amounts 2.8 and 0.2%, respectively (3). In the combustion analysis, propane was necessarily calculated as $2C_2H_6 - CH_4$. Propylene should be calculated as $CH_4 - {}^5/_3C_3H_6$ and $C_2H_6 + {}^7/_3C_3H_6$ in Method A, and as $CH_4 - {}^2/_3C_2H_6$ and $C_2H_6 + {}^5/_3C_3H_6$ in Method B. These corrections are more readily seen from inspection of the stoichiometric equations expressing the reactions:

Method A $CH_4 = {}^1/_3(4TC - 5CO_2) + {}^1/_3(3C_3H_8 + 5C_3H_6)$

$C_2H_6 = {}^1/_3(4CO_2 - 2TC) - {}^1/_3(6C_3H_8 + 7C_3H_6)$

Method B $CH_4 = {}^1/_3[7(CO_2 + TC) - 9O_2] + {}^1/_3(C_3H_8 + 2C_3H_6)$

$C_2H_6 = {}^1/_3[6O_2 - 4(CO_2 + TC)] - {}^1/_3(6C_3H_8 + 5C_3H_6)$

If the most probable spectrometric values for propane and ethane are accepted, the net errors in the calculated values by Method A would be: methane 3.1% too low, ethane 6.1% too high; by Method B: methane 2.9% too low, and ethane 5.9% too high. Thus the value 77.0% methane reported by Method A should actually have been 80.1 if the known amounts of propane and propylene had been properly accounted for. The spectrometric value was 77.6, and thus Method A does not agree with

the spectrometer in the determination of methane. Similarly, the value 18.5% ethane reported by Method A should actually have been 12.4%, with propane and propylene properly accounted for, and this does not agree with the 14.7% found by the mass spectrometer. On the other hand, Method B reports 75.0% methane; and when this is corrected as indicated above, the resulting 77.9% essentially agrees with the spectrometric value 77.6. Similarly, the 20.5% ethane of Method B, when corrected, is 14.6%, which agrees with the spectrometric value of 14.7.
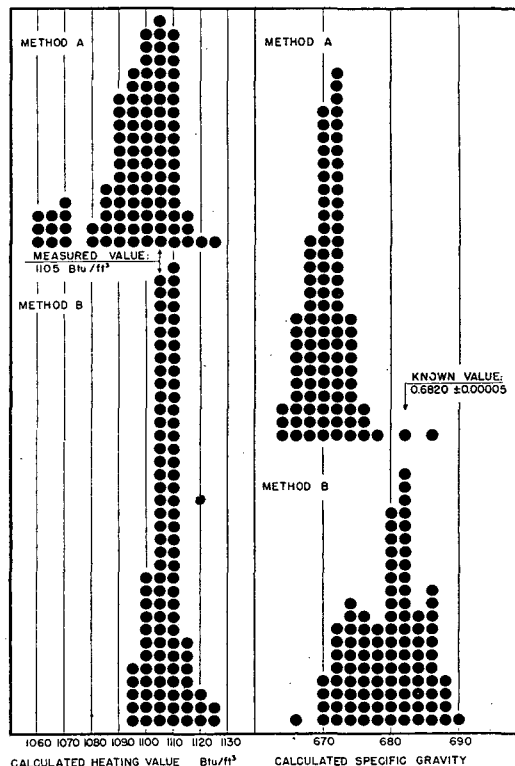

Figure 4. Frequency Distribution Plot for Calculated Heating Value and Specific Gravity

Table I. Comparison of New with Old Results by Method A

	Laboratory								
Component	4	5	8	11	17	18	22	24	28
CO₂									
Old	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.1
New	1.1	1.1	1.0	1.0	1.0	1.1	1.0	1.0	1.0
Δ	0.1	0.1	0.1	...	...	0.1	...	...	0.1
O₂									
Old	0	0.3	0.2	0.4	0.1	0.1	0	0	0.1
New	0.1	0.3	0	0.5	0.2	0	0	0	0
Δ	0.1	...	0.2	0.1	0.1	...	...	...	0.1
N₂									
Old	3.0	3.8	1.9	2.1	2.8	2.5	4.0	3.2	4.0
New	2.7	2.9	2.7	4.5	2.9	2.7	2.9	3.6	2.7
Δ	0.3	0.9	0.8	2.4ᵃ	0.1	0.2	1.1	0.4	1.3ᵃ
CH₄									
Old	76.7	76.6	78.4	79.4	77.1	77.4	73.9	76.7	74.4
New	77.3	77.1	76.8	77.0	77.4	78.3	76.3	77.1	76.9
Δ	0.6	0.5	1.6ᵃ	2.4ᵃ	0.3	0.9	2.4ᵃ	0.4	2.5ᵃ
C₂H₆									
Old	19.4	18.3	18.5	17.0	19.1	19.1	21.1	18.5	20.6
New	18.8	18.7	19.5	16.9	18.4	18.7	19.8	18.3	19.4
Δ	1.6ᵃ	0.4	1.0	0.1	0.7	0.4	1.3ᵃ	0.2	1.2ᵃ
Calcd., B.t.u./cu. foot									
Old	1105	1086	1106	1092	1105	1106	1108	1106	1103
New	1102	1098	1110	1065	1096	1106	1111	1091	1105
Δ	3	12ᵃ	4	27ᵃ	9	...	3	15ᵃ	2
Calcd., sp. gr.									
Old	0.673	0.672	0.665	0.659	0.671	0.670	0.686	0.675	0.683
New	0.670	0.671	0.672	0.670	0.669	0.669	0.675	0.670	0.672
Δ	0.003	0.001	0.007ᵃ	0.011ᵃ	0.002	0.001	0.011ᵃ	0.005	0.011ᵃ

ᵃ Differences greater than 1%, or greater than 10 B.t.u., and 0.007 specific gravity.

The extent of such agreement is shown graphically on the frequency distribution plots by reversing this correction and translating the spectrometric values to correspond to the combustion values. These translated values are indicated by the arrows marked "MS Values." It is seen how nearly the chemical Method B is in agreement with the spectrometric method, while Method A is not.

Calculated Heating Value. The frequency distribution plot for the calculated heating value (Figure 4, left section) shows a greater reproducibility and perhaps a slightly greater accuracy yielded by Method B. Highest frequency for Method B lies between 1105 and 1110 B.t.u. per cu. foot, while that for Method A is centered at 1105. However, the median for Method A is 1100, and that for Method B is 1105. The mean for Method B is 1107 and that for Method A is 1097. Thus the most probable value for Method B lies nearer the measured value, 1105, than does the most probable value for Method A. [Heating value was measured by J. H. Eisman and Ralph Jessup, National Bureau of Standards (see *6*, p. 30).]

Calculated Specific Gravity. The calculated specific gravity is an over-all measure of the accuracy of the analysis, and is accordingly of interest. The known value, 0.68200 ± 0.00005, is neatly matched by the highest frequency of Method B, while the highest frequency of Method A, 0.672, is considerably to the left of this value. The mean and median of Method B are 0.680. The mean of Method A is 0.671; the median is 0.670. Thus, although Method A has yielded better reproducibility in this instance, the accuracy obtained is relatively poor. [The specific gravity was measured by Carroll Creitz, National Bureau of Standards. The method used is described in (*2*).]

Comparison of New with Old Results Obtained by Method A. Because sample A.S.T.M. D 3-VII-4 was the same as A.S.T.M. D 3-VII-2, the opportunity occurs of comparing the analyses of the same sample made by the same laboratory several years apart. The laboratory averages have been used for this purpose and are tabulated (Table I) to show the old and new results and the difference between the two, for each component and for calculated heating value and gravity. Differences greater than 1.0%, or greater than 10 B.t.u. and 0.007 specific gravity, are indicated.

On the whole the earlier results are in agreement with the later ones. There are only two notable disagreements in the determination of nitrogen, four in the determination of methane, three for ethane, three in calculated heating value, four in calculated specific gravity, and none in the determinations of carbon dioxide and oxygen.

REVIEW

Method B, which takes account of the oxygen consumed during a combustion as well as the contraction and carbon dioxide produced, gives a better analysis than Method A, which takes account of only contraction and carbon dioxide. In particular, Method B gives greater accuracy in the determinations of carbon dioxide, oxygen, nitrogen, methane, and ethane and in calculated heating value and calculated specific gravity. Method B yields greater reproducibility in the determination of carbon dioxide, oxygen, and nitrogen and in calculated heating value; Method A gives better reproducibility in the determination of methane and in calculated specific gravity. In the determination of ethane, reproducibility appears about equal. The results from Method B can be made to agree with those obtained by the mass spectrometer, but this is not true for Method A. Thus, in this instance, two totally different analytical methods, one chemical and the other physical, can be brought into agreement.

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(4) *Ibid.*, 22, 23 (1950).
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(6) *Ibid.*, 38, 19 (1947); **RP 1759.**
(7) *Ibid.*, 38, 491 (1947); **RP 1789.**
(8) *Ibid.*, 44, 509 (1950); **RP 2098.**
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Analysis of a Carbureted Water Gas

By Volumetric Chemical Methods and by Mass Spectrometer

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Fifty-one laboratories throughout the country have analyzed a standard sample of the carbureted water gas type by the conventional volumetric chemical methods and the mass spectrometer. The analytical data are compared in a series of frequency distribution plots which show the strong and weak points of these totally different methods.

THIS is the sixth of a series dealing with the cooperative analysis of standard samples of fuel gases. (These samples are not to be confused with the regular standard samples prepared and offered for sale by the National Bureau of Standards. Instead, they are mixtures prepared especially for the laboratories cooperating on this project with the American Society for Testing Materials.) The analyses were conducted to furnish basic information for the preparation of standard methods by Subcommittee VII of Committee D-3, American Society for Testing Materials. The procedure for the development of these standards has been outlined in previous reports (*3*, *4*), and includes the evalua-

tion of apparatus and methods by means of performance with standard samples.

The 51 laboratories cooperating in the analysis of this sample are widely distributed throughout the United States, and represent gas, oil, steel, and various chemical industries as well as college and federal research groups. Their work is typical of the better grade of gas analysis by laboratories using modern equipment.

The preparation and distribution of this standard sample of the carbureted water gas type have been previously described (*3*), and its analysis by the conventional chemical methods (*3*) and by

the mass spectrometer (6) has been reported. These reports give a general account of the cooperating laboratories, apparatus, and specific methods of analysis employed—information which is desirable in fully evaluating the data presented in this paper. The analytical data from both of these cooperative analyses are assembled here in such a manner that comparisons and contrasts between these widely different chemical and physical methods are brought into sharp focus. These data again show the real state of gas analysis in this country, and are worth a few moments' reflection by those who analyze gases or use gas analyses.

MANNER OF PRESENTING ANALYTICAL DATA

Although the usual tabulation of the data has been made, prolonged contemplation of the tabulated version does not disclose what may be seen in a moment's study of frequency distribution plots of these same data. The plots are really actual pictures of the analytical data and make most of the conclusions self-evident. Thus, little of the usual discussion is necessary.

In each plot the results of the chemical analyses have been given in the lower or left section, and are marked C. The results of the mass spectrometric analyses are marked MS, and appear in the upper- or right-hand sections. Each circle of a plot represents a single determination of the gas indicated in the legend. The circles are plotted equidistant on the ordinates. Thus the abscissas are values derived from the analyses, and the ordinates indicate the frequency with which they occur. For example, in the plot for the chemical determination of carbon dioxide (Figure 1, left section), the following values for carbon dioxide have been reported: 2 determinations of 3.7%, 1 of 4.0%, 5 of 4.2%, 20 of 4.3%, etc.

[In reporting the arithmetical mean of chemical determinations, the values given are for the preferred chemical method unless otherwise noted. This is designated as Method II in the complete report of the chemical analyses (3), and involves a combustion over copper oxide for hydrogen and carbon monoxide rather than the absorption of carbon monoxide in cuprous chloride.]

DISCUSSION OF ANALYTICAL DATA

Determination of Carbon Dioxide. Continuing the study of the frequency distribution plot for carbon dioxide (Figure 1), the highest frequencies for both chemical and spectrometric methods occur at 4.5%. Mean and median of the chemical method are both 4.5, and these values are neatly matched by the spectrometric approach. Everything is in agreement. The spread of values is slightly greater for the spectrometric method, although the Gaussian distribution is evident in both sections of the plot. The chemical method appears to give somewhat greater reproducibility.

Determination of Oxygen. The oxygen originally present in this sample, when it was analyzed as No. A.S.T.M. D 3-VII-1 by chemical methods, was 0.5%. Most of this was removed before the sample was analyzed as No. A.S.T.M. D 3-VII-5 by the mass spectrometer, leaving less than 0.05%. When rounded off, the spectrometric values should indicate 0% if the determination is correct; the chemical values should indicate 0.5%. Thus, if the abscissa 0.5 on the C plot is changed to 0, the two plots (Figure 2) can be directly compared.

It is seen at once that the chemical method found considerably more oxygen than was present, and the spectrometric method did not have this fault. This duplicates the history of the analysis of a natural gas by these two methods (2). These analyses give convincing evidence of the superiority of the mass spectrometer with respect to the determination of small amounts of oxygen in fuel gases of these types, and clearly demonstrate the need of improved chemical methods.

Determination of Nitrogen. The values for nitrogen obtained by both methods are rather diffused over the frequency distri-
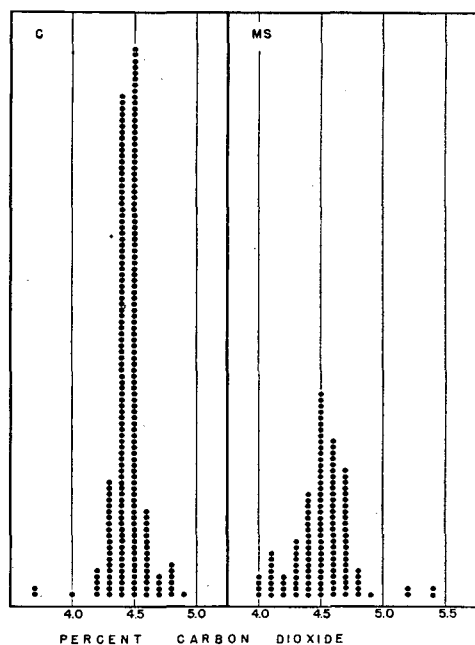

Figure 1. Frequency Distribution Plot of Carbon Dioxide

bution plots (Figure 3). The chemical plot seems more to suggest the Gaussian pattern, but not overstrongly. The chemical mean is 6.3 ± 0.3 (average deviation), and the median is 6.3. The spectrometric mean is 5.9 ± 0.8 (including values from 4.2 to 8.2 only), and the median is 5.8 (dropping the high ones). These values are more closely in agreement with the best chemical value, 5.74 + 0.06. The 12 high rogues noted on the MS plot attest to some confusion of nitrogen with carbon monoxide in the mass analysis.

Determination of Hydrogen. The frequency distribution plot (Figure 4) reveals the fact that neither the chemical nor the mass spectrometric method is altogether happy with this determina-
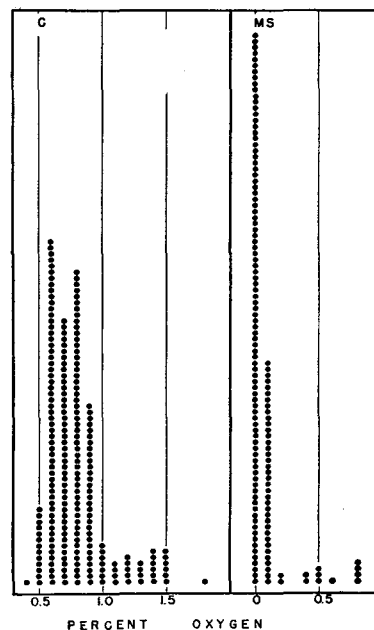

Figure 2. Frequency Distribution Plot of Oxygen

tion. Of the two, the spectrometric values are more widely scattered over a range of 7.4% and the plot shows no really significant highest frequency. The chemical values are somewhat more clustered, the total spread being 5%, with the majority of the determinations grouped between 34 and 35.5%. The mean of the chemical values is 34.4 ± 0.25 and the median is 34.8. The mean of the spectrometric values (33 to 37.8, inclusive) is 35.1 ± 0.8, and the median is 35.1. These values are not in disagreement but their derivation is from data too widely scattered to warrant dependence upon the data of any laboratory selected at random.
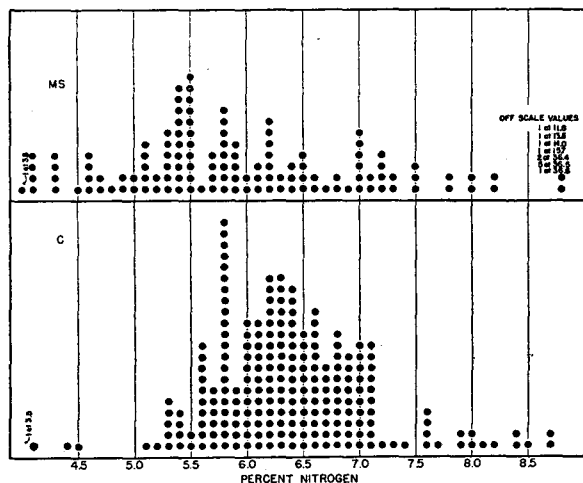

Figure 3. Frequency Distribution Plot of Nitrogen

Determination of Carbon Monoxide. The frequency distribution plot (Figure 5) clearly shows the effect of two independent chemical methods [one absorption, the other combustion (3)], with two high frequencies apparent at about 29.5 and 30.0%. Even so, all the chemical values are more closely grouped than the spectrometric values, which are indeed inconveniently various. The spectrometric values show no adherence to the Gaussian pattern, and the wide dispersion causes the uncomfortable feeling that, if the results of but a single laboratory were available, they might be 6 or 7% away from the results of another, 3% away from the mean of, say, 30 laboratories, and probably no closer to the mean than 1%. (These observations are based on the laboratory averages.) In spite of all this, the mean of the spectrometric values (28.4 to 32.3, inclusive) is 30.3 ± 0.9, which is in reasonable agreement with the mean of all chemical values, 29.8 ± 0.2. The median of the spectrometric values is 30.4; that of the chemical values is 29.7. From the chemist's viewpoint, the problem is to determine whether absorption or combustion is the preferable method. From the physicist's viewpoint, the direction of required improvement should be decided. This may involve increasing the sensitivity of the relatively weak 12 peak of carbon monoxide, or the chemical removal of carbon
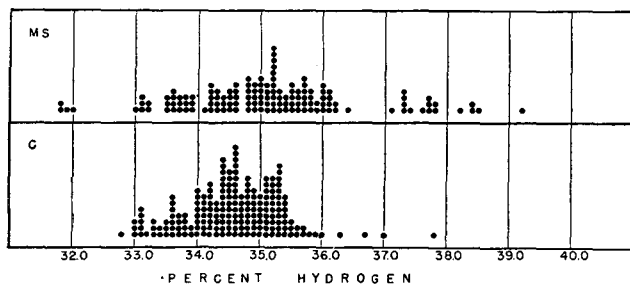

Figure 4. Frequency Distribution Plot of Hydrogen

monoxide to determine the resulting difference in the sensitive 28 peak, or a better method of computation to unscramble the overpopulous 28 peak.

Determination of Methane. With the first of the hydrocarbons in this sample, the mass spectrometer is obviously competent to deal with the situation, and the chemical methods are relatively less adequate (see Figure 6). In the nature of things this must be so; for, as is well known, the chemical methods cannot (as a matter of simple algebra) determine more than two of a related series of hydrocarbons. Thus, if propane is present together with methane and ethane (as it almost invariably is), it is calculated from the combustion data as $2C_2H_6 - CH_4$, and would never be identified in the actual analysis to compensate in any way for the error its presence had caused.

The spectrometric mean is 8.0 ± 0.4 (with three low values dropped); the chemical mean is 8.6 ± 0.3. The spectrometric median, 8.0, is in agreement with the highest frequency, 8.1; the chemical median is 8.7; the highest frequency is 8.6. The preferred chemical method, using a combustion procedure rather than absorption for the determination of carbon monoxide prior to the combustion of the hydrocarbons, gave a mean of 8.4.
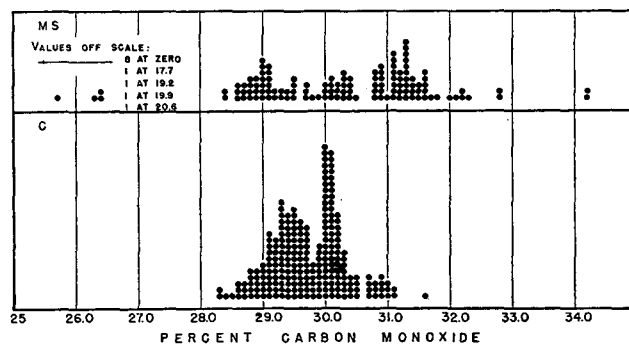
Figure 5. Frequency Distribution Plot of Carbon Monoxide
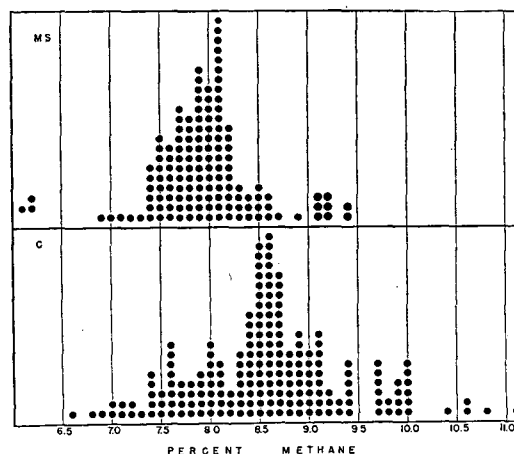
Figure 6. Frequency Distribution Plot of Methane

Determination of Ethane. The mass spectrometer offers a clean-cut determination of ethane with values well grouped between 2.7 and 3.7% (see Figure 7). The highest frequency occurs at 3.3, the median at 3.3, and the mean at 3.3 ± 0.15. In contrast, the chemical values are more scattered between 0.5 and 3.7. The highest frequency is about 2.8, the median is 2.8, and the mean is 2.9 ± 0.17—all lower than the spectrometric values.

Determination of Ethylene. If two outside values are eliminated, the mass spectrometer indicates from 11.8 to 13.7% of ethylene; eliminating three values from the chemical determinations leaves a range of 12.1 to 15% (see Figure 8). However, almost all the chemical values lie between 12.1 and 13.7%. The chemical plot is more nearly along the Gaussian lines, with two peaks, the lesser of which is caused by absorption in bromine, the greater by absorption in fuming sulfuric acid. The highest frequency (chemical) is at 13.0%, and the mean is 12.9 ± 0.10, corresponding to the median, 12.9. The highest frequency of the spectrometric plot is not so apparent, although the blocklike structure may be estimated to center around 13%. The mean is 12.9 ± 0.4, and the median is 12.9. Agreement between the physical and chemical methods is good.

Figure 7. Frequency Distribution Plot of Ethane

Other Hydrocarbons. The right section of Figure 8 gives a record of the small amounts of other hydrocarbons reported by a few of the spectrometric laboratories. Out of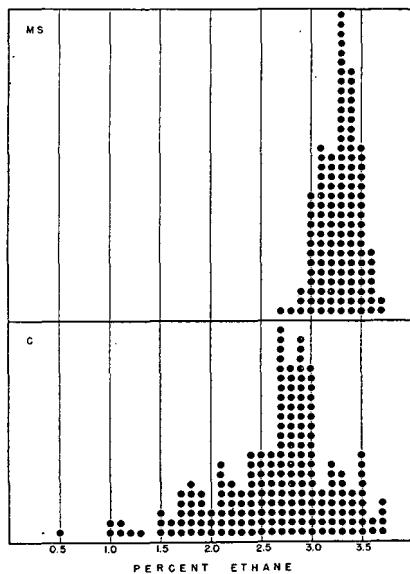 138 analyses, propane was reported 15 times, propylene 18 times, n-butane 6 times, butenes 6 times, "C_3" three times, C_4^+ 12 times, and acetylene 3 times. One of the delicate decisions sometimes to be made in mass spectrometric analyses is illustrated by these minority reports; small or trace amounts of such components may actually be present in the sample, or may be contributed by desorption of lubricant, glass, or metal within the spectrometer or sampler. Extremely careful evacuation, flushing, and equilibration of the spectrometer and sampler are always necessary if such difficulty is to be avoided.

CALCULATED HEATING VALUE

The heating values calculated from all the analyses are plotted in Figure 9. The spectrometric values show no decisive Gaussian pattern. The mean of values from 529 to 566 is 550 ± 7; the median is 551. The chemical plot also shows widely scattered values, but the approximately central portion is well shaped, with a high frequency at 545, and a median of 545. The mean of the chemical values is 545 ± 3.3. The measured heating value is 549. [This measurement was made by John Eiseman and Ralph Jessup of the National Bureau of Standards (3, p. 327).] Thus, it appears that the spectrometric approach may give the greater accuracy, and the chemical approach the greater reproducibility, although the matter is somewhat vague.
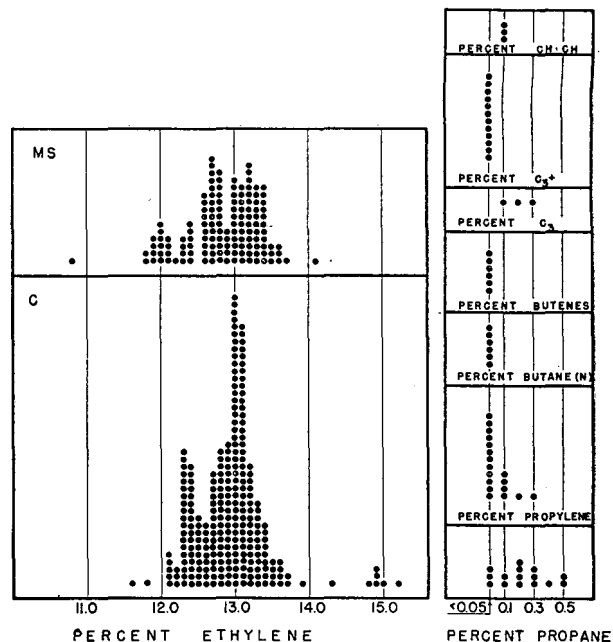
Figure 8. Frequency Distribution Plot of Ethylene, Propane, and Other Hydrocarbons
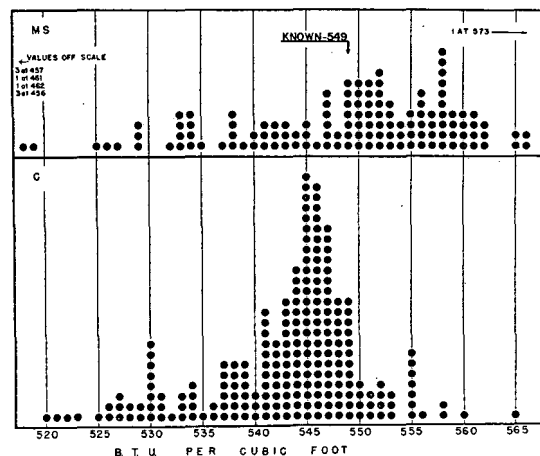
Figure 9. Calculated Heating Values

CALCULATED SPECIFIC GRAVITY

The calculated specific gravity is an over-all measure of accuracy, inasmuch as the specific gravity of this standard sample had been carefully determined to a significance at least an order of magnitude greater than the values calculated from the analyses. The known value was 0.6475 [measured by Carroll Creitz of the National Bureau of Standards; for the method used, see (1) and (3, p. 324)]. The calculated values obtained from both chemical and spectrometric analyses are somewhat scattered, although in both cases the greater proportion lies between 0.640 and 0.660 (Figure 10). The high frequency for the chemical method appears at 0.648, the median at 0.650. The mean is 0.648 ± 0.002. These values agree well with the known. The spectrometric mean (0.626 to 0.677) is 0.650 ± 0.007. The median is 0.651, and the Gaussian pattern is too distorted to permit the clean selection of a high frequency. Thus, although greater accuracy may have been expected from the spectrometric method because it discloses more complete composition than does the chemical

Figure 10. Calculated Specific Gravity

Youden [7] remarks: "It is a fact of experience that a set of measurements made by different operators at different times or in different localities is subject to greater variation than a set of measurements made by one operator using the same apparatus on the same day." The data presented here offer no exception to this fact of experience. Thus, for example, the mean of all spectrometric values of calculated specific gravity (between 0.626 and 0.677) is 0.650 $\pm$ 0.007; the mean of the laboratory averages is 0.648 $\pm$ 0.009; but the reproducibility of each laboratory varies from 0.0005 to 0.004, with an average of 0.0017—three times better than the reproducibility obtained from the laboratory averages.

approach, it has not been attained. Improvements in the determinations of hydrogen and carbon dioxide are needed to correct this situation.
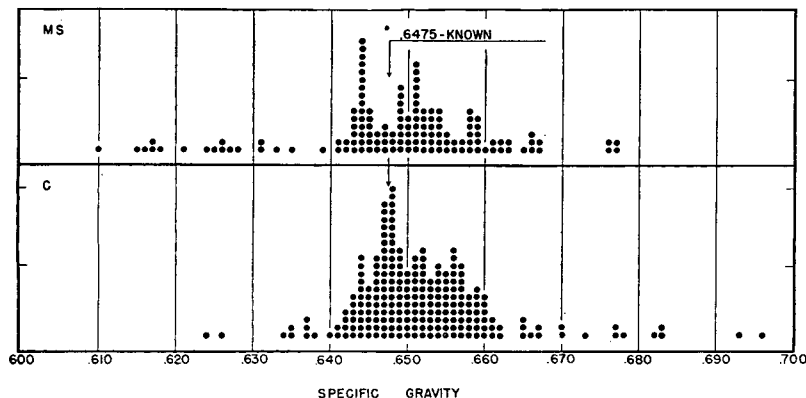
TABULATED DATA

No attempt has been made to set forth all the statistical inferences that can be derived from the data given in this report. The whole object of the report is to present a general integrated picture of the real state of analysis of this kind without, for the moment, distracting particulars. This is not to say that a statistical study will not prove of equal or greater value, but it should be presented separately. To tempt someone to do this, the tabulated data have been given in two other papers [3, 6].

Without invoking a formal statistical study, a few observations may be briefly made. In the instance of calculated specific gravity, which is a good over-all measure of the success of the analysis and involves all the components determined, these facts are evident in glancing at the spectrometric data:

The differences between two calculators using the same spectrogram in the same laboratory were small. The average difference is about 0.001.

The differences between two operators using the same instrument in the same laboratory were small. The average difference is about 0.001.

The differences between spectrograms were larger than between operators and calculators. The average difference is about 0.0025.

These observations agree with those made previously in the analysis of a natural gas by the mass spectrometer [5].

REVIEW

Although the superiority of the mass spectrometer over volumetric methods was clearly demonstrated in the analysis of a natural gas [2], the same superiority is limited to the hydrocarbon fraction of the carbureted water gas discussed in this report. The full significance of this is not indicated by the data presented, for the sample itself contained few of the heavier saturated, unsaturated, and ring hydrocarbons that are ordinarily present in fuel gases of this type, and the spectrometer is capable of analyzing a mixture of 20 or more components that would prove a vexing and rather durable problem to one employing conventional chemical methods. As in the analysis of a natural gas [2], oxygen was correctly determined in the present sample by the spectrometer and not by the volumetric chemical method. However, in the spectrometric method needs considerable improvement in the determination of hydrogen and particularly carbon monoxide. It may be that a combined physical-chemical analysis will offer the best solution for gases of this type.

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Coulometric Titrations with Chlorine

Titration of Arsenic and Use of an Amperometric End Point

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THE secondary type of coulometric process involves an intermediate half-cell reaction which is caused to take place with 100% current efficiency at a generating electrode. Szebelledy and Somogyi [6] and Meier, Myers, and Swift [2] have discussed the advantages of this type of process and the characteristics of suitable intermediate half-cell reactions; the latter discussion has particular reference to titrations with amperometric end points.

Until the present work only three intermediate half-cell reactions had proved satisfactory for coulometric determinations. For the titration of reducing agents, bromine has been employed rather extensively [1, 3, 5, 7, 8] and recently Ramsey, Farrington, and Swift [4] have shown that iodine can be used for the titration of arsenic. Cuprous copper has been used for the coulometric titration of certain oxidizing agents [2].

In order to increase the number of substances which could be titrated by such processes, a stronger oxidizing intermediate than bromine was sought. Because the halogen half-cells are

so readily reversible at electrodes, chlorine seemed to be the logical choice for investigation. Wooster, Farrington, and Swift (8) used chlorine as an intermediate in the coulometric titration of iodine in 2 F hydrochloric acid and observed positive errors of from 0.5 to 1%. Because these errors may have arisen from the iodine monochloride formed in those titrations, the oxidation of tripositive arsenic by electrolytically generated chlorine has been studied and the results are presented below.

EXPERIMENTAL

Reagents. All chemicals used were reagent grade.

One volume formal sodium chloride solutions, prepared from the salt, were found to contain no extraneous oxidizing or reducing agents.

Sulfuric acid (2.5 F) was prepared and chlorine gas was bubbled through the solution for 2 to 3 minutes. After the acid had boiled for 1 hour, no excess chlorine remained in solution and only a very small amount of reducing material was detected.

The reducing material present in the reagent grade hydrochloric acid used was determined by coulometric titration with chlorine. A stock solution of 8 F hydrochloric acid was prepared by adding the stoichiometric amount of potassium chlorate and allowing the solution to stand. After 1 day essentially all the chlorate had reacted and the acid was ready for use.

Standard solutions of tripositive arsenic were prepared in the following way: Bureau of Standards arsenious oxide was dried for 2 hours at 110° to 115° C. A 0.5-gram sample of the oxide was accurately weighed out and dissolved in 10 ml. of water containing 1 gram of sodium hydroxide. The resulting solution was neutralized with 8 ml. of 2.5 F sulfuric acid, about 180 ml. of boiled distilled water were added, and the total weight of the stock solution was determined. Weighed samples of the stock solutions were diluted to appropriate volumes to provide standard solutions for analysis. Stock solutions were discarded after 5 days; dilute standard solutions were used only on the day of preparation.

Laboratory distilled water was boiled 15 to 20 minutes to remove a small amount of oxidizing agent, presumably chlorine.

Apparatus. The apparatus described by Meier, Myers, and Swift (2) was used with the following changes: The cathode instead of the anode was enclosed in a shield. In order to improve current regulation, the laboratory direct current supply was replaced by a simple voltage-regulated rectifier. The indicator electrodes were made the same size, 2 × 2.5 cm.

Preliminary Adjustment. The current of the generation circuit was determined by measuring the voltage drop across a standardized resistance through which the generation current was passing. All voltage measurements were referred to a cell which had been checked against a bank of cells obtained from the Bureau of Standards. Generation rates of about 10^{-8} and 10^{-7} equivalent per second were used.

When not in use the indicator electrodes were shorted together and stored in a solution 0.5 F in sulfuric acid and 0.2 F in sodium chloride. Before each series of titrations both indicator electrodes were connected to the generator anode and chlorine was generated at the high rate for about 30 seconds. To maintain the sensitivity of the electrodes, they were given the same treatment for 10 seconds after each blank and every titration.

Titration Procedure. All solutions had a total volume of 45 ml. and were 0.5 F in sulfuric acid and 0.2 F in sodium chloride; the initial indicator potential was set at 0.30 volt. The considerations influencing the selection of the various conditions of the procedure are discussed below. A correction for reducing material in the reagents was made by generating in a blank solution of the composition given above for short intervals of time and recording the values of the indicator current. A plot of indicator current against generation time was constructed and the linear curve was extrapolated to zero time; the intercept on the time axis was designated as the "blank time."

When the apparatus had not been in use for several hours, the first one or two blank time values were usually erratic and were not included in the average blank time value. At least three consistent values were used in obtaining the average blank time.

To make a titration, the proper amounts of sulfuric acid and sodium chloride solutions were mixed in a titration cell with sufficient water to make the volume either 35 or 20 ml. A 10- or 25-ml. portion of standard arsenite solution was pipetted into the cell and the total volume was then 45 ml. As soon as the titration cell was attached to the stirring apparatus, generation was started. By means of the built-in potentiometer the generating current could be checked during the course of the titration and the current was held constant by making small adjustments. Near the end point the indicator current underwent a momentary

reversal, and at this point generation was stopped immediately. After a few seconds the indicator current rose slowly and reached a steady value of less than 10 μa. Generation was continued for short intervals and values of the indicator current and time were recorded. The linear curve of indicator current vs. time was extrapolated to the time axis, and the point of intersection was taken as the "titration time," inasmuch as the chlorine excess is assumed to be zero at the extrapolated zero indicator current. By subtracting the average blank time from the titration time a corrected titration time was obtained. The weight of arsenic was calculated from the values of the corrected titration time and the rate of generation.

DISCUSSION

Potential Difference Applied across Indicator Electrodes. With an applied potential difference of 500 mv. between the indicator electrodes, chlorine was generated in a blank solution until the indicator current was 25 μa. The indicator potential was then varied between values from 50 to 1000 mv. and values of the indicator current were recorded. Before each change of indicator potential the current was adjusted to 25 μa. at 500 mv. by generating chlorine. The data thus obtained were plotted, and the curve of indicator current vs. indicator potential was similar in form to the one obtained by Ramsey for iodine (4), except that the flattest portion of the curve was from 400 to 600 mv. Although it would have been desirable to use an indicator potential which lay on this flat portion of the curve, this was not practicable because high initial indicator currents—that is, before beginning generation—were obtained in blank solutions. In order to reduce this initial value of the indicator current to 1 μa. or less, it was necessary to use a potential of 300 mv. This potential proved to be satisfactory for the titrations; linear curves of indicator current vs. time were obtained for blank titrations, and the electrode sensitivity was good.

Table I. Confirmatory Analyses

| No.[a] | Arsenic, Micrograms | | | |
	Taken	Found	Error	% Error
I	29.8	30.2	0.4	1.34
		29.9	0.1	0.33
		29.9	0.1	0.33
		29.9	0.1	0.33
I	82.4	83.1	0.7	0.85
		82.7	0.3	0.36
		82.6	0.2	0.24
		82.6	0.2	0.24
I	321.9	321.9	0.0	0.0
		321.9	0.0	0.0
		322.3	0.4	0.13
		321.9	0.0	0.0
I	802.5	802.2	−0.3	−0.04
		801.8	−0.7	−0.09
		803.5	0.5	0.06
		802.6	0.1	0.01
II	819.1	818.6	−0.5	−0.06
		817.8	−1.3	−0.16
		817.9	−1.2	−0.15
		817.8	−1.3	−0.16
		817.8	−1.3	−0.16
III	795.6	796.1	0.5	0.06
		794.8	−0.8	−0.10
		794.5	−1.1	−0.14
		796.1	0.5	0.06
		795.3	−0.3	−0.04

[a] Roman numerals indicate stock solutions used.

Effect of pH on Indicator Current. Inasmuch as chlorine tends to hydrolyze even in slightly acid solutions, it was desirable to determine the maximum pH at which a stable indicator current could be obtained when the chloride was 0.2 F. In a solution buffered to a pH of 3 with phosphoric acid and dihydrogen phosphate no indicator current could be observed when the low rate of generation was used. For a solution in which the pH was 2 an indicator current was obtained, but it decreased at the rate of 1 μa. in 4 seconds as soon as generation was stopped;

The conditions under which electrolytically generated chlorine can be used for secondary coulometric titrations with an amperometric end point have been studied. A procedure is described by which tripositive arsenic has been titrated in quantities of from 30 to 800 micrograms with an average error without regard to sign of less than 0.5 microgram.

this is not adequate stability for quantitative measurements. A stable indicator current was obtained in 0.05 F sulfuric acid; however, to provide a factor of safety, solutions 0.5 F in sulfuric acid were used in the titrations.

Indicator Current Phenomena. The indicator current response was slower for chlorine than that which has been found for bromine or iodine. When either a blank chloride solution or such a solution containing arsenic was placed in the cell and a potential was applied between the indicator electrodes, the indicator current surged to a high value, then decreased slowly. In either case several minutes elapsed before the current reached a steady value of about 0.2 μa. In practice, generation was started in a blank solution as soon as the indicator current dropped to 1 μa. instead of waiting until 0.2 μa. was reached; no difference in blank time was observed. When arsenic was titrated, generation was begun immediately after closing the indicator circuit because the indicator current always dropped rapidly and underwent a reversal near the end point and the value of the indicator current during the titration had no significance.

After the first period of generation in a blank solution and after the current reversal at the end of a titration, the indicator current rose so slowly that a period of 1 to 3 minutes was necessary for a steady state to be attained. For all other readings of indicator current a steady state was reached in 10 to 15 seconds.

The current reversal near the titration end point is similar to the one observed by Myers and Swift (3); however, with the present apparatus no hydrogen enters the solution from the generator cathode. When the potential is first applied to the indicator electrodes, the current surges to a high value (more than 50 μa.), then decreases. During the passage of this current a small quantity of hydrogen or possibly metallic arsenic is probably being produced on the indicator cathode; because of the small quantities involved, no visible evidence of either reaction was observed. Near the titration end point the concentration of chlorine increases rapidly and there is a transition of indicator electrode potentials and reactions. If there is a significant lag in removing adsorbed hydrogen (or possibly arsenic) from the indicator cathode, a cell would be established in opposition to the applied potential and a current would flow in the reverse direction.

Effect of Chloride and Acid on Coulometric Titration. In view of the positive errors obtained by Wooster in the titration of iodide with chlorine in 2 F hydrochloric acid (8), it seemed advisable to use the lowest practicable chloride and hydrogen ion concentrations. As discussed above, 0.5 F sulfuric acid was taken as a safe minimum acid concentration. With a chloride ion concentration of 0.05 F there was evidence that the generator anode efficiency was slightly less than 100%, while 0.1 F chloride ion seemed perfectly satisfactory. Confirmatory titrations were made using the chloride and acid concentrations given in the procedure above, and the results are listed in Table I. To investigate the effects of varying acid and chloride concentrations, titrations were made according to the conditions listed in Table II. Each stock solution was titrated by the regular procedure, so that the data in Table II may be directly compared with the data for the corresponding stock solution in Table I. The arsenic found when titrating in 0.05 F sodium chloride

solution was about 0.2% greater than the value obtained in 0.2 F sodium chloride solution; this indicates that the current efficiency may not have been 100% in the 0.05 F chloride solution.

Table II. Effect of Acid and Chloride Ion Concentrations

No.[a]	Solution	Arsenic, Micrograms Taken	Found	% Error
II	0.5 F H$_2$SO$_4$	819.1	819.4	0.04
			819.4	0.04
	0.05 F NaCl		819.0	-0.01
			819.8	0.09
II	0.5 F H$_2$SO$_4$	819.1	817.4	-0.21
			817.4	-0.21
	3.0 F NaCl		817.4	-0.21
II	0.5 F H$_2$SO$_4$	819.1	817.9	-0.15
			817.9	-0.15
	Saturated NaCl		817.8	-0.16
III	2 F HCl	795.6	794.9	-0.09
			794.9	-0.09
			796.4	0.10
			795.7	0.01
III	6 F HCl	795.6	798.4	0.35
			800.5	0.62
			799.2	0.45

[a] Roman numerals indicate stock solutions used.

Considering that chlorine would be expected to oxidize the platinum anode in the presence of such high chloride concentrations, it is surprising that significant positive errors were obtained only in the titrations in 6 F hydrochloric acid.

CONCLUSIONS

Chlorine can be used as the intermediate for a secondary coulometric process in which use is made of platinum electrodes and an amperometric end point. The acid concentration should not be lower than 0.1 volume F, and the chloride concentration should be between 0.1 and 2 F. In the coulometric titration of arsenic by this method an accuracy of ±0.2% was obtained for 300- to 800-microgram quantities of arsenic; 30- to 100-microgram quantities were titrated with an average error of less than 1%.

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Use of Physical Constants in Analysis

Extension to Liquid Halogen and Oxygen Organic Compounds

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Charts showing the relation between structure and refractive index, density, and boiling point of representative liquid halogen compounds and compounds of carbon, hydrogen, and oxygen are presented. How these charts can be used to shorten and simplify the analysis needed in connection with research work is described and illustrated.

THE main feature of the procedure described here is the use of physical constants, usually used to help in final identification, to serve also in the classification of an unknown. The classification requires the use of charts showing the relation between molecular structure and refractive index, density, and boiling point of pure compounds. These three physical constants, when compared with the plotted data of known compounds, limit the class possibilities very sharply and show quickly which tests and chemical derivatives, if any, are needed for final identification.

A search of the literature shows that Smith in 1930 plotted refractive index against density to aid in the identification of individual compounds (17). He recognized the value of the chart, but did not plot enough data at that time to show the segregation of classes in limited fields. Samygin in 1936 showed that several classes of aliphatic compounds fell in separate and distinct fields when so plotted (15). Similar graphs have been published in connection with hydrocarbon analysis (10, 16). That the general principles involved have received wide attention
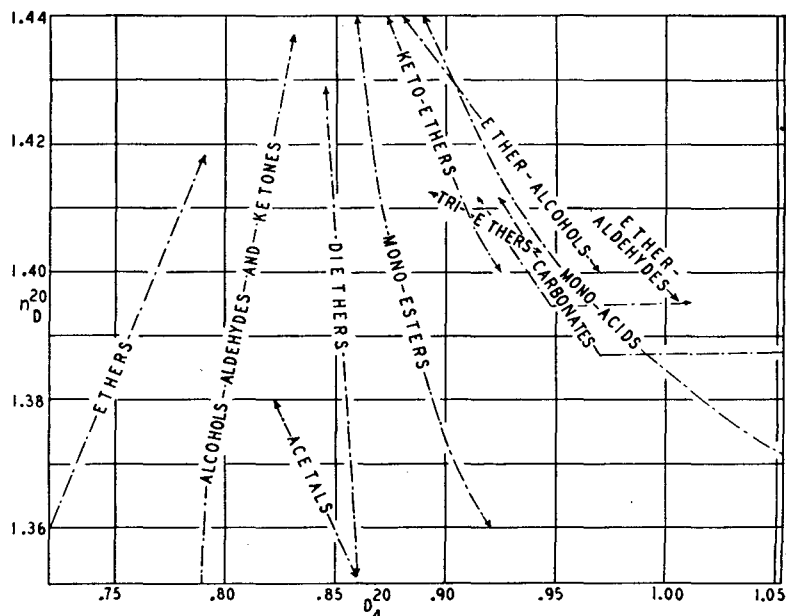
Figure 2. Density and Refractive Index of Some Classes of Saturated Aliphatic Compounds
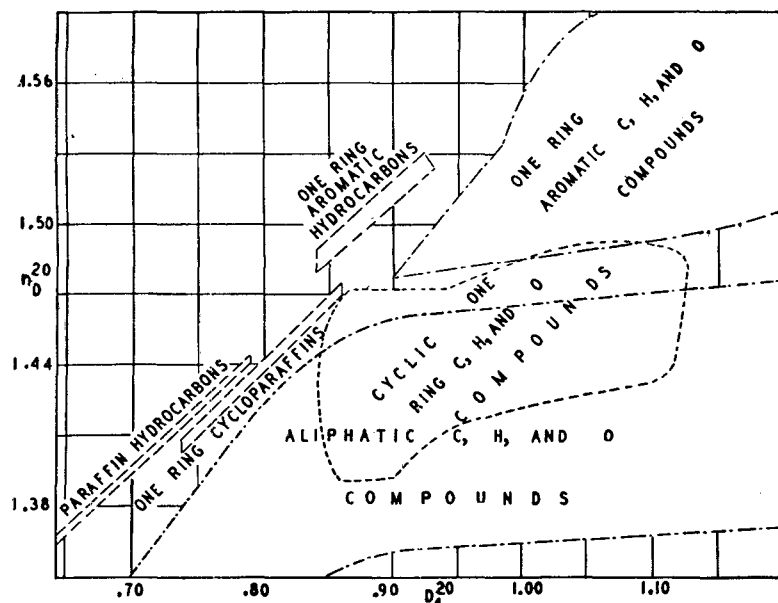
Figure 1. Density and Refractive Index of Oxygenated Saturated Compounds Compared to Parent Hydrocarbons

in the petroleum industry is shown very strikingly by many other outstanding discussions correlating physical constants and structure of hydrocarbons (1–6, 9, 11–14, 18–20). The present paper, based on work with halogen- and/or oxygen-containing compounds, extends the ideas developed in connection with hydrocarbon research to the analysis of other liquid organic compounds (16).

CONSTRUCTION OF GRAPHS

An ideal method for plotting the data on any one class of compounds would be to plot a reference series in the class completely, and then to plot not more than two or three compounds in each isomeric series (1). For example, on Figure 6, the straight-chain primary alcohols in the aliphatic monoalcohol class are plotted completely enough to serve as a reference series. Data for the members omitted can be easily estimated by interpolation. On this same figure, 2-pentanol can be used to illustrate how one compound serves to estimate data on an isomeric series. Its boiling point is 18.2° C. lower than that of 1-pentanol, its density is 0.0056

Figure 3. Density and Refractive Index of Several Classes of Saturated Aliphatic Compounds

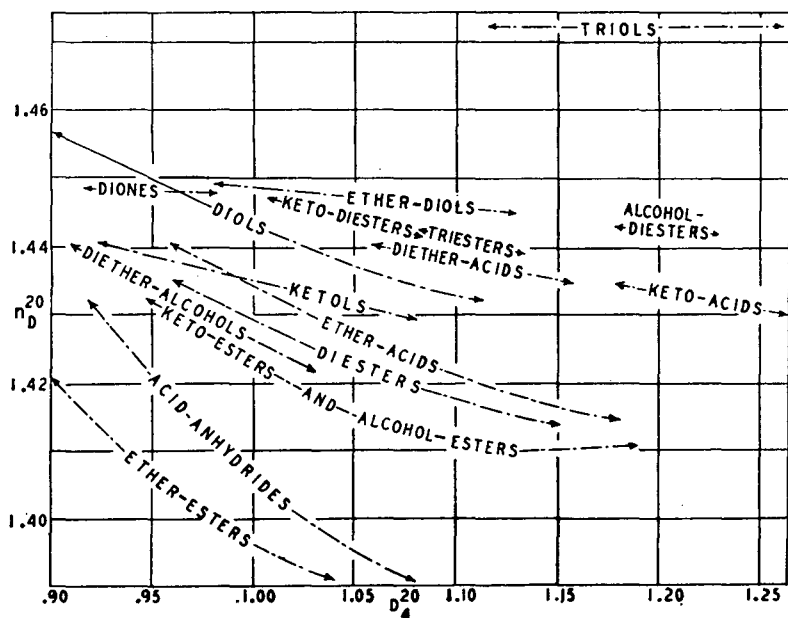data on chlorine compounds, the book by Huntress is available (7), and for additional data *Chemical Abstracts* seems to be the best source. The chemical handbooks and reference books which contain tabulated data are also good supplementary sources.

The halogen derivatives, which have been studied in some detail, present a more difficult problem in analysis than do the carbon, hydrogen, and oxygen compounds. The possible number of halogen compounds is probably in the millions. At present, fewer than 5000 can be found even partially described in chemical literature. If a halogen compound be chosen at random, the chance of its being mentioned in chemical literature is very slight; hence, some method of interpolating and extrapolating data is necessary in any scheme of analysis. Charts of the kind presented here simplify the interpolation appreciably. Figures 7 and 8 give data for a very few of the simpler halogen compounds. The dash-dot lines on these two figures show direction for finding other members of a particular series of compounds whose successive members differ by a —CH₂— group. By interpolation in

lower, and its refractive index is 0.0039 lower. Other members of the 2-ol series should differ similarly from their isomers in the reference series. The differences in constants will be larger for isomers of smaller molecular weight and a little smaller for the isomers of larger molecular weight.

It is self-evident that the physical constants for the compounds of any one series of a given class should vary in some regular pattern as the molecular weight increases, and that the differences in constants between isomers of two series should have some uniformity. These are the basic ideas to use with the charts.

The relative positions of the fields for paraffins, one-ring cycloparaffins, one-ring aromatic hydrocarbons, and the saturated oxygenated derivatives of these three types of hydrocarbons are shown on Figure 1. Figures 2 and 3 show approximately which class of saturated aliphatic oxygenated derivatives can be found at any given density and refractive index. Figure 5 serves similarly for aromatic compounds. Figure 4 shows the position of different classes of cyclohexane derivatives; how a change in ring structure affects the position on the chart is also shown by the five different ether series. The smaller the ring, the lower the compounds will be on the chart, and an oxygen atom in the ring lowers the position on the chart. Figures 2, 3, 4, and 5 can be used for preliminary classification of an unknown and in the case of mixtures, where the point representing the unknown will be in between those of the components, for forecasting classes present so that the purification will not be entirely blind trial and error.

Figure 6 illustrates the kind of detailed graph needed for maximum help in an analysis. The dash-dot lines are for the reference series plotted most completely. Boiling points are given in degrees centigrade at atmospheric pressure, or at the pressures indicated by superscripts. For carbon, hydrogen, and oxygen compounds, the textbook by Huntress and Mulliken has considerable data easily available for plotting other such charts (8). For

Figure 4. Density and Refractive Index of Cyclohexane Derivatives and of Several Ether Series

such a series, the structure of an unknown may be deduced. Figure 9 illustrates other kinds of series which may be similarly used.

ANALYTICAL PROCEDURE

In an analysis of a liquid sample, many variations in the use of charts such as the ones presented here can be made. In any case, the first step is to determine density at 20° C. and refractive index for the sodium *D* line at 20° C. Corrections of 0.001 per ° C. on density and 0.00045 per ° C. on refractive index will be found accurate enough for most cases, if it is inconvenient to make the tests at exactly 20° C. Data on the unknown are compared with those plotted on Figures 1 to 8 and on other similar graphs constructed by the analyst, and used with history of the sample to judge what class or classes of compounds are probably present.

Figure 5. Refractive Index and Density of Saturated Aromatic Compounds

Figure 6. Saturated Aliphatic Ethers, Alcohols, and Oxides

appreciably by their use. Another feature which should be emphasized is the amount and accuracy of detail which can be predicted about the structure of an unknown from the three physical constants only. For example, an unknown with d_4^{20} = 0.785, n_D^{20} = 1.404, and boiling point = 98–100° C. cannot only be classified immediately as an aliphatic monoether, but the boiling point in relation to its position on Figure 6 and the averages given below for effect of unsaturation show that it is unsaturated. Assuming that this particular compound is not yet described in the literature, its probable structure can be quickly deduced by interpolation and extrapolation of data known for other unsaturated ethers, when such data are plotted on a graph similar to Figure 6.

Another example was a cut obtained by fractionating the products from the oxidation of ethylene in the presence of sodium acetate. The data on this cut were: boiling point = 160–170° C. (uncorrected), d_4^{20} = 0.836, n_D^{20} = 1.4042. These data, plotted on Figure 2, indicated that the compound was probably a diether. The data plotted with known diethers on a detailed chart not given here lined up very well with straight-chain diethers having the oxygen atoms separated by two carbon atoms. Interpol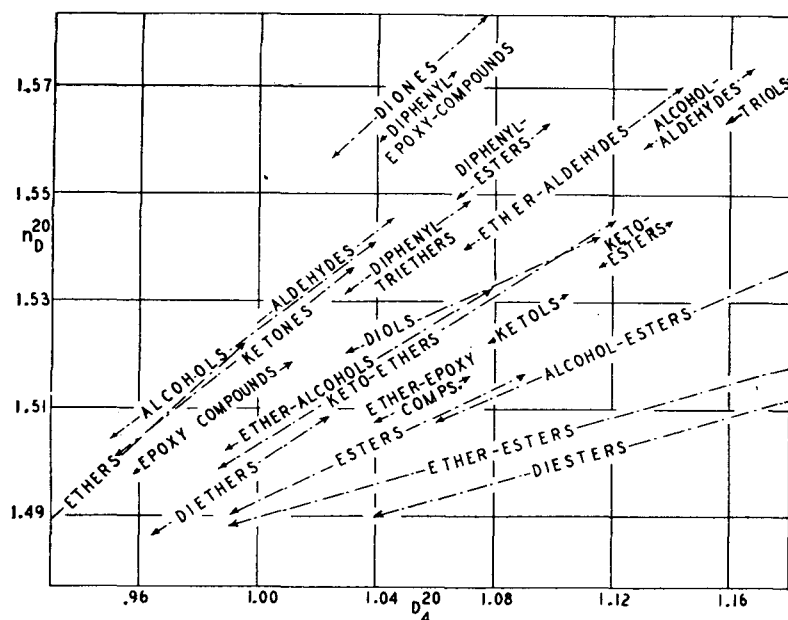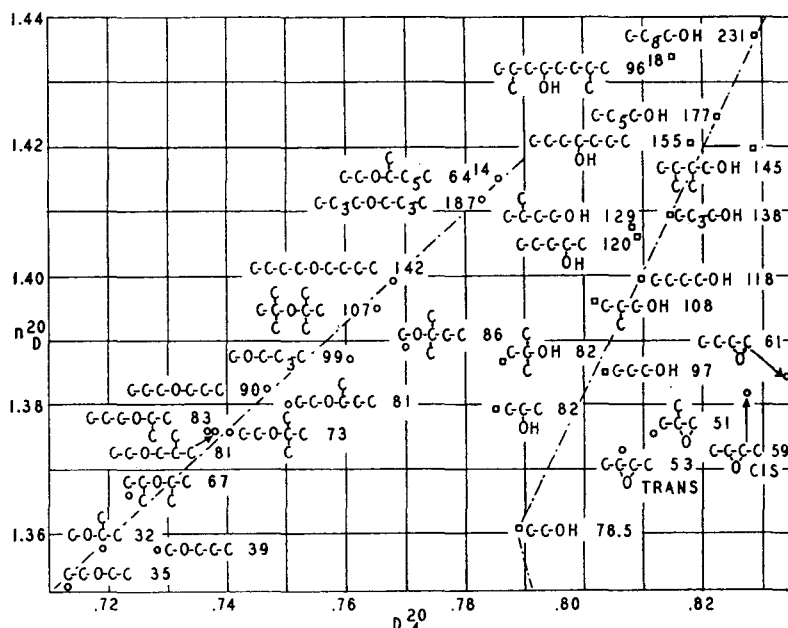ation of boiling points indicated a molecule containing approximately eight carbon atoms. Because boiling point was obtained incidental to purification, less than 5 minutes was needed to obtain the remainder of the experimental data used in classification. The information on structure might be complete enough in some research work to allow omitting the further testing by breaking up into alcohols or alkyl halides, as would probably be done if older classification methods were used.

When two or more functional groups are in the same molecule, such will usually be indicated when its data are compared with data plotted on an auxiliary chart similar to Figure 6. Consider a compound such as ethoxyacetaldehyde, with d_4^{20} = 0.942, n_D^{20} = 1.3956, and boiling point = 105° C. Its refractive index and density place it in the aliphatic acid field, but its boiling point does not match the acids at that particular position in the field. A class test might be needed to show the presence of the aldehyde group, and with that confirmed, it would be obvious that there is another functional group in the molecule, an ether group. This emphasizes a point already brought out, that the position of the point representing the unknown and its boiling point must be completely accounted for by the structure and functional groups of the molecule.

In the case of mixtures, the point representing the unknown will be in between those of the main components on the charts, and closer to the one present in largest amount. Hence, some idea of the components present is obtained, which helps in choosing methods of separation to use. It is not likely that a main component will be missed, as has happened in using older methods of analysis.

Several general rules can be given about the position of the different classes on the charts. If the oxygenated compounds are considered as being derived from the corresponding hydrocarbons, introducing an oxygen atom to make an ether group has the least effect on the constants. The next least effect is for the oxygen atom to be in an alcohol, aldehyde, or ketone group. Still farther

To obtain maximum help, a detailed chart such as Figure 6 should be constructed. If, during separation and purification, refractive index and density are determined occasionally and plotted on such a chart, successive points will line up toward the point representing the compound being purified. Properties of individual compounds, or of classes indicated to be present by their position on the graph, determine each step in procedure until final identification is made. Boiling point often serves to distinguish between saturated and unsaturated compounds or between compounds in two different classes whose fields overlap on the graph. It can also be a distinguishing property in choosing between compounds of two isomeric series of the same class.

DISCUSSION

Even where the usual class tests are not entirely eliminated by use of the charts, the time for an analysis usually will be shortened

away from the hydrocarbons are acetals and diethers, then esters, and finally the acids. The distance of difunctional compounds from their parent hydrocarbon is roughly the sum of the distances of the monofunctional compounds from the parent hydrocarbon. The effect of any group in a big molecule is less than that of the same group in a small molecule. Therefore, as molecular size increases, the field for any class of compounds moves closer and closer to the field for the parent hydrocarbon, and the difference between isomers is less for large molecules than for small ones.

From data now available on the oxygenated and halogenated compounds, the average effects of creating a double bond by eliminating hydrogen from molecules of molecular weight between 100 and 160 are approximately: an increase of 0.035 in density, an increase of 0.030 in refractive index, and very little change in boiling point. The effects are largest in aromatic compounds and next largest in other cyclic compounds. The effects also vary widely with position of the double bond in relation to other groups which possibly activate the double bond. Compounds which might be expected to polymerize readily seem to have the higher constants. For example, a comparison of data on the two 1-phenylpropenes shows that the one having the double bond conjugated with the benzene ring has approximately 17° C. higher boiling point, 0.017 higher density, and 0.034 higher refractive index than the other isomer. The average difference in density of saturated and unsaturated bromine and iodine compounds is appreciably higher than the average for other halogen compounds. In an analysis, use of the above averages will help in judging whether the unknown is unsaturated when using graphs containing only data on saturated compounds. Once the unknown is established as an unsaturate, enough individual data on unsaturated compounds should be plotted to place the unknown in one particular series if possible.

Correlation of unsaturation and change of structure with change in physical constants has been by far more extensively studied in connection with hydrocarbons than with any other class of compounds. The discussions referred to above are a few of the better known papers on this subject. Qualitatively, the same conclusions reached for hydrocarbons apply to oxygenated and halogenated compounds. A methyl group in 2-position results in the compound's having lower refractive index and density than the corresponding n-compound, but branching farther away from the end of the molecule raises both refractive index and density. An ethyl or larger side branch has about the same effect on boiling point as a methyl side branch, and about double the effect on refractive index and density. The effect of several changes in structure is roughly additive, except that adjacence of groups may cause an additional effect. For example, two adjacent tert- or neo-carbon atoms result in appreciably higher constants than those for isomers where they are not adjacent. Usually, cis compounds have higher constants than the trans isomers. An oxygen atom or a halogen atom can be considered qualitatively as being like another carbon atom, but the effects of their position are greater. Thus, secondary straight-chain alcohols have, on an average, about 18° C. lower boiling point than the corresponding primary alcohols, compared to about 8° C. lower boiling point for isomers where a methyl group is shifted from the end to make

a side branch. Switching the position of two halogen atoms has very little effect on the constants. For example, 1-chloro-2-fluoropentane will have practically identical constants with 1-fluoro-2-chloropentane, but both will be noticeably different from an isomer, such as 1-chloro-5-fluoropentane. Data can be found to contradict any of the above rules. However, it is believed that most of these contradictions are due to inaccuracies in published data.

The amount of variation from averages made to show the effect of unsaturation and also to show the effect of isomerization indicates that the published data on an individual compound may be very inaccurate. Hence, some method of checking accuracies is desirable. If all data available on two isomeric series are plotted on a graph such as Figure 6, it will be easy to see the approximate amount of error in individual data, inasmuch as some regular pattern is to be expected between successive members of each series, as well as between isomers in the two series.

Figure 7. Fields for More Common Aliphatic Halogen Compounds

Figure 8. Fields for Simpler Cyclic Halogen Compounds

Figure 9.   Illustration of Different Ways to Interpolate

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Coulometric Titrations with Electrically Generated Ferrous Ion

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Ceric sulfate and potassium dichromate solutions were titrated with ferrous ion generated at a platinum cathode. The end point was obtained potentiometrically using a platinum-tungsten electrode system. The reductions were carried out at constant current, and the time of the electrolysis was measured.

COULOMETRIC methods of analysis are made possible by Faraday's fundamental researches upon electrochemical equivalence. Quantitative experiments using the coulometric principle have long been included in courses in physical chemistry. Quinn and Hulett (16) utilized the method with silver and cadmium coulometers in series for estimating the equivalent weight of cadmium. The first extensive analytical studies of the coulometric method were those of Szebelledy and Somogyi (19).

The method depends upon the measurement of the amount of current, working at 100% efficiency, necessary to complete a chemical oxidation or reduction. These procedures fall into two general classes: those that are carried out at constant controlled electrode potential, and those at constant current.

In the former method, originally devised by Hickling (8), the potential of the anode or cathode is controlled so that only the desired reaction is able to take place. The process is allowed to continue until only a small residual current flows which in-

dicates complete reaction. The amount of current involved is measured by means of a coulometer which could be chemical (11), electronic (1), or mechanical (18). This method, though possibly more versatile than the constant current procedures, is at present limited by the lack of a simple indicating coulometer having an accuracy of at least 0.1%. Lingane applied this method, using chemical coulometers, to the determination of copper, bismuth, and lead (11), as well as the halides (10).

Constant current procedures have been applied to electrolytic stripping of plated deposits. Because the degree of polarization is less in electrolytic solution of an electrode, such processes can often occur with theoretical efficiency at constant current. Zakhar'evskiĭ (22) determined copper and lead in this fashion. Metallic copper and lead dioxide were first deposited and then stripped off an electrode with a measured amount of current.

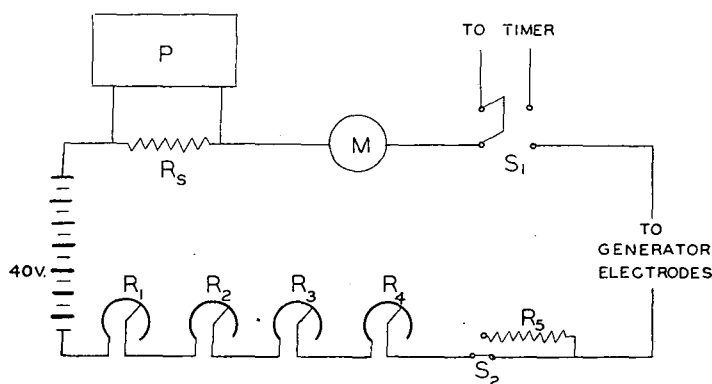Campbell and Thomas (3, 4), as well as Francis (6), used this principle to measure the thickness of metal films.

Figure 1. Wiring Diagram

M. Milliammeter, 0-10, 0-100 ma.
P. Leeds & Northrop student potentiometer
R_1. 10-ohm, 4-watt wire-wound variable resistor
R_2. 100-ohm, 10-watt wire-wound variable resistor
R_3. 1000-ohm, 50-watt wire-wound variable resistor
R_4. 5000-ohm, 20-watt wire-wound variable resistor
R_5. 5000-ohm, 20-watt wire-wound fixed resistor
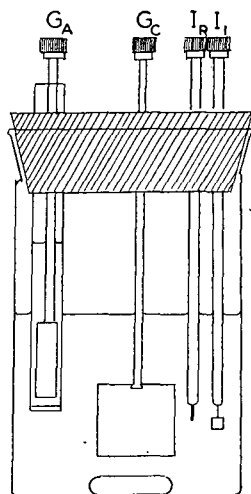R_s. Standard resistor (10-ohm or 100-ohm)
S_1. D.p.s.t. switch
S_2. S.p.d.t. switch

Figure 2. Titration Cell

Ga. Isolated generator anode
Gc. Generator cathode
Ii. Platinum indicator electrode
Ir. Tungsten reference electrode

Indirect constant current procedures depend upon the electrolytic generation of an oxidant or a reductant. Such procedures have been called coulometric titrations (14) because a definite known amount of reagent is added to the solution electrolytically. However, in this type of titration, the standardization of solutions is unnecessary, and the storage problem of unstable solutions is avoided.

The end point of the titration is obtained by chemical indicators (19), amperometrically (2, 12, 14, 17, 21), or, as in the work presented here as well as by others (5, 15, 20), potentiometrically. The number of equivalents involved in the reaction is known from the magnitude of the current and the time of generation.

The latter method has advantages in that no coulometer is necessary, and reactions which cannot be carried out directly at 100% efficiency can be successfully performed in this fashion. For example, dichromate solutions cannot be reduced at a platinum cathode with theoretical efficiency (7); however, the indirect generation of ferrous ions allows this determination to be

accomplished. On the other hand, there must be some indication of the end point which is dispensed with in the controlled potential procedures.

Coulometric titrations employing amperometric end points are limited to the use of currents of about 10 ma. (1). Higher currents through the generator circuit induce parasitic currents in the indicator circuit which obliterate the end point. This difficulty, plus the fact that the titrations should not require an excessive period of time, limits the application of such procedures to dilute solutions.

The use of potentiometric measurements to follow the titration is free of this difficulty, and the magnitude of the generating current is only limited to values at which the process can be carried out at 100% efficiency. Oelsen and Gobbels (15) titrated permanganate and vanadate solutions electrolytically by the reduction of ferric ions. The value of the current was variable, and was averaged by taking readings at 10-second intervals.

Ceric sulfate and potassium dichromate solutions were titrated with ferrous ion generated by a constant current at a smooth platinum cathode. The concentration of the ferric ion was kept high to prevent appreciable polarization. It was found that the presence of a small amount of phosphoric acid was essential for theoretically efficient reduction.

APPARATUS

The constant current source was the laboratory direct current power supply furnished by a bank of large capacity storage batteries delivering 40 volts. Currents of 100 ma. could be drawn from these batteries for extended periods with negligible voltage change. The wiring diagram is shown in Figure 1. There was a slight drift in the current during electrolysis caused by heating effects in the external resistances, and small changes in the conductivity of the cell. The former effect was decreased by using high wattage values in the external resistances. Changes in the current through the circuit were compensated manually by adjustment of the variable resistances.

Although the current in this instance was manually controlled, any of the available constant current circuits could be applied to this type of analysis (9, 12, 13).

The value of the current was determined by measuring the IR drop across a standard resistance with a potentiometer. An electric timer, accurate to 0.1 second, was ganged into the circuit. It was found necessary to check this timer frequently against a chronometer.

The end point of the reaction was determined potentiometrically using platinum-tungsten bimetallic electrodes, and measuring the voltage change by means of a Beckman Model G electronic voltmeter. Because the titrant could be added in very small increments, in most instances it was not necessary to plot the voltage change. The current and the time-measuring device may be shut off near the end point in order to allow the potential of the indicator electrode to become fairly constant. This part of the process is in every way analogous to a conventional potentiometric titration, except that the reagent is added to the solution by electrolytic generation rather than in the form of a standard solution.

The titrations were carried out in a 50-ml. cell of the type shown in Figure 2. The pair of generator electrodes consisted of a platinum cathode with an area about 10 sq. cm., and an isolated anode of approximately the same size. The anode was curled inside a 1-cm. glass tube fitted with a medium porosity sintered-glass disk. This anode compartment was filled with a 5% solution of sodium sulfate, the level of which was kept above that of the solution to prevent diffusion losses.

A large cathode was used to decrease electrode polarization. The anode was large, so that bubble formation did not cause fluctuations in the resistance of the cell.

The solutions were vigorously stirred with a magnetic stirrer (Arthur H. Thomas Company, Catalog No. 9235-R), but not so much as to cause cavitation.

REAGENTS

A standard solution of potassium dichromate was prepared by weight from reagent grade salt. The ceric sulfate solution was

Table I.   Titration of Ceric Sulfate and Potassium Dichromate

	Sample Wt. *Mg.*	Current *Ma.*	Time Calcd. *Sec.*	Time Obsd. *Sec.*	Error *%*
Cerium	144.4	100.0	994	994.0	0
				996.7	+0.3
				996.6	+0.3
				994.8	+0.1
	57.76	48.40	822	823.8	+0.2
				822.2	0
				821.7	0
				821.3	−0.1
	14.44	20.00	497.2	498.0	+0.2
				497.6	+0.1
				496.4	−0.2
				497.6	+0.1
	7.19	20.00	247.6	247.7	0
				247.3	−0.1
				248.1	+0.2
				247.8	+0.1
	1.444	10.00	99.4	98.4	−1.0
				99.8	+0.4
				100.1	+0.7
				99.5	+0.1
Chromium	8.63	100.0	480.3	480.6	+0.1
				481.1	+0.2
				480.5	0
				480.5	0
				480.7	+0.1
	1.732	35.00	275.4	274.3	−0.4
				275.5	0
				275.8	+0.1
				275.7	+0.1
				275.8	+0.1
	0.867	20.00	241.3	241.1	−0.1
				241.2	0
				240.8	−0.2
				241.4	0
				241.5	+0.1
	0.1732	5.00	192.8	192.2	−0.3
				197.5	+2.3
				196.0	+1.6
				193.2	+0.2
				193.6	+0.4

standardized against Bureau of Standards arsenious oxide, using osmium tetroxide as catalyst. The mean of the five determinations was 0.1032 ± 0.00007 N.

A 0.6 N solution of ferric ammonium sulfate acidified with sulfuric acid (to 4 N) was used to supply ferric ions. The concentration of ferric ion used was much greater than that of the solution titrated. Thus, the presence of a small percentage of ferrous ion in the ferric ammonium sulfate was found to introduce a negative error in the titration of the more dilute solutions. This error was in direct proportion to the amount of ferric ion present, as is shown graphically in Figure 3, for the titration of 10 ml. of 0.01 N potassium dichromate solution.
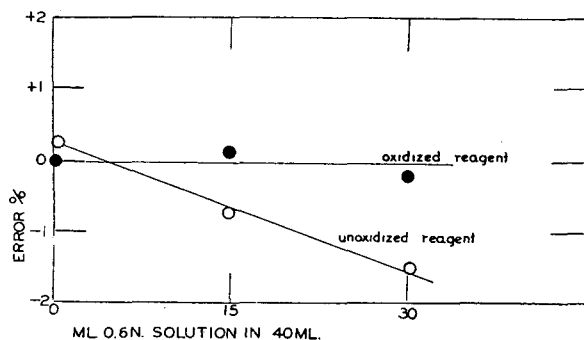

Figure 3.   Error Caused by Presence of Ferrous Ion in Ferric Ammonium Sulfate Solution

The values for 0 ml. were determined by pipetting 10 ml. of the 0.01 N solution into a solution which had been brought just to the end point. The magnitude of the error indicates that the ferric ammonium sulfate contained 0.0012% ferrous ion, which is in reasonable agreement with the value of 0.001% given by the manufacturer. The errors that were caused by ferrous ion in

the ferric reagent were proportionally greater the smaller the amount of oxidant that was determined.

The ferrous ion was removed from the ferric ammonium sulfate solution by treatment with manganese dioxide. One-half liter of the ferric ammonium sulfate solution was treated with 1 gram of finely divided manganese dioxide. The solution was boiled, cooled, and decanted through a sintered-glass crucible of fine porosity. The filtrate was passed through the same crucible a second time to assure complete removal of the manganese dioxide. This solution was stored without noticeable change during this work.

PROCEDURE

The titrations in this work were performed at current values, determined by the amount of material present, which would require a reasonable period of time. The external resistance was set approximately before the titration by short-circuiting the generator electrodes and decreasing the resistance until the correct value was reached.
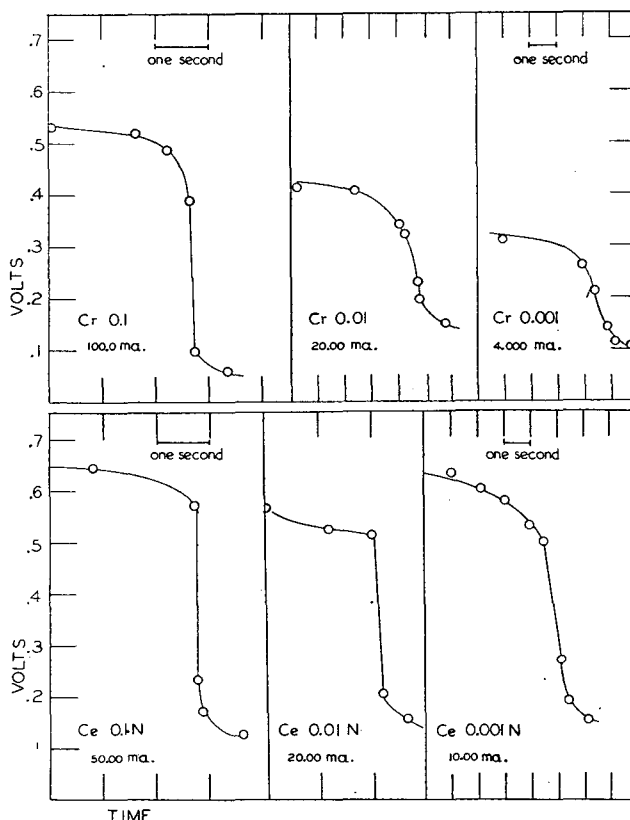

Figure 4.   Potential-Time Curves in Vicinity of End Point

The solution to be analyzed was pipetted into the titration vessel. Two milliliters of 18 N sulfuric acid and 1 ml. of 85% phosphoric acid were added, along with the ferric ammonium sulfate solution. About 15 ml. of the ferric ion solution were used for currents up to 30 ma., and 30 ml. for currents above this value. The solution was then diluted sufficiently to cover the electrodes. With amounts below 10 mg. of cerium, or 2 mg. of chromium, it was necessary to sweep dissolved air from the solutions and titrate in an inert atmosphere. Appreciable positive errors were caused by the presence of oxygen in the titration of 10 ml. of the 0.001 N solutions.

To carry out the titration, the current was adjusted to the desired value and the electrolysis begun. The IR drop across the standard resistance was frequently checked and adjustment of the resistance was made, when necessary, to maintain the current at a constant value.

The voltage change across the indicator electrodes was followed as the titration proceeded. Near the end point, the

generating current was momentarily interrupted to allow the system to reach equilibrium. As shown in Figure 4, the voltage change was abrupt at the stoichiometric point and could be ascertained in most cases without recourse to plotting the voltage-time curves. With generation currents below 10 ma., however, plotting of these curves was necessary.

In the titrations of ceric sulfate in the 0.001 N range, the indicator electrodes acquire equilibrium potentials rather slowly. It was necessary to wait 2 or 3 minutes near the end point before making the readings.

RESULTS

Aliquot portions of ceric sulfate and potassium dichromate solutions were titrated with satisfactory accuracy. The results obtained are shown in Table I.

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Fluorometric Determination of Pyruvaldehyde

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A method for determining pyruvaldehyde, based on a reaction with chromotropic acid, is described. The reaction appears to be specific for pyruvaldehyde, and the proposed method is subject to relatively few interferences. Formaldehyde and diacetyl interfere, owing to formation of the purple dye with chromotropic acid. Reducing sugars which are partially converted to pyruvaldehyde or diacetyl in strong acids also interfere. The fluorescent product of the pyruvaldehyde–chromotropic acid reaction undergoes a gradual nonphotochemical decay. The effect of this decomposition is minimized by measuring the fluorescence of unknown samples against that of samples prepared from pyruvaldehyde standards. A procedure for preparation and standardization of pyruvaldehyde solutions is described.

PYRUVALDEHYDE reacts with chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid) in concentrated sulfuric acid with the formation of a soluble yellow condensation product of unknown constitution. This reaction has not been previously described for pyruvaldehyde, although apparently it was observed by Eegriwe (5) upon allowing chromotropic acid-sulfuric acid mixture to react with glyceraldehyde.

Irradiation of sulfuric acid solutions of the condensation product with light of wave length 380 to 510 mμ produces an intense green fluorescence. This property is the basis of the proposed analytical method.

PREVIOUS WORK

Pyruvaldehyde has been estimated gravimetrically after conversion to substituted dihydrazones by reaction with 2,4-dinitrophenylhydrazine (10), as well as with m-nitrobenzohydrazide, p-bromophenylhydrazine, and p-nitrophenylhydrazine (13). The 2,4-dinitrophenylosazone has also been measured colorimetrically (3). Other colorimetric methods are based on the color formed with α-methylindole (4) and that given by pyruvaldehyde with arsenophosphotungstic acid in the presence of cyanide ion (1). Fischler and Boettner (6) oxidized pyruvaldehyde with alkaline hypoiodite to oxalate ion, which was then determined. The compound has also been estimated by titration of the acids formed upon hydrogen peroxide oxidation (7) and of lactic acid produced on alkaline rearrangement (2).

PROCEDURE

A standard solution containing approximately 1.5 mg. of pyruvaldehyde per liter is made up from an aliquot of a concentrated stock solution, the preparation and standardization of which are described below. A second standard, if used, is made up in the same way to a somewhat lower concentration.

One milliliter of the unknown solution, containing 0.5 to 2 micrograms of pyruvaldehyde, and 1 ml. of freshly prepared 2% chromotropic acid solution are placed in a 25-ml. glass-stoppered volumetric flask. Separate solutions containing the pyruvaldehyde standard (or standards) and the blank (distilled water) are prepared in the same way. To each of these solutions are then gradually added 10 ml. of ice-cold concentrated sulfuric acid (specific gravity 1.84); the flasks are cooled during the addition by swirling in an ice-water mixture so that the temperature of the reaction mixture does not rise above 25° C. After addition of sulfuric acid, each flask is stoppered and placed in a shallow bath containing ice-water mixture. It is preferable to make the addition to the blank solution last. The flasks are then transferred together to a water bath maintained at 50° where they are swirled for 5 minutes. At the end of this time the flasks are transferred together to a cool water bath where they are quickly brought to room temperature. Each flask is then diluted to the mark with concentrated sulfuric acid and the fluorescence of the

Table I. Analysis of Pyruvaldehyde Stock Solutions

	Pyruvaldehyde Found, G./L.[a]		
Experiment	Disemi-carbazone	Periodic acid oxidation	2,4-Dinitro-phenylosazone
1	4.978	4.98	...
2	3.649	..	3.680

[a] Average of two determinations.

Table II. Effect of Time in Oxidation of Pyruvaldehyde by Periodic Acid

Reaction Period, Min.	Sample Aliquot, Ml.	Periodic Acid Utilized, Me.
60	3	1.342
125	3	1.341
240	3	1.340
245	3	1.342

unknown is compared with that of the standard, employing a blue primary and a yellow secondary filter for the measurements (excellent results are obtained with the PC-2 and B-2 filters supplied with the Coleman photofluorometer for the determination of riboflavin).

EXPERIMENTAL

Materials. Glyceraldehyde used in these experiments was prepared by the Organic Syntheses procedure (14). The purified dimer melted at 138°. Technical chromotropic acid was obtained from Eastman Kodak Company and Paragon Testing Laboratories. The solutions of this compound were filtered before use; otherwise, the reagent was not purified. Acetol was prepared by the Organic Syntheses procedure (9); it was also purchased from Bios Laboratories. Other materials employed for this work were either Eastman Kodak best grade or C.P. quality.

Apparatus. A Model 12 Coleman photofluorometer, equipped with a B-2 primary filter and a PC-2 secondary filter, and the standard cuvettes supplied for this instrument were used in making all fluorescence measurements.

Pyruvaldehyde Stock Solutions. Stock solutions of pyruvaldehyde were prepared by distillation of a solution of 1 gram of glyceraldehyde in 25 ml. of 1 M sulfuric acid. Fifteen milliliters of distillate were collected, diluted to 100 ml. with redistilled water, and stored at 5° C. These stock solutions were not acidic and varied in concentration from 2 to 5 grams of pyruvaldehyde per liter, depending upon the rate of distillation. The usual distillation time was 15 minutes; this gave a concentration of approximately 3 grams per liter.

The pyruvaldehyde stock solutions were standardized by precipitation of the compound as the slightly soluble disemicarbazone. To a 10-ml. aliquot of the solution to be standardized was added a filtered solution of 1 gram of sodium acetate (hydrate) and 1 gram of semicarbazide hydrochloride in 15 ml. of water. Although the disemicarbazone precipitates immediately, the mixture was allowed to stand for 24 hours to ensure completion of the reaction. Longer reaction periods were avoided on account of the danger of forming insoluble biurea. The precipitate was collected in a filter crucible, washed with a few milliliters of cold water, and dried in an oven at 110°. The disemicarbazone melted at 254°, with decomposition, in agreement with the literature value (8). Its solubility (1.7 mg. under these conditions) was determined by equilibrating a weighed amount of the compound with a solution of 1 gram of semicarbazide hydrochloride and 1 gram of sodium acetate in 25 ml. of water, washing, and drying the undissolved material as described above.

Further indication of the purity of these pyruvaldehyde solutions was obtained in comparing analytical values found by the disemicarbazone precipitation with those found by periodate oxidation and by precipitation as the 2,4-dinitrophenylosazone. Data from typical determinations are given in Table I.

The periodic acid oxidations were carried out as follows: A 10-ml. aliquot of the pyruvaldehyde solution was added to a mixture of 20 ml. of 0.2 N periodic acid and 15 ml. of acetate buffer (3 M each in sodium acetate and acetic acid). The resulting mixture was allowed to stand at room temperature (approximately 25°) for 4 hours. At the end of the reaction period the mixture was almost neutralized by adding slightly less than the required amount of sodium hydroxide solution and then saturated

with sodium bicarbonate. One milliliter of 5% sodium iodide and excess standard arsenite were added, and the mixture was back-titrated with 0.01 N iodine. The completeness of the reaction between pyruvaldehyde and periodic acid under these conditions is indicated by the data in Table II.

As a further check on the quantitative nature of the periodic acid oxidation of α-dicarbonyl compounds, a solution of carefully purified diacetyl, made up by weight, was analyzed by the periodic acid method used for pyruvaldehyde. The following results were obtained: molarity of diacetyl solution weighed, 0.1417; molarity found by periodic acid oxidation, 0.1409.
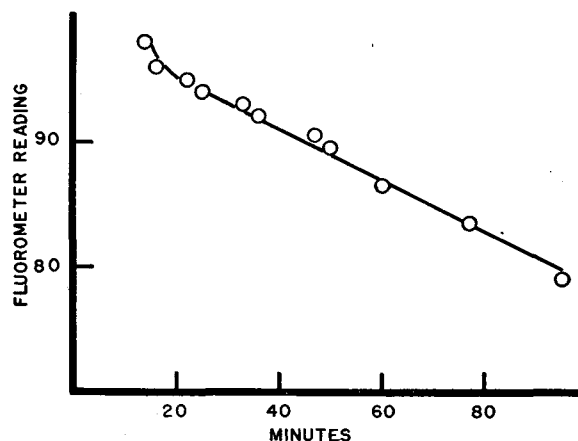

Figure 1. Decay of Fluorescence

Zero time is time of initial addition of sulfuric acid

The following procedure was used for precipitation of pyruvaldehyde as the 2,4-dinitrophenylosazone.

The reagent was prepared by dissolving 4 grams of 2,4-dinitrophenylhydrazine in a mixture of 100 ml. of 72% perchloric acid and 200 ml. of water. This solution was allowed to stand for 24 hours before use and the small quantity of insoluble material present was removed by filtration. To 25 ml. of the reagent was added a 5-ml. aliquot of the pyruvaldehyde solution. The osazone precipitated immediately. After the mixture had stood at room

Table III. Effect of Temperature on Development of Fluorescent Compound

Temperature, ° C.	Fluorometer Reading
0	33
25	48
50	54
75	54

Table IV. Effect of Time of Heating at 50° C.

Time, Min.	Fluorometer Reading
5	60
10	59
15	58

Table V. Effect of Chromotropic Acid Concentration

Concentration of Chromotropic Acid Reagent, %	Fluorometer Reading
1	45
2	52
3	52

Table VI. Effect of Sulfuric Acid Concentration

Molarity of Sulfuric Acid[a]	Fluorometer Reading
18.8	55
18	48
16	34
14	19
12	2

[a] Concentration of acid used in both development and dilution.

temperature for 1 hour, the precipitate was collected in a filter crucible, and washed several times with a solution of 50 ml. of 72% perchloric acid in 200 ml. of water in order to remove excess reagent, and then thoroughly with water. The precipitate was dried to constant weight at 110° to 120° C.

Fluorescein Solutions. Fluorescein reference solutions used in determining the development and decay characteristics of the fluorescent compound were prepared by diluting a stock fluorescein solution (4.6 mg. per liter) 1 to 15.

Decay of Fluorescent Compound. The nonphotochemical decay of the fluorescent compound, shown in Figure 1, was determined by measuring the fluorescence obtained by the recommended procedure with samples of the same pyruvaldehyde concentration. At the end of the reaction period, the solutions were allowed to stand at 25° for varying periods of time. A fluorescein standard was used as a reference for the measurements.

Effect of Reaction Conditions and Interferences. The data given in Tables III, IV, V, and VI, which show the effects of temperature, time of heating, chromotropic acid concentration, and sulfuric acid concentration on the development of the fluorescent compound, were obtained by carrying out reactions with sets of pyruvaldehyde samples of the same concentration. The factor being studied was varied. Other conditions were those of the recommended procedure. Measurements were made against fluorescein.
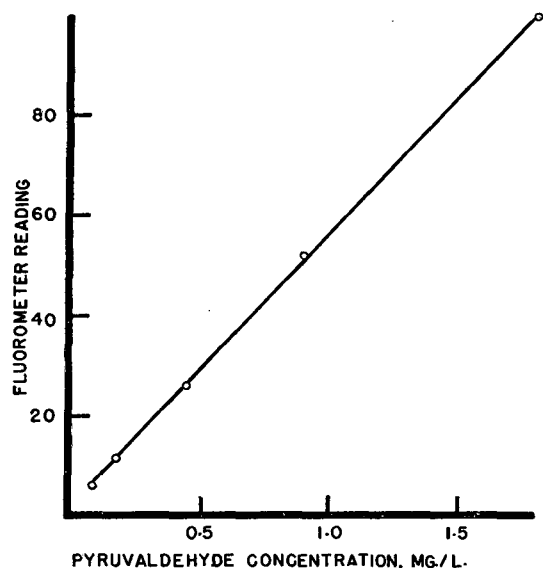

Figure 2. Fluorescence vs. Pyruvaldehyde Concentration

Concentration is that in aliquot taken for analysis

Data for several interfering compounds (Table VII) were obtained with solutions containing the indicated concentrations of pyruvaldehyde and the compound being tested. After development of the fluorescent compound, the fluorescence of these solutions was compared with that of solutions prepared from standards of the same pyruvaldehyde concentration.

Data indicating the precision of the method (Table VIII) were obtained by simultaneous development of the fluorescent compound in six samples of the same pyruvaldehyde concentration. Measurement was made against the first of the series.

DISCUSSION

Qualitatively, pyruvaldehyde, glyceraldehyde, and dihydroxyacetone all react with chromotropic acid–sulfuric acid mixture to form the same highly fluorescent condensation product. The reaction has not been observed with any other substance, except
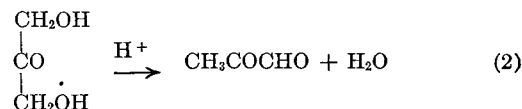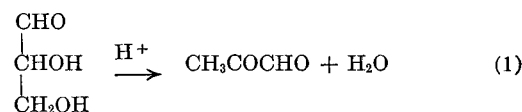
Table VII. Interferences

Sample	Pyruvaldehyde Concentration, Mg./L.	Concentration of Interfering Substance, Mg./L.	Fluorometer Reading
Pyruvaldehyde	1.49	..	50
Pyruvaldehyde–D-glucose	1.49	1000	35
Pyruvaldehyde–D-glucose	1.49	500	31
Pyruvaldehyde–D-xylose	1.49	1000	>100
Pyruvaldehyde–D-xylose	1.49	500	95
Pyruvaldehyde-diacetyl	1.49	1000	7
Pyruvaldehyde-diacetyl	1.49	500	22
Pyruvaldehyde	0.91	..	100
Pyruvaldehyde-formaldehyde	0.91	50	0
Pyruvaldehyde-formaldehyde	0.91	5	55

Table VIII. Precision

Sample No.	Fluorometer Reading
1	72
2	72
3	73
4	70
5	70
6	71

those that are converted to pyruvaldehyde under strongly acidic conditions. Hence, in view of the facile and irreversible conversion of glyceraldehyde and dihydroxyacetone to pyruvaldehyde in acid solution (Equations 1 and 2), it is probable that the formation of the fluorescent product is a property of pyruvaldehyde only.

$$\begin{array}{c} CHO \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{H^+} CH_3COCHO + H_2O \qquad (1)$$

$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ CH_2OH \end{array} \xrightarrow{H^+} CH_3COCHO + H_2O \qquad (2)$$

The pyruvaldehyde–chromotropic acid product undergoes a considerable nonphotochemical decay, as shown in Figure 1. Accordingly, its fluorescence may be measured in either of two ways: (1) at some fixed time, after completion of the reaction, against a standard reference such as fluorescein, or (2) against solutions from standard pyruvaldehyde samples for which the chromotropic acid reaction is carried out simultaneously with that of the unknown. The latter procedure was chosen in this work because decay effects cancel out and operation on a rigid time schedule is unnecessary. The conditions recommended for carrying out the development of the fluorescent compound are those which appear to give the greatest sensitivity and precision for this method of measurement.

Inasmuch as the curve representing concentration versus fluorometer reading is linear over the range of concentrations studied and extrapolates nearly to 0 (Figure 2), it has been convenient and sufficiently accurate in most applications of the method to employ a single pyruvaldehyde reference solution. Nevertheless, no difficulty is introduced in the use of two pyruvaldehyde standards of different concentration. Newer photofluorometer models such as the Coleman 12B permit the measurement of considerably lower concentrations of pyruvaldehyde. Doubtless the fluorescence-concentration relationship is also linear at these levels.

Of the substances investigated, those which cause significant interference in this method are: formaldehyde, diacetyl, xylose, glucose, and fructose. The presence of formaldehyde or diacetyl results in low values owing to the formation of the purple dye with chromotropic acid (5, 11). This dye absorbs strongly in the visible range with maxima at 485 and 570 $m\mu$, which is sufficient to account for the interference (by absorption of the fluores-

cence). The interference by formaldehyde is more pronounced on account of the greater rate of dye formation with this substance. Attempts to eliminate this interference by initial reaction of pyruvaldehyde samples containing formaldehyde with dimedone were unsuccessful. Apparently pyruvaldehyde also undergoes a rapid reaction with dimedone.

The presence of reducing sugars at fairly high concentrations may result in either high or low values, depending on the mode of degradation of the carbohydrate under these conditions. D-Xylose causes high values, which increase with time of standing, because of appreciable conversion to pyruvaldehyde (*12*). D-Glucose appears to undergo sufficient degradation to diacetyl or formaldehyde (*11, 12*) to cause low results, although in view of the greater interference by the lower concentration of this substance, as shown in Table VII, it seems that formation of pyruvaldehyde is in this case a competing reaction which may be more concentration dependent.

The following substances did not interfere at a weight ratio of substance tested to pyruvaldehyde of 1000 to 1: furfural, acetol, methyl ethyl ketone, pyruvic acid, lactic acid, levulinic acid, acetic acid, propionic acid, acetone, acetaldehyde, isobutyraldehyde, methanol, ethanol, and 1-butanol.

PRECISION

The precision of the method indicated by the data in Table VIII is slightly outside the limits of reproducibility by the fluorometer. However, the handling of this number of samples is a rather severe test of precision, owing to the considerable elapsed time

between the first addition of sulfuric acid to the first sample and the placing of the six samples in the 50° bath. In a number of applications of the method where development for only two or three samples has been carried out at one time the precision has been generally better than that indicated in the table.

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Fluorometric Determination of Acetol

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The fluorescence of 3-hydroxyquinaldine, which is formed in the reaction of o-aminobenzaldehyde with acetol, has been applied in a method for determining acetol. The effects of the following variables have been determined: concentration of sodium hydroxide, reagent concentration, acetol concentration, time, and final pH. The proposed method is sufficiently sensitive to permit determination of acetol at concentrations of 0.3 mg. per liter. Its usefulness is limited by pronounced interference of furfural, diacetyl, and formaldehyde.

RECENT work in this laboratory involving investigation of products from reaction of amino acids with reducing sugars has led to a search for a method for determining acetol at low concentrations in the presence of other carbonyl compounds. The proposed analytical procedure, which has been developed in an attempt to meet these requirements, is based upon a reaction first described by Baudisch (*1, 2*) in which acetol combines with o-aminobenzaldehyde in alkaline solution to form 3-hydroxyquinaldine (Equation 1). Upon irradiation with ultraviolet light, 3-hydroxyquinaldine gives a strong blue fluorescence.

$$
\text{(image of reaction)} \quad + 2H_2O \quad (1)
$$
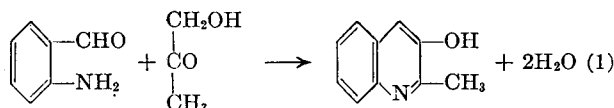
RECOMMENDED PROCEDURE

One milliliter of the unknown solution, containing 0.30 to 6 micrograms of acetol, is placed in a 25-ml. volumetric flask equipped with a glass stopper. To this is then added 1 ml. of the o-aminobenzaldehyde reagent (0.2 mg. of o-aminobenzaldehyde per ml.) followed by 5 ml. of 0.2 N sodium hydroxide. A blank is also prepared by adding the same amounts of the o-aminobenz-

aldehyde and sodium hydroxide solutions to 1 ml. of distilled water. The flasks are immersed in a bath of boiling water and the stoppers are inserted. Heating is continued for a total of 30 minutes, after which the flasks are transferred to a cold water bath and rapidly brought to room temperature. To each solution are then added 2 ml. of 0.5 N hydrochloric acid and 5 ml. of pH 6.6 McIlvaine buffer (*3*). The solutions are diluted to the mark with distilled water, and the fluorescence of the unknown is determined in a fluorometer equipped with standard filters used in the vitamin B₁ determination. The instrument is calibrated by determining the fluorescence obtained by the above procedure with solutions of known acetol content. Two points are sufficient to establish a curve, as it is perfectly linear over the recommended concentration range. Temperature control is recommended during fluorescence measurements.

EXPERIMENTAL

Materials. Acetol used in these experiments was obtained from Bios Laboratories and was purified by ordinary distillation at reduced pressure. The fraction collected boiled at 42° to 45° C. at 15 mm. and was stored in a desiccator over Drierite. For preparation of acetol stock solutions, approximately 100 mg. of such a fraction were accurately weighed into a 50-ml. volumetric flask and diluted to the mark with redistilled water. The purity of the acetol was checked by oxidation of aliquots of these stock solutions with periodic acid. In a typical determination,
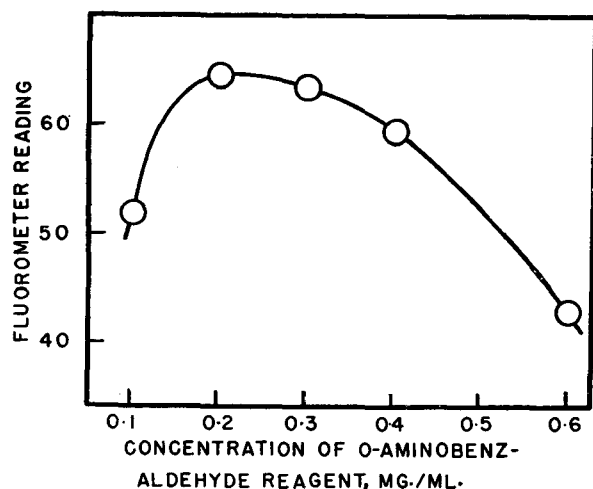
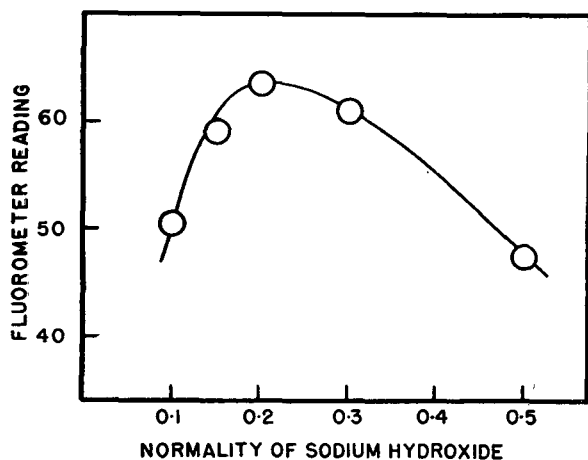Figure 1. Effect of o-Aminobenzaldehyde Concentration

Figure 2. Effect of Sodium Hydroxide Concentration Used in Condensation upon Final Reading

the acetol concentration found by periodic acid oxidation was 2.080 grams per liter, as compared with 2.076 grams per liter actually weighed.

o-Aminobenzaldehyde was purchased from Bios Laboratories and was not purified before use. Diacetyl was obtained from Forest Products Chemical Company and was fractionally distilled. Other compounds tested as possible interferences were either Eastman Kodak best grade or c.p. chemicals. Hydrochloric acid, sulfuric acid, sodium hydroxide, citric acid, and disodium phosphate used in this work were all c.p. quality. Mallinckrodt U.S.P. quinine sulfate was used to prepare reference standards.

Apparatus. A Model 12B Coleman electronic photofluorometer, equipped with a B-1 primary filter and a PC-1 secondary filter, and the standard cuvettes supplied for this instrument were employed for fluorescence measurements. A Beckman pH meter with glass electrode was used for pH determinations.

Preparation of o-Aminobenzaldehyde Reagent. Solid o-aminobenzaldehyde undergoes polymerization upon standing, with the formation of water-insoluble material. This reaction may be reversed by solution in concentrated hydrochloric acid, and, providing neutralization is carried out immediately after solution is effected, the resulting solutions contain only a negligible amount of insoluble material and remain clear. Accordingly, the following procedure was adopted for preparation of solutions of this compound:

Fifty milligrams of o-aminobenzaldehyde were dissolved in 25 ml. of concentrated hydrochloric acid (specific gravity 1.19). The solution was then adjusted to pH 7.0 (glass electrode) with

Table I. Effect of Time of Heating

Time, Minutes	Fluorometer Reading
5	33.0
10	54.0
15	63.5
30	75.0
45	76.5

Table II. Interferences

Mixture	Weight Ratio	Fluorometer Reading
Acetol	....	68.0
Furfural-acetol	100:1	> 100
	10:1	84.0
Pyruvic acid–acetol	1000:1	60.5
	100:1	65.0
Diacetyl-acetol	10:1	5.0
Formaldehyde-acetol	1000:1	> 100
	100:1	5
Acetaldehyde-acetol	1000:1	38.5
	100:1	57.0

sodium hydroxide solution, cooled during the neutralization, and diluted to 250 ml. with distilled water.

Effect of Reaction Conditions. In order to test the effect of variation of reaction conditions on the formation of the fluorescent compound, sets of identical samples were treated according to the recommended procedure, with the exception of the condition being studied which was varied from sample to sample. In all cases separate blanks were prepared for each sample, and a quinine sulfate solution (0.3 mg. of quinine sulfate per liter, 0.1 N in sulfuric acid) was employed for maintaining a reference point (100 on the scale of the instrument). The results of variation in the time of heating are shown in Table I. The relationship between fluorescence and the concentrations of o-aminobenzaldehyde and of sodium hydroxide is shown in Figures 1 and 2, respectively.
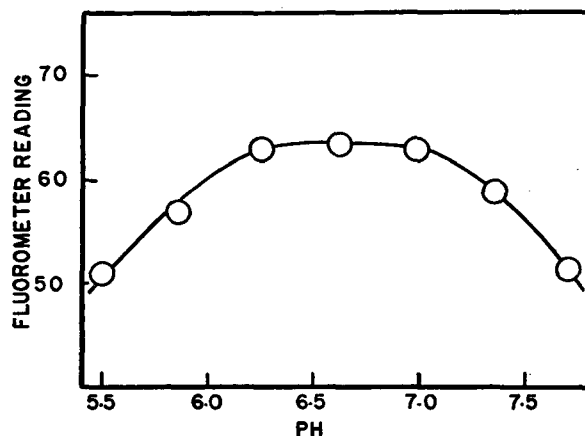

Figure 3. Effect of pH on Fluorescence

Effect of pH on Fluorescence. The fluorescence obtained with acetol-o-aminobenzaldehyde reaction mixtures is dependent upon the final acidity of the solution. Data showing this variation of fluorescence with pH (Figure 3) were obtained by carrying out the reaction of identical samples of acetol with o-aminobenzaldehyde according to the recommended procedure and varying the pH of the buffer solution added after neutralization. Separate blanks were again prepared, and the quinine sulfate solution was used as the reference.

Interferences. The data in Table II, which indicate interference by several compounds, were obtained with solutions containing the same aliquot of acetol standard stock solution and the compound to be examined for interference in the weight ratio indicated. The most pronounced interference is that of diacetyl.

Table III. Precision

Acetol Weighed, Mg./L.	Found, Mg./L.
0.82	0.8, 0.9
1.64	1.6, 1.6
2.40	2.5, 2.5
3.28	3.2, 3.3
4.09	4.2, 4.2
4.91	4.8, 4.9
5.73	5.7, 5.8
6.55	6.6, 6.5

Formaldehyde, in large excess, forms colored solutions which fluoresce beyond the range measurable by the fluorometer. At lower concentrations of formaldehyde, in which case little coloration develops, low values are obtained, possibly due to reaction of formaldehyde with acetol. The presence of furfural results in high values. Acetaldehyde interferes only when present in very large excess, whereas the interference by pyruvic acid is small. The following substances do not interfere when present in a weight ratio of 1000 to 1: methanol, ethanol, acetone, lactic acid, and levulinic acid.

DISCUSSION

This quantitative application of Baudisch's qualitative test for acetol gives good results in the absence of the interfering sub-

stances mentioned above. As shown in Table III, the precision of the method appears to be nearly within the limits of the fluorometer. The fluorescence is dependent on temperature. However, the fluorescent compound is stable, exhibiting no decay, in the absence of strong illumination, during 2 hours. A single determination requires approximately one hour, and several can be run simultaneously.

As yet, no means has been found for reducing the effect of any of the interfering substances. This is unfortunate, for the interferences of diacetyl and furfural limit the usefulness of the method in application to certain problems in carbohydrate chemistry.

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Spectrochemical Analysis of Brines

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A spectrographic procedure for the analysis of most of the cations in brine solutions utilizes an alternating current spark form of excitation on 0.5-inch briquets combined with a series of synthetic standards. A relative standard method is used to obtain the concentrations of the major constituents. The shortcomings of the method as well as its advantages are discussed. An error of ±10% is claimed for the procedure.

THE complete quantitative chemical analysis of brines has always been a difficult and tedious task. In the determination of the cations this has been occasioned both by the difficult chemical separations as, for instance, small amounts of potassium from large amounts of sodium, or small quantities of barium and strontium from larger amounts of calcium, and the determination of very small amounts of some constituents. In addition, there is difficulty in determining the anions in the form in which they occur in the original sample. Contact of the brine solutions with the air continually changes the form of the anion—i.e., bicarbonate changes to carbonate.

As the result of these chemical difficulties, shortened and approximate methods of brine analysis have been developed in many laboratories. All alkalies are reported as sodium. Barium and strontium are not determined, but are partially precipitated with and determined as calcium. Aluminum and iron are precipitated as the hydroxides, along with any other materials that would be precipitated at this point, and reported as R_2O_3. Many of the elements such as boron, manganese, and lithium, present only in small amounts, are not detected in a sample of the size usually taken for chemical analysis.

The investigation reported here has been carried out to develop a more rapid method for the quantitative analysis of brines. In addition, more information can be provided by the spectroscopic method than by the usual chemical analysis.

QUALITATIVE ANALYSIS

Before any attempt is made to analyze a sample quantitatively, a so-called qualitative analysis is made. The sample is evapo-

rated to dryness over an open flame in the presence of a little hydrochloric acid. Three 10-mg. portions of the dried residue are weighed and arced, using 10-ampere direct current and a large Littrow quartz prism spectrograph. The purpose of using an exact weight of sample is to enable the operator to estimate more accurately the quantities of elements present. These qualitative results become of value to the quantitative analysis only as the operator learns to place them in the proper percentage groupings. On the basis of many other samples that have been analyzed chemically, the operator is able to place the elements in their correct groupings by remembering the densities of lines

Table I. Qualitative Analysis of a Typical Brine Residue

(% refers to cations detected)

%	
> 10	Na
1–10	Ca Mg
0.1–1	K Sr Si B
0.01–0.1	Fe Li Al Cu
< 0.01	Pb Ba Ti Ag Cr

of samples of known composition and comparing them with the unknowns. However, such results are obtained by visual means. The sum of the elements with the exception of sodium, calcium, and magnesium is estimated for use in the quantitative analysis of the aforementioned elements. Table I illustrates a typical qualitative brine analysis.
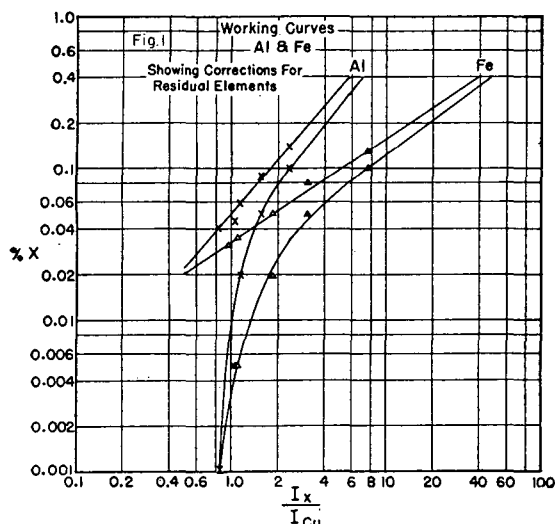
QUANTITATIVE ANALYSIS

Once the constituents of a brine are known, it is possible to prepare standards for their quantitative analysis. One of the assumptions made at the beginning of this investigation was that the major constituents were present as the normal hydrated chlorides. In a few cases this is a poor assumption, and then a poor analysis results. However, even in the worst case, where the calcium is present as sulfate rather than chloride, an error of only about 15% of the amount present would result because the molecular weight of calcium chloride dihydrate is 147 whereas that of calcium sulfate dihydrate is 172. In the case of sodium chloride against sodium carbonate, the error would only be 10%. In most samples the constituents of the brine are present as chloride and little error is introduced. The same approximate composition of both standards and samples is attained by evaporating the brine to dryness with hydrochloric acid.

From the qualitative analysis it is possible to bracket the impurities—that is, potassium might be between 0.1 and 1%. Using these estimated ranges of values, standards are made up by adding known quantities of impurities to a base mixture containing sodium chloride, calcium chloride dihydrate, and magnesium chloride hexahydrate. It is the usual practice to add the highest desired percentage of impurities to a sample of the base mixture and to make other standards by diluting portions of the high standard with varying amounts of base mixture. In this manner the author has prepared a series of brine standards from approximately an order of magnitude below the ordinary concentration of impurity in a brine to an order of magnitude above this normal impurity level.

A series of standards was prepared for the major constituents, sodium, calcium, and magnesium. The sodium chloride was varied from 70 to 99% of the total salt mixture, the magnesium chloride hexahydrate from 10 to 0.5%, and the calcium chloride dihydrate from 10 to 0.5%. In the case of both series of standards, the materials were dried at 110° C. before weighing, and efforts were made to see that no moisture was picked up during the weighing step of the procedure. The materials were thoroughly ground together by means of a mortar and pestle before weighing. Both the samples and standards were hygroscopic and special care was taken in order to be certain that the ma-

terials were dry and in a reproducible state. These standards were then available for any form of excitation.
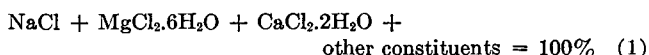
Because it had been used previously with nonmetallic samples, an alternating current spark form of excitation was used. After some experimentation, aliquots of the standards were weighed up with natural graphite and internal standard in the ratio of 4:1:1. Natural graphite was chosen over synthetic graphite because of its favorable briquetting properties. Copper oxide was chosen as the internal standard for the minor impurities, and a relative standard method was chosen for the major constituents.

Table II gives the conditions used for the analysis of the constituents in brine solutions. Figure 1 gives working curves obtained upon running the series of standards. The curved lines are those obtained without making any correction. Theoretically, such a curve should have been a straight line if there had been no background, no self-absorption of the spectrum lines used, or no contamination or impurities present. The background was low and corrections applied to this background did not appreciably change the curve. The curvature of the lines was in the wrong direction to be explained by self-absorption, and self-absorption does not usually occur at such low concentration levels. Because both background and self-absorption can be ruled out, it has been assumed that the curvature arose from contamination or impurities within the standards themselves. Qualitative analyses of the base materials substantiate this assumption. Corrections have been applied to the added percentages of impurities with the resulting straight lines shown. These corrections are relatively large, but chemical analyses in this range are usually too poor to prove or disprove the hypothesis. Figure 2 is a series of similarly corrected working curves for some of the minor constituents.
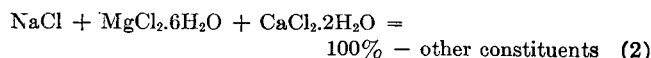
Table II. Conditions for Determining Constituents in Brines

|	B, Si, Fe, Al	K, Ba, Sr	Na, Mg, Ca
Spectrograph	Large Littrow quartz prism		
Range, A.	2413–3160	3687–8000	2739–4071
Emulsion used	SA1	1L	SA1
Power, kv.-amp.	2	2	4/3
Capacitance, μf.	0.021	0.021	0.014
Inductance, mh.	0.36	0.36	0.36
Primary voltage	75	75	75
Prespark, sec.	5	5	5
Exposure time, sec.	40	15	15
Distance from slit, inches	18	18	33
Slit width, microns	30	30	30
Upper electrode		0.5-inch briquet	
Lower electrode	Hemispherical cone, 0.25-inch graphite rod		
Internal standard	CuO	CuO	None
Development		D-19, 4 minutes	
Analysis lines	B 2496.8 Cu 2703.2	K 7699.0 Cu 5153.2	Na 3302.3
	Si 2516.1 Cu 2703.2	Ba 4554.0 Cu 5153.2	Mg 2779.8
	Fe 2599.4 Cu 2703.2	Sr 4607.3 Cu 5153.2	Ca 3180.5
	Al 3082.2 Cu 2703.2		

The relative standard method is convenient for use in determining major constituents [1–3]. To the extent that the working curves formed using this method have a 45° slope, the method is theoretically sound. As the working curves depart from the 45° slope, it is necessary that standards of similar composition be used in order to bracket the concentration ranges covered. This method is based on the fact that the sum of all the constituents in any mixture is equal to 100%. Therefore, by assuming all of the major constituents of the brine to be chlorides, we are justified in writing Equation 1. The hydrates given are those normally present from room temperature to about 110° C. The percentage of "other constituents" can be estimated from the qualitative analysis. The error involved in this estimation, although it may be large for the constituent itself, is relatively minor when compared with the 100% total. Dividing Equation 2 by NaCl and transposing, Equation 3 is obtained.

$$NaCl + MgCl_2.6H_2O + CaCl_2.2H_2O + \text{other constituents} = 100\% \quad (1)$$

Hence:

$$NaCl + MgCl_2.6H_2O + CaCl_2.2H_2O =$$
$$100\% - \text{other constituents} \quad (2)$$

$$NaCl = \frac{100\% - \text{other constituents}}{1 + \dfrac{MgCl_2.6H_2O}{NaCl} + \dfrac{CaCl_2.2H_2O}{NaCl}} \quad (3)$$

Fig. 2 Working Curves, Minor Constituents in Brines
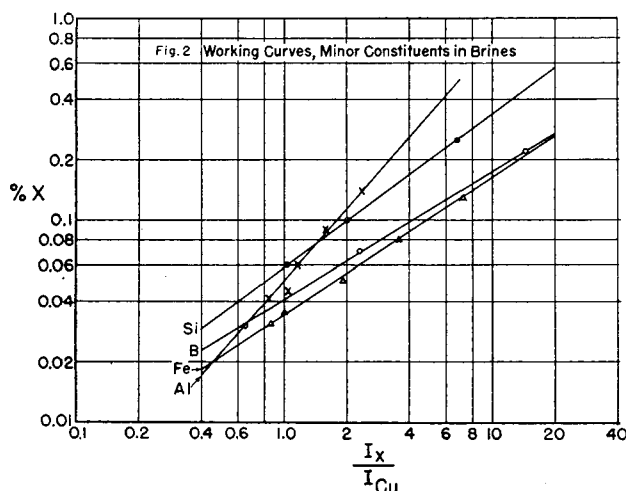
The standards for the major constituents are made up of known proportions of sodium chloride, calcium chloride dihydrate, and magnesium chloride hexahydrate. The quantity that is measured on the photographic plate is the transmittance of light through the spectrum lines. These values are converted to intensity ratios by referring them to the calibration curve of the particular emulsion involved. Thus, while the value obtained is the intensity ratio of either calcium and sodium or magnesium and sodium, this value is a measure of the concentration ratios of calcium chloride dihydrate to sodium chloride or magnesium chloride hexahydrate to sodium chloride. The values for the intensity ratios are plotted against the percentage ratios of the compounds involved and a working curve is drawn. The percentage ratios of samples treated in the same fashion are obtained by referring the intensity ratios to this working curve and are substituted in Equation 3. This results in an expression with only one unknown—namely, sodium chloride—which can be solved. Upon getting the percentage of sodium chloride, this value can be substituted into the ratio expression—i.e., calcium chloride dihydrate to sodium chloride—and a value obtained for the other member. Once percentage values have been obtained for the three compounds, sodium chloride, magnesium chloride hexahydrate, and calcium chloride dihydrate, the parts per million can be calculated in a straightforward manner. Figure 3 gives working curves of the percentage ratio of compounds to intensity ratio of elements. Tables III and IV give typical results obtained with the method as well as a limited number of routine chemical analyses. Although the individual errors of the calcium and magnesium are rather large, the combined calcium and magnesium result in a much smaller error. This could be caused by compensating errors. Table V shows the reproducibility of the method on different photographic plates taken on different days. This table illustrates the type of accuracy and precision that could be obtained if accurate chemical values for standards and samples were available. It is possible that the reproducibility of the method coincides with the accuracy, but in the absence of an independent check, such a conclusion would be open to doubt.

Table III. Comparison Analyses of Brines

Element	Concentration, Mg./L. Chemical	Concentration, Mg./L. Spectrographic	% Deviation from Chemical
Sample 3			
Na	a	8607	0.7
Ca	1,030	1160	12.6
Mg	398	294	26
K	...	134	...
Li	...	8	...
Sr	...	220	...
Fe	...	5	...
Al	...	3	...
Al + Fe	12	8	33
Si	24	21	12
B	...	24	...
Na, K, + Li	8.663	8749	0.9
Ca + Mg	1,428	1454	1.9
Total dissolved solids	27,476	...	...
Sample 8			
Na	a	6587	0.4
Ca	964	1116	16
Mg	289	232	19.7
K	...	114	...
Li	...	9	...
Sr	...	78	...
Fe	...	6	...
Al	...	2	...
Al + Fe	14	8	42.8
Si	24	21	13.3
B	...	23	...
Na, K, + Li	6,613	6710	1.5
Ca + Mg	1,253	1348	7.6
Total dissolved solids	21,460	...	...

a Figure used here was total Na, K, + Li.

Table IV. Comparison Analyses of Brines, Sample S-1

Element	Concentration Added, Mg./L.	Concentration Found, Mg./L. Chemical	Concentration Found, Mg./L. Spectrographic	% Deviation from Calculated Values Chemical	% Deviation from Calculated Values Spectrographic
Na	17,098	17,030	16,940	0.4	0.9
Ca	1,038	1,040	1,172	0.2	13.0
Mg	90.1	105	84	16.7	6.7
Total dissolved solids	47,136	...	...	...	...
Li	<10	...	...	...	...
Sr	<10	...	...	...	...

DISCUSSION OF RESULTS

The method is somewhat tedious because it is necessary to carry out so many dryings on both samples and standards during the procedure. Usually the samples and standards are kept in a drying oven at 110° C. and are only removed before analytical work is actually commenced. In addition, three photographic plates are necessary for the analysis of any batch of samples. One SA1 emulsion is used for the minor impurities in the region 2300 to 3000 A. Another SA1 emulsion is used for the determination of the major constituents, which requires a different set
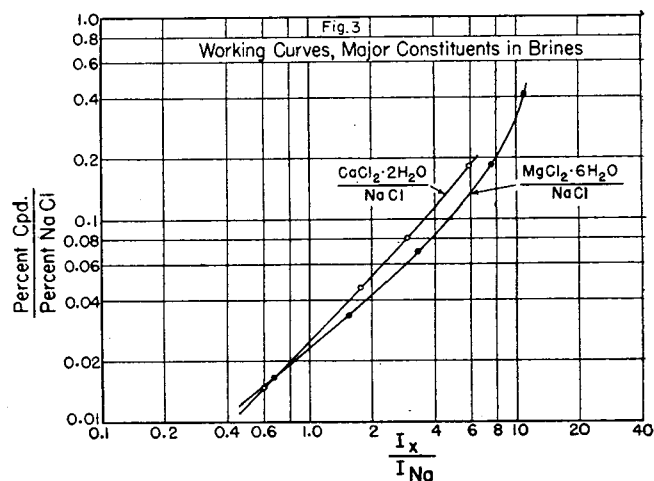

Fig. 3 Working Curves, Major Constituents in Brines

Table V. Spectroscopic Reproducibility Data for Brine Analysis

	Sample 8	Sample 1		Sample 8	Sample 1
B	0.045	0.092	Na	30.8	35.5
	0.040	0.068		30.3	35.5
	0.044	0.078		30.1	
Si	0.188	0.141	Ca	0.30	1.41
	0.152	0.128		0.30	1.39
	0.150	0.150		0.36	
Fe	0.034	0.029	Mg	2.49	0.46
	0.036	0.030		2.67	0.47
	0.040	0.030		2.68	
Al	0.37	0.042			
	0.22	0.045			
	0.23	0.035			

of standards and different exposure time than the first plate. A 1L emulsion is used for the detection of barium, strontium, and potassium in the visible region.

In view of the reproducibility of the method, it should be capable of results within ±10% of the actual quantities of elements present, especially if the samples approach the standards in composition. Lack of complete reliable chemical information regarding the accuracy of the procedure makes an actual percent-age value somewhat difficult. The method is much more rapid than regular chemical analyses and gives information not ordinarily obtained in the chemical analyses. A single sample can be analyzed in about 6 hours, though 5 to 10 samples can be analyzed almost as quickly. As an adjunct to chemical analyses, such a procedure would be valuable. The assumption that the major constituents of the samples are chlorides places a limitation on the procedure which is not serious, for in most cases it will introduce an error of less than ±10%.

ACKNOWLEDGMENT

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Thermomagnetic Determination of Hägg Carbide in Used Iron Fischer-Tropsch Catalysts

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Being capable of measuring the Curie points and magnetic moments of ferromagnetic materials, the magnetic balance is suitable for the relatively rapid qualitative and quantitative determination of the ferromagnetic phases present in used iron Fischer-Tropsch catalysts. Because of the nature of the samples and of the method, special consideration must be given to the magnetic field strength, elastic effects, remanent force, sampling technique, shape of sample, and heating schedule. These points are discussed, and it is shown how a composite thermomagnetic curve may be resolved into its components when their characteristic magnetic constants are known. In connection with x-ray and chemical analyses, and by means of a few simple equations, the relative abundance of ferromagnetic phases can be calculated. This procedure is illustrated for the three-component system Fe_2C–Fe_3O_4–α–Fe, and the significance of the magnetically nondetectable iron is discussed.

EXPERIMENTAL

THERMOMAGNETIC analysis is the study of the temperature dependence of the force experienced by a ferromagnetic substance in a constant, inhomogeneous magnetic field—that is, the variation with temperature of the magnetic moment of the ferromagnetic material. A convenient instrument for this type of investigation is the magnetic balance, which permits qualitative identification and quantitative estimation of relative amounts of ferromagnetic phases present in a substance. At the Bureau of Mines laboratories, Bruceton, Pa., thermomagnetic analysis has been applied to iron Fischer-Tropsch catalysts, and some of the results were presented at the 1949 Gordon Research Conference on Catalysis.

For qualitative information about the known interstitial alloys of carbon in iron, thermomagnetic analysis is superior to chemical analysis, by which no distinction between these alloys can be made as yet. In conjunction with x-ray diffraction and chemical analyses, thermomagnetic analysis can be used to determine quantitatively the bulk changes in catalysts during their use. Magnetic measurements have been used qualitatively for analysis of Fischer-Tropsch catalysts (11) and quantitatively for study of the iron-nitrogen system in connection with iron synthetic ammonia-type catalysts (4, 5).

The choice of the magnetic field strength is determined by two considerations: The field should be as weak as possible for a clear definition of the Curie points (10) (qualitative analysis), and it should be as strong as possible to ensure that the saturation value of the specific magnetization (12) has been attained over the temperature range of the analysis for all ferromagnetic phases present (14) (quantitative analysis). Determinations at either high or low field strength may be carried out, or an intermediate field strength may be used. Thus, a field strength of 2160 gausses was decided upon for routine measurements, that being also the limiting safe field strength for continuous, long-time operation of the available electromagnet. Although the Curie points are not as sharply defined as possible and this field strength is not always sufficient for saturation magnetization (errors due to this limitation are discussed below), this compromise proved to be satisfactory.

Elastic hysteresis effects of the torsion wire make it necessary to interrupt the current and to allow the magnetic field to decay after each reading, thus preventing a drift of the null position of the sample. A small remanent force on the sample persists after the current is interrupted unless the apparatus is jarred a number

of times. It has been found more convenient to avoid any such mechanical disturbance during analysis. In this way, reproducible results can be obtained, and the accuracy of the measurements is not affected seriously.

The sampling technique is important, particularly when the catalyst is not homogeneous—for example, in the initial stages of its use in the synthesis. It is necessary, in the case of fixed-bed converters, to remove the total catalyst charge while preventing any contact with air and to mix it thoroughly in order to obtain a representative sample. This may be stored under an inert atmosphere, or preferably (for ease of handling) under a liquid such as n-hexane, n-heptane, or petroleum ether. In order to obtain representative samples and, thus, reproducible thermomagnetic curves, the samples are ground in a steel mortar under an inert liquid. This is of particular importance in the case of inhomogeneous samples, because only about 0.10 to 0.30 gram is used for each determination. Subsequent manipulations of samples, the general course of the analysis itself, and the magnetic balance have been described (7). The shape of the crushed catalyst—when filled into the borosilicate glass or silica sample holder (7)—is that of a fairly thin, round disk, oriented with its essentially plane sides parallel to the lines of force, thus minimizing the demagnetization factor (9) as much as possible.
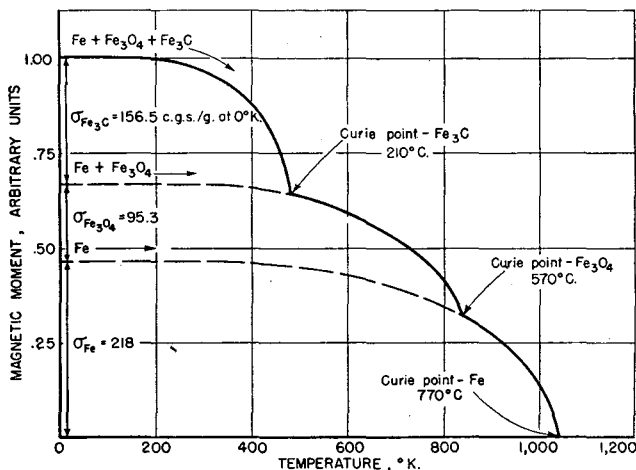

Figure 1. Ideal Thermomagnetic Curve of Mixture of Equal Amounts of α-Fe, Fe_3O_4, and Fe_3C

Because of the reactivity and thermal instability of some of the phases present in used catalysts, the analysis must be carried out fairly rapidly. Yet the heating must be slow enough to avoid temperature gradients between the sample and the point of temperature measurement. Both conditions appear to be fulfilled when samples of used catalysts are heated from room temperature to 530° C. in 26 to 29 minutes. Cooling curves are generally not characteristic of the original mixture of solid phases because of reactions that have occurred during heating.

EVALUATION OF THERMOMAGNETIC CURVE

Thermomagnetic curves can be evaluated quantitatively only if it is known that no changes take place in the material tested over the ranges of temperature and time of the analysis or if any such reactions, their rates, and their temperature coefficients are known well enough to make proper allowance for them. The reactions occurring in used Fischer-Tropsch catalysts during thermomagnetic analysis will be described elsewhere. It has been found that in most cases no serious errors are introduced into the calculations by assuming that no reactions take place at least up to 330° C. with fairly rapid heating. Any reactions

Table I.   Magnetic Constants of Solid Phases Found in Used Iron Fischer-Tropsch Catalysts

Phase	Curie Point, ° C.	Specific Magnetization at Saturation and Room Temperature, $\sigma_\infty, 298°$ K., C.G.S./G.
α-Fe	770	218
Fe_3O_4	570	95.3
Fe_2C-Hägg	247	About 140
Fe_2C, h.c.p.[a]	380	About 140
Fe_3C	210	139

[a] Hexagonal close-packed.

occurring above that temperature do not interfere with the quantitative analysis of mixtures of Hägg iron carbide (Fe_2C), magnetite, and metallic iron. (These three phases are the most common ferromagnetic constituents found in used Fischer-Tropsch catalysts.) When hexagonal close-packed iron carbide (Fe_2C) is present with Hägg carbide, the amount of carbide can be roughly estimated, but no fully satisfactory method for quantitative determination has been developed as yet.

Table I is a compilation of the magnetic constants of some of the ferromagnetic phases that may be present in appreciable amounts in used Fischer-Tropsch catalysts. As is indicated there, the specific magnetizations of the modifications of iron carbide, Fe_2C, are not yet accurately known, but the values given deviate at most only a few per cent from the true values. The Curie points may vary somewhat with differences in composition of individual preparations—for example, that of Fe_3C from 205° to 220° C.—but will leave no doubt about the identity of the phases.

The thermomagnetic curves for the various phases in a mixture are simply additive, and each phase exhibits a magnetic moment which is the product of its specific magnetization and its relative abundance in the mixture. Thus, Figure 1 represents an ideal thermomagnetic curve of a mixture of equal amounts of magnetically saturated metallic iron, magnetite, and cementite. It was constructed from experimental thermomagnetic curves by arbitrarily neglecting the paramagnetic contribution to the magnetic moment near the Curie point (10) and eliminating the low-temperature magnetic anomaly of magnetite (14). Discontinuities appear on the resultant curve wherever a phase loses its ferromagnetism (the Curie point). As the shape of a thermomagnetic curve of a pure, magnetically saturated ferromagnetic substance is characteristically invariant and as its specific magnetization at saturation at any temperature and its Curie point are characteristic constants, it is theoretically possible to resolve any thermomagnetic curve into its components by characterizing these components by their Curie points (and hence to identify the corresponding ferromagnetic phases), and to determine their relative abundance by their respective contributions to the total magnetic moment.

The ideal conditions under which a curve such as Figure 1 is possible are virtually never obtained in practice. Even if saturation of all phases can be attained by the use of a sufficiently high field strength, Curie points usually appear as points of inflection rather than discontinuities (10), and reactions may introduce spurious kinetic effects. A typical family of calculated curves such as might be obtained with used iron Fischer-Tropsch catalysts is shown in Figure 2. This figure was constructed from actual thermomagnetic curves obtained in this laboratory with the pure phases. In each case, Hägg carbide amounts to 50% of the ferromagnetic components, the remainder consisting of various proportions of magnetite and free iron. Obviously, the contribution of Hägg carbide to the total magnetic moment becomes insignificant not at its Curie point (247° C.) but only at about 330° C. (see also 6, Figure 4). Estimation of the relative amounts of iron and magnetite in used catalysts is seldom possible by magnetic means (2) because of the metastability and reactivity of these catalysts at higher temperatures (1, 3). However, x-ray analysis can

provide the ratio of iron to magnetite, and curves such as those shown in Figure 2 can then be resolved into their three components. X-ray diffraction analysis is suitable for this estimation, because the patterns of iron and magnetite are simple and intense owing to the high symmetry and relatively small lattice parameters of these substances. This simplicity does not exist in Hägg carbide (iron percarbide according to Jack, 8).
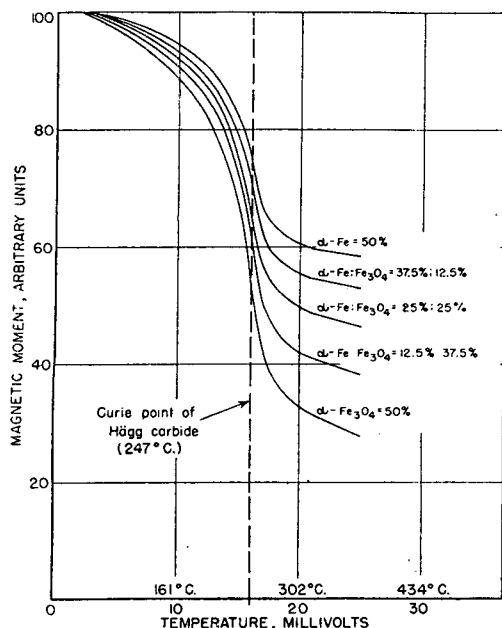

Figure 2. Calculated Thermomagnetic Curves for Mixtures of α-Fe, Fe₃O₄, and Fe₂C–Hägg (50% Fe₂C–Hägg)

If the sensitivity of the magnetic balance is known—that is, movement of balance beam per unit of specific magnetization—it is possible to calculate the mass of iron in each phase (assuming saturation) and thus the magnetically measured total mass of iron in a catalyst sample. If this mass is the same as that found directly by chemical determination following thermomagnetic analysis, the ferromagnetic phases in the catalyst are saturated, and all the iron can be accounted for magnetically. If, however, the magnetically determined mass of iron is less than that found chemically, the difference represents magnetically nondetectable iron. Its existence may be due to the general magnetic hardness of the sample, small crystallite size, unfavorable crystallite orientation, type of magnetic anisotropy of the crystal, strains, etc. For example, crystallites too small to be magnetized may be formed during phase changes at temperatures which are too low to permit coalescence into larger crystallites. Thus, carburization of iron at comparatively low temperatures may lead to the formation of small, nonsaturable, or even paramagnetic crystallites of either modification of Fe₂C, simultaneously leaving similar small, unreacted crystallites of iron. As there is an intermediate range of sizes between nonferromagnetic crystallites and those in which saturation magnetization can be attained (13), the apparent amounts of detectables and nondetectables are not necessarily exact and may also vary to some extent with the field strengths employed. Nevertheless, such discrepancies between the magnetically and chemically measured amounts of iron in used catalysts are of great interest because of the possibility of a relationship between them and catalytic activity. Therefore, a combination of magnetic, x-ray, and chemical analyses yields more complete information about used iron Fischer-Tropsch

catalysts than can be obtained by the use of any one or two of these methods alone.

CALCULATIONS

The following equations apply to a system of three ferromagnetic components, the total magnetic moment of which is measured at room temperature and at an elevated temperature, T, at which the magnetic moment of one of these phases is negligible. (Examples of such systems are Fe₂C–Hägg–Fe₃O₄–α-Fe, $T = 330°$ C., or Fe₃C–Fe₃O₄–α-Fe, $T = 300°$ C.) It is assumed that nonferromagnetic substances, such as promoters and supports, are simply diluents and do not affect the analysis. If reaction between them and one of the ferromagnetic phases takes place, proper allowance must be made for the possible ferromagnetic effect of the product formed or for the apparent disappearance of iron caused by its incorporation into a nonferromagnetic compound.

The magnetic moment, M, of a substance is the product of its specific magnetization, σ, and its mass, m:

$$M = \sigma m \qquad (1)$$

Experimentally, M is measured by the movement, D, of the substance in the magnetic field:

$$M = D/k \qquad (2)$$

where k is the sensitivity constant of the magnetic balance. If three ferromagnetic substances are present, then, as their magnetic moments are simply additive, from Equations 1 and 2,

$$\sigma_1 m_1 + \sigma_2 m_2 + \sigma_3 m_3 = D_1/k + D_2/k +$$
$$D_3/k = D(d_1 + d_2 + d_3)/k = D/k \qquad (3)$$

where $D = D_1 + D_2 + D_3$, $d_1 = D_1/D$, etc., are the fractions of the total movement due to the respective substances. Also from Equation 3,

$$d_1 = k\sigma_1 m_1/D \qquad (4A)$$

and

$$d_2 + d_3 = k(\sigma_2 m_2 + \sigma_3 m_3)/D =$$
$$k(m_2 + m_3)\left(\sigma_2 \frac{m_2}{m_2 + m_3} + \sigma_3 \frac{m_3}{m_2 + m_3}\right)/D \qquad (4B)$$

and at temperature T,

$$(d_2 + d_3)_T = k(m_2 + m_3)\left(\sigma_{2T} \frac{m_2}{m_2 + m_3} + \sigma_{3T} \frac{m_3}{m_2 + m_3}\right)/D \qquad (5A)$$

so that

$$(d_2 + d_3)/(d_2 + d_3)_T =$$
$$\left[\sigma_2 m_2/(m_2 + m_3) + \sigma_3 m_3/(m_2 + m_3)\right]/$$
$$\left[\sigma_{2T} m_2/(m_2 + m_3) + \sigma_{3T} m_3/(m_2 + m_3)\right] \qquad (5B)$$

whence $d_2 + d_3$ is known. As

$$d_1 = 1 - (d_2 + d_3) \qquad (6)$$

d_1 can be found, and likewise m_1 from (4 A), and m_2 and m_3 from (5 A) when $m_2/(m_2 + m_3)$ is known.

Letting the subscripts 1, 2, and 3 stand for Fe₂C, α-Fe, and Fe₃O₄, respectively, the magnetically measured mass of iron is

$$m_m = 0.9030\, m_1 + m_2 + 0.7236\, m_3 \qquad (7)$$

If the chemically determined mass of iron is m_c, the amount of magnetically nondetectable iron is $m_c - m_m$. Hence, the distribution of iron in the mixture is

$$\% \text{ iron in Fe}_2\text{C} = 90.30\, m_1/m_c \qquad (8A)$$

$$\% \text{ iron in } \alpha\text{-Fe} = 100\, m_2/m_c \qquad (8B)$$

$$\% \text{ iron in Fe}_3\text{O}_4 = 72.36\, m_3/m_c \qquad (8C)$$

$$\% \text{ nondetectable iron} = 100\, (m_c - m_m)/m_c \qquad (8D)$$

The following example illustrates the use of these equations: Using pure nickel, the torsion suspension of the magnetic balance was found to twist 22.5° per gram of nickel. As $\sigma_\infty = 56.2$ c.g.s./gram for nickel at room temperature,

$$k = 22.5°/56.2 \text{ c.g.s.} = 0.4004°/\text{c.g.s.}$$

A catalyst sample having a ratio of $\alpha\text{-Fe}:\text{Fe}_3\text{O}_4 = 76:24$—that is, $m_2/(m_2 + m_3) = 0.76$—as found by x-ray diffraction, showed a deflection at room temperature, $D = 8.20°$. At $T = 330°$ C., the deflection was $5.85°$; hence, $(d_2 + d_3)_T = 5.85/8.20 = 0.713$. Furthermore, it has been found that, under the conditions of measurement, the specific magnetizations of metallic iron and of magnetite at $330°$ C. are 96.5 and 76%, respectively, of their specific magnetization at room temperature. Hence, from Equation (5B), $d_2 + d_3 = 0.713 (218 \times 0.76 + 95.3 \times 0.24)/(210.4 \times 0.76 + 72.4 \times 0.24) = 0.758$.
From (5A), $0.758 = 0.4004 (m_2 + m_3)(218 \times 0.76 + 95.3 \times 0.24)/8.20$, and $m_2 + m_3 = 0.0824$ gram. Thus $m_2 = 0.76 \times 0.0824 = 0.0626$ gram and $m_3 = 0.24 \times 0.0824 = 0.0198$ gram. Also from Equation 6, $d_1 = 1 - 0.758 = 0.242$, and from (4A), $0.242 = 0.4004 \times 140 \times m_1/8.20$, $m_1 = 0.0354$ gram.
From Equation 7, $m_m = 0.9030 \times 0.0354 + 0.0626 + 0.7236 \times 0.0198 = 0.109$ gram of iron. The chemically determined mass of iron was 0.140 gram. Hence, from (8A to D),

$$\% \text{ iron in Fe}_2\text{C} = 90.30 \times 0.0354/0.140 = 22.9\%$$

$$\% \text{ iron in } \alpha\text{-Fe} = 100 \times 0.0626/0.140 = 44.8\%$$

$$\% \text{ iron in Fe}_3\text{O}_4 = 72.36 \times 0.0198/0.140 = 10.3\%$$

$$\% \text{ nondetectable iron} = 100(0.140 - 0.109)/0.140 = 22.0\%$$

The errors in this type of analysis are those of sampling and of the chemical, x-ray, and magnetic analyses. The chemical analysis determines the accuracy of m_c and the x-ray analysis that of $m_2/(m_2 + m_3)$ and $m_3/(m_2 + m_3)$ only. Sampling errors become apparent from the reproducibility of the shape of thermomagnetic curves obtained with two or more samples of the same preparation. The mean total error—that is, those errors just described plus errors in k, σ_T, D, $(d_2 + d_3)_T$, errors caused by

remanent magnetization, and errors caused by promoter-iron complexes (such as, magnesioferrite)—is estimated to be about ±8% of the calculated percentages. In the case of fluidized beds, the sampling error is probably much less, and the mean error may thus be reduced considerably. The largest error, however, is that caused by the use of a low field strength. As a result, the saturation values of the specific magnetizations are probably not attained, and the degree of unsaturation may be different for each phase. The error from this source is included in the magnetically nondetectable fraction, the composition of which is unknown. By the use of a more powerful magnet, this error should be considerably decreased.

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Titration of Nitric Acid in Solutions of Aluminum Nitrate

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Concentrations of nitric acid as low as 0.001 M may be determined in solutions of aluminum nitrate as high as 2 M by titration with standard base. Through the use of potassium oxalate to complex aluminum and prevent its hydrolysis as the titration proceeds, fairly good end points are obtained with the pH meter. The procedure is simple and gives consistent results under a variety of conditions.

THERE exists a real need for a rapid and accurate method of determining acid or base in solutions of hydrolyzable metal salts, such as those of aluminum, iron, and uranium. Samples of these salts almost invariably contain a small proportion of either basic salts or excess acid, depending on the conditions of preparation—for example, different samples of reagent grade aluminum nitrate may contain up to 0.02 equivalent of excess acid or base per mole of aluminum. Determination of this excess acid or base in solutions containing the metal ions is of paramount importance in quantitative studies of the hydrolysis or solvent extractability of these ions. The chemical literature contains many questionable data on the hydrolysis of heavy metal ions, simply because there are no methods sufficiently precise for analysis of the heavy metal salts used to obtain these data.

This paper is restricted to the analysis of solutions containing aluminum salts only. However, fragmentary data exist which indicate that a similar approach is applicable to solutions of many other metal ions which form insoluble or complex oxalates.

If a solution of aluminum nitrate contains a small proportion of nitric acid, the acid may be titrated with standard base neither easily nor accurately. The aluminum hydrolyzes appreciably at the equivalence point for nitric acid, and the inflection in the titration curve is almost imperceptible. Figure 1 contains a typical titration curve. The end point is poor, and the error may be large.

An article by Eder (3) contains a study of many methods proposed earlier for the titration of acid in solutions of aluminum sulfate, using standard base with indicators to establish the end
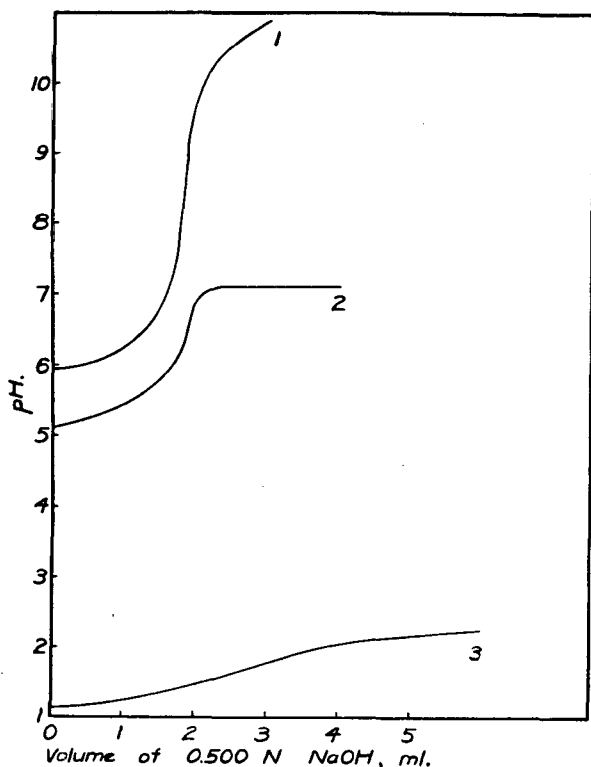
Figure 1. Titration of Nitric Acid in Aluminum Nitrate Solutions

1. 25-ml. sample of Al(NO₃)₃-HNO₃ stock solution titrated in volume of 100 ml. at 10° to 15° C. after adding 30 grams of KF.2H₂O. No blank correction made
2. As in 1, except 60 grams of K₂C₂O₄.H₂O added instead of KF
3. As in 1, except 50-ml. sample used, and no KF

point. The following procedures are investigated and rejected as unsuitable:

Direct titration.

Methods involving removal of aluminum (as ammonium alum from alcoholic solution or as aluminum ferrocyanide) and filtration, after which the acid in the filtrate is titrated. These procedures are subject to large, systematic errors.

Titration of the acid after binding aluminum into a soluble, nonhydrolyzable, complex ion, using sodium oxalate. This is rejected because of critical dependence of the end point on the aluminum and oxalate concentrations.

Gravimetric determination of aluminum as the oxide and sulfate as barium sulfate, wherewith the free acid may be found by difference. Not only is the precision of such difference procedures poor when the proportion of acid to aluminum is low, but work in this laboratory shows them highly susceptible to systematic error.

The only method found satisfactory by Eder is that proposed by Craig (2) and modified by Scott (5), in which aluminum is precipitated as potassium aluminum fluoride with potassium fluoride, and the excess acid is titrated without removal of the precipitate, using phenolphthalein as an indicator. Many workers have employed this method with satisfactory results (1, 3). A typical titration curve is given in Figure 1. It may be seen that a very sharp end point is obtained. However, there are many disadvantages to the use of potassium fluoride. As a substitute for potassium fluoride, potassium oxalate complexes aluminum sufficiently to give a fairly good end point (see Figure 1), but does not possess the disadvantages. This is shown in the work which follows, and conditions are selected for the use of potassium oxalate to allow direct titration with standard base of nitric acid in aluminum nitrate solutions.

There exists a conductometric method for the determination

of acid in aluminum sulfate solutions, but it fails when the proportion of acid to aluminum becomes only moderately low (4).

SELECTION OF CONDITIONS

Search for a Complexing Agent. Several easily available reagents were compared to potassium fluoride for ability to complex aluminum ion.

The following reagent grade or c.p. chemicals were used: potassium sodium tartrate, sodium citrate, potassium thiocyanate, potassium acetate, potassium ferrocyanide, potassium ferricyanide, sodium formate, and potassium, sodium, and ammonium oxalates. Only the oxalates exhibited complexing ability approaching that of fluoride. In addition to poor complexing ability, many of the substances contained acidic or basic impurities. Potassium oxalate was chosen in preference to the other oxalates because of its greater solubility. This is an important consideration. In attempting to remain within the solubility limits of sodium oxalate, Eder (3) found the free acid end point to be too critically dependent on conditions and therefore rejected this reagent. The greater solubility of potassium oxalate avoids this difficulty.

Reagents. A stock solution of aluminum nitrate was prepared by dissolving Mallinckrodt reagent grade aluminum nitrate in water and adding excess concentrated nitric acid to 0.06 M, because there were basic salts present. The solution was boiled to drive off nitrous fumes and carbon dioxide. After filtering and cooling, the aluminum content was determined in two ways: (1) Weighed samples of the solution were evaporated, ignited to aluminum oxide, and weighed. (2) Weighed samples were dissolved in an excess of concentrated, carbonate-free sodium hydroxide, and then titrated with standard acid according to Bushey (1). Both procedures checked within a few tenths of 1% to give an aluminum nitrate concentration of 2.23 M (29° C.).

Determination of the excess nitric acid in the aluminum nitrate stock solution by direct titration with 0.500 N sodium hydroxide was attempted, but the result was uncertain. Titration of 50-ml. samples of the stock solution in 50 ml. of water at different temperatures gave for the nitric acid concentration: 0.020 M at 30° C., 0.029 M at 12° C., and 0.035 M at 0° C. The end point became sharper as the temperature decreased. At 0° C., the upper part of the titration curve was flatter and more horizontal than for the curves obtained at the higher temperatures. This was interpreted to mean that the low temperature value was probably most correct. The volume of the system had no appreciable effect on the end point. Four titrations at 0° C., at volumes from 50 to 500 ml., gave 0.035 M for the nitric acid concentration of the aluminum nitrate stock solution. The average deviation was 0.003 M.

Standard nitric acid and sodium hydroxide solutions, each at 0.500 N, were prepared from Acculute solutions (E. H. Sargent and Company). The nitric acid was checked against primary standard sodium carbonate. The two standard solutions were also checked against each other, using both phenolphthalein and methyl orange indicators. The base contained 0.002 M carbonate.

Mallinckrodt analyzed reagent grade potassium oxalate monohydrate was used without pretreatment of any sort.

Effect of Temperature on End Point. Twenty-five-milliliter portions of the aluminum nitrate-nitric acid stock solution were mixed with boiled, carbonate-free water to give a volume of 100 to 125 ml. at the end point. These solutions were cooled prior to titration by immersion in an ice bath, and an excess (about 60 grams) of solid potassium oxalate was added to each. The cold solutions were then titrated with the standard base. No attempt was made to thermostat the solutions, which warmed up as much as 5° C. in the course of titration. This warming caused a slight drift of pH, which did not interfere with establishment of the end point. The blank, determined by titrating 60 grams of potassium oxalate in 100 ml. of water to the point of maximum inflection of the titration curve, amounted to 0.08 ml. of 0.500 N sodium hydroxide. Titrations above room temperature were also performed. A second series of runs was carried out similarly, using only 10-ml. samples of stock solution.

In Figure 2A the volume of standard base required for titration of the nitric acid in the sample is plotted as a function of temperature at the end point. It may be seen that consistent

results are obtainable if the titrations are carried out below 10° to 15° C. Here, the average deviation is about 0.05 ml. of 0.500 N standard base for the 25-ml. sample and less for the 10-ml. sample.

The end points are much less sharp at higher temperatures. Below 10° to 15° C., the upper parts of the titration curves are flat and horizontal (see Figure 1), indicating that the aluminum oxalate complex is adequately undissociated at the end point, and that the end point is probably close to the nitric acid equivalence point. This is apparently not true above 10° to 15° C., at least for the higher aluminum nitrate concentrations.

Effect of Volume on End Point. Twenty-five–milliliter portions of the aluminum nitrate–nitric acid stock solution were diluted with different volumes of carbonate-free water. After being cooled to 5° to 10° C. in an ice bath and saturated with solid potassium oxalate, each portion was titrated with standard base. The blank was determined for each titration by titrating an equal quantity of potassium oxalate in the same volume in the absence of aluminum nitrate. The blanks varied from 0.03 ml. of 0.500 N base at the lowest volume to 0.32 ml. at the highest volume.

In Figure 2B, the volume of standard base required for titration of the nitric acid in the sample is plotted as a function of the volume of the titrated solution at the end point. It may be seen that the volume of standard base required for the 25-ml. sample is independent of the titration volume over a considerable range (50 to 300 ml.). The average deviation in this range is about 0.04 ml. of 0.500 N base. As the volume increases, the sharpness of the end point decreases and the size of the blank increases. It is therefore best to work at low volume (ca. 100 ml.).

Effect of Potassium Oxalate Concentration on End Point. Twenty-five–milliliter portions of the stock solution were titrated at 5° to 15° C. in the presence of different quantities of potassium oxalate. End-point volumes were 100 to 125 ml. The blank was determined for each titration, and was proportional to the amount of oxalate used. In this series of runs, the blanks ran from 0.01 to 0.10 ml. of 0.500 N base. In like manner, a second series of runs was performed on 5-ml. portions of the stock solution.

In Figure 2C, there is plotted the volume of standard base required for the titration of the nitric acid in the sample as a function of the amount of potassium oxalate monohydrate added. On the curves are indicated the weights of potassium oxalate roughly equivalent to the aluminum present in each of the two samples used. (These amounts are easily determined experimentally by observing the pH of the solution as solid potassium oxalate is added; the pH rises abruptly in the region where the potassium oxalate is equivalent to the aluminum present.) There are also indicated the amounts of potassium oxalate required to saturate the solution. At low concentrations of aluminum, saturation with respect to potassium oxalate is indicated by the presence of crystals in the system. At high concentrations of aluminum, this is not a reliable criterion, for granular potassium aluminum oxalate precipitates before the solution is saturated with respect to potassium oxalate. In such cases, evidence of saturation may be obtained easily by adding potassium oxalate until a 5- to 10-gram portion produces only a small change in pH of the solution.

Inspection of Figure 2C shows that the volume of base required for titration of the sample is independent of the amount of oxalate used, providing the oxalate is more than equivalent to the aluminum present. If this condition is met, the average deviation from constancy is 0.05 ml. of standard base or less, even though the oxalate may be manyfold in excess of that required to complex the aluminum. The sharpness of the end point decreases as the amount of oxalate used decreases, becoming poor for amounts of oxalate less than that required to complex the aluminum. For these reasons, it is best in practice to saturate the solutions with potassium oxalate before titration.
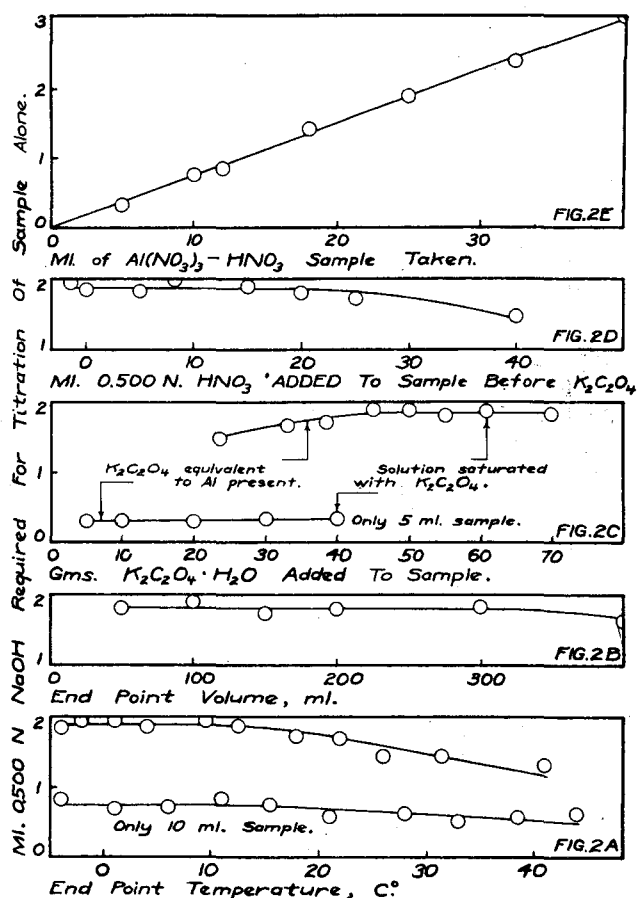

Figure 2. Effect of Conditions on End Point in Titration of Nitric Acid in Aluminum Nitrate Solutions

Standard conditions for all titrations as follows, except where noted differently on graphs: Volume at end point, 100 to 125 ml. Volume of Al(NO₃)₃–HNO₃ stock solution used for sample, 25.00 ml. Temperature, 5° to 15° C. Potassium oxalate, 50 to 70 grams of monohydrate

Effect of Excess Acid on End Point. In order to ascertain that acid or base was not incorporated into the aluminum oxalate complex, different volumes of standard nitric acid were added to 25-ml. portions of the stock solution. Each portion was diluted with sufficient water to give a volume of 100 to 125 ml. at the end point, cooled to 5° to 10° C., saturated with potassium oxalate, and titrated with standard base. The blank in all runs was 0.10 ml. of 0.500 N sodium hydroxide.

In Figure 2D, the volume of standard base required for titration of the sample alone—i.e., total volume of base used in titration minus volume of base equivalent to the standard acid added—is plotted against the standard acid added to the sample before the potassium oxalate. Within a precision of 0.5 ml., the volume of standard base required for titration of the sample alone is independent of the amount of standard acid present, providing this amount is less than 20 ml. This indicates no incorporation of acid or base into the potassium aluminum oxalate precipitate in this range. Above this limit, there is apparently a slight coprecipitation of acid. When the acid in samples is this high, it should be partially neutralized with a measured volume of standard base before adding oxalate, after the method of Eder (3).

There is in Figure 2D a point signifying that a negative amount of nitric acid was added to the sample before addition of potassium oxalate. Actually, a small quantity of 0.500 N sodium hydroxide was added in this determination. This quantity of base was less than equivalent to the acid in the sample, so the

resulting solution still required standard base for titration, and the end point was approached from the acid side.

Data not presented show that at concentrations of aluminum low enough to prevent precipitation of the potassium aluminum oxalate (10 ml. of stock solution or less), there is no inclusion of acid, and consistency is obtained for all acid concentrations.

It was not convenient to study samples that contained an excess of base and required standard acid for titration. The approach to the end point from the basic side required a much longer time and was less precise than the approach from the acid side. After each increment of standard solution was added, the time required for the pH meter to reach equilibrium was only 0.5 to 1 minute in the latter case as compared to 5 to 10 minutes in the former.

Potassium aluminum oxalate should never be thrown down prior to titration from a solution which contains excess base, because the tendency for coprecipitation of the base is pronounced. Furthermore, when acid is added to such a system, the coprecipitated base is liberated very slowly. For this reason, when samples contain excess base, a measured excess of standard acid should be added before the potassium oxalate. The end point may then be approached from the acid side by titration with standard base, and coprecipitation of hydroxyl ion is avoided.

Effect of Aluminum Nitrate Concentration on End Point. To determine finally the effect of aluminum nitrate concentration on the end point, different sized samples of the stock solution were diluted with sufficient water to give end-point volumes of 100 to 125 ml. After being cooled to 5° to 10° C., the solutions were saturated with potassium oxalate and titrated with standard base. The blank determinations varied from 0.10 to 0.15 ml. of 0.500 N base.

In Figure $2E$ is plotted the volume of standard base required for titration of the nitric acid in the sample as a function of sample size. Inasmuch as the same stock solution is used in all titrations, the nitric acid is proportional to the sample size, and the plot of Figure $2E$ should be a straight line. Inspection of the graph shows an average scattering for all the determinations corresponding to only 0.03 ml. of base from the best straight line.

In the determinations involving 18 ml. or more of the stock solution, a granular precipitate appears slowly, even before the solution becomes saturated with potassium oxalate. This is probably a potassium aluminum oxalate compound. Figure $2E$ indicates that no appreciable amount of acid or base is coprecipitated with this compound, because there is no deviation from linearity, even for samples containing as much as 0.09 mole of aluminum. However, because Figures $2A$ to $2D$ obtain for 0.05 mole or less, it is necessary to restrict the sample size to this in application of the method, even though Figure $2E$ indicates the possibility of using larger samples without increasing the error.

Precision and Accuracy. The average value of the nitric acid concentration of the aluminum nitrate stock solutions may be calculated as 0.037 M with an average deviation less than 0.001 M from the many determinations summarized in Figure 2.

This value agrees reasonably with the value of 0.035 M found by direct titration at low temperature. In addition, the oxalate procedure is consistent under a wide variety of conditions. The shape of the titration curve is such that the end point and equivalence points for nitric acid are probably close together. It may therefore be concluded that systematic error is probably absent, and that the error of the method is of the same order of magnitude as the above average deviation, which corresponds to 0.05 ml. of 0.500 N sodium hydroxide for a 25-ml. sample, or to 2×10^{-5} equivalent of acid in the sample.

It seems possible to determine the nitric acid concentration with an error about 0.001 M in a sample containing over 2 M aluminum nitrate. This error is reduced as the proportion of free acid to aluminum nitrate increases, eventually approaching that of a strong acid–strong base titration.

Other Aluminum Salts. Titrations were performed for free acid or base on several reagent grade aluminum salts. Results as consistent as those for aluminum nitrate were obtained under a variety of conditions. Aluminum chloride hexahydrate contained 0.008 equivalent of free base per mole of aluminum. Potassium alum, ammonium alum, and hydrated aluminum sulfate contained 0.002, 0.003, and 0.007 equivalent of free acid per mole of aluminum, respectively. Contrary to the supposition of Eder (3), the alums are not strictly neutral.

Interferences. Any anion which precipitates aluminum in such a form that acid or base is easily coprecipitated, or which forms an acid so weak that it is not neutralized at pH 6 to 7, might cause error. Any cation which hydrolyzes strongly or precipitates as a hydroxide at a pH less than 6 to 7 might cause error unless it is strongly bound or precipitated by oxalate.

A very few substances were tested for interference by adding them to 25-ml. portions of the stock solution used in the preceding experiments. Titrations were carried out as described in the section on procedure. Reagent grade or c.p. chemicals were used. Phosphate and acetate were added as acids, fluoride as potassium fluoride, and iron and lead as the nitrates. Results are shown in Table I.

Of the impurities studied, only phosphate interfered, undoubtedly because of incomplete neutralization of the third hydrogen of phosphoric acid at the end point. Phosphate also decreased the sharpness of the end point. Because the precision of all the determinations was about 0.001 equivalent of nitric acid per mole of aluminum, it was concluded that fluoride, acetate, ferric, and plumbous ions did not interfere under conditions of the experiment.

If a sample contains substances other than those studied here, possible interference should be determined in the manner outlined above before using the method. There are too many factors involved to predict safely whether or not a particular substance would cause error in the titration.

Inadequacy of Potassium Fluoride as a Complexing Agent. The advantage of a sharp end point when potassium fluoride is used is offset by many disadvantages. The following statements are supported by data that are not reproduced in this report because of limited space.

Table I. Interferences in Titration of Nitric Acid in Solutions of Aluminum Nitrate

Impurity Added	Mole of Impurity per Mole of Al	Equiv. of HNO₃ per Mole of Al		
		Present	Found	Error
Phosphate	0.007	0.037	0.030	−0.007
Fluoride	0.20	0.015	0.015	0.000
Acetate	0.010	0.025	0.024	−0.001
Fe(III)	0.015	0.015	0.015	0.000
Pb(II)	0.010	0.015	0.015	0.000

The best grades of potassium fluoride are very impure. The principal impurities are carbonate and fluosilicate, both of which interfere and cause a blank corresponding to 0.4 to 0.6 ml. of 0.5 N base in a typical titration. In contrast, the blank for potassium oxalate is usually 0.10 to 0.15 ml. Unless the potassium fluoride is recrystallized, the end-point sharpness is considerably poorer than that indicated in Figure 1; and the inflected portion of the curve is not smooth but wavy, owing to the presence of more than one impurity. This causes error and confusion in locating the end point.

Data analogous to those in Figure 2 were obtained for recrystallized potassium fluoride. The volume of standard base required for titration of a given sample of stock solution showed a greater variation with all conditions studied except temperature, com-

pared to potassium oxalate. The coprecipitation of acid and base is particularly bad. The error due to such coprecipitation may be greatly reduced by careful partial neutralization (*3*) of the acid prior to adding the potassium fluoride. This is troublesome, however, because it requires an approximate knowledge of sample composition.

In short, the behavior of potassium fluoride seems such that no simple set of conditions similar to those for use of potassium oxalate may be formulated to give consistent results for the analysis. This is so even if a prior knowledge of sample composition is assumed. Inconsistencies corresponding to 0.5 to 1.0 ml. of 0.5 N base are observed in the analysis of solutions containing a high ratio of aluminum salts to free acid. This is roughly the precision noted by Eder (*3*), who has investigated the use of fluoride more thoroughly than any other worker known to the authors.

PROCEDURE

Reagents. Standard 0.500 N nitric acid. Standard 0.500 N sodium hydroxide, carbonate-free. Potassium oxalate, reagent grade.

Apparatus. pH meter, with calomel and glass electrodes. Mechanical stirrer.

Procedure. A sample containing 0.05 mole (1.5 grams) of aluminum or less and 0.01 equivalent of acid—i.e., 0.6 gram of nitric acid—or less should be used. [If the aluminum content of the sample is much greater than 0.05 mole (1.5 grams), so much precipitate forms that mixing becomes difficult. This is easily noticeable, and the volume of the solution may be increased by adding more water and potassium oxalate, or a smaller sample may be chosen for analysis. If the sample contains more than 0.01 equivalent of acid, it should be partially neutralized with a measured volume of standard base to a value less than this before adding potassium oxalate. If the aluminum content is less than 0.02 mole (0.5 gram), however, this partial neutralization is unnecessary.]

Boiled, carbonate-free water is added to the sample in a 250-ml. beaker to give an end point volume around 100 ml. The beaker and contents are cooled to 10° C. or less by immersion in an ice bath for a few minutes. (It is not necessary to cool further than this. Potassium oxalate, when added, dissolves endothermically, cooling the system several degrees more.)

The beaker is placed on the titration stand, and solid potassium oxalate is added in 15- to 20-gram portions with mechanical stirring until the solution is saturated. [When an amount of potassium oxalate equivalent to the aluminum is added, there is a sudden rise of pH. An excess of oxalate is present when addition of a small portion does not cause much further change in pH. A large excess of oxalate does no harm, except to increase the blank and interfere with stirring. Fifty to 70 grams of potassium oxalate monohydrate are required per determination, the exact amount depending on the volume, the quantity of aluminum present, and the temperature. It is convenient to add the solid from a small measure (ca. 20 grams) adding an integral number of these for a determination.]

The solution is then titrated with 0.500 N sodium hydroxide, using the pH meter to establish the end point. [In the region of the end point, the standard base is added in 4-drop (or 0.2-ml.) increments, and the pH is observed and plotted against volume of standard base as the titration proceeds. A rough plot, drawn over a 1-ml. interval in the region of the end point, serves to establish the end point with a precision of 0.05 to 0.10 ml. of 0.500 N sodium hydroxide. The end point is taken as the midpoint of that portion of the curve with the steepest slope. About a minute is required for the pH meter to reach equilibrium after each addition of standard base. Before the end point is reached, the drift during this minute is toward higher pH; after the end point, it is toward lower pH. This behavior affords a useful and reliable indication of whether the end point has been passed. After a minute, the pH is read, even though there may be a residual drift. This procedure allows ample time for plotting as the titration proceeds. Under conditions of this procedure, the end point occurs at pH 6 to 7. If the conditions vary radically from these, the end point pH may be different. However, such variations cause no appreciable error, provided they are held within the ranges dictated by Figure 2. There is no need to thermostat the titration vessel. The starting temperature (ca. 5° C.) is low enough so that the solution does not warm above the desired limit of 10° to 15° C. in the course of a normal titration. The warming of the solution produces a negligible drift in pH which causes no trouble in

locating the end point. Because only pH changes are needed to determine the end point, the temperature compensator on the pH meter is simply left fixed at room temperature as the titration proceeds, even though the solution temperature may change greatly.]

A blank determination should be made on the reagents. [A good way of determining the blank is as follows: After the sample containing aluminum has been titrated, and the end point found, a measured amount (ca. 1 ml.) of standard acid is added to bring the system back to the acid side of the end point; 100 ml. of water and an amount of potassium oxalate equal to that used in the determination are added, and the solution is retitrated with standard base to the end point. The blank is then found by difference, and usually amounts to 0.10 to 0.15 ml. of 0.500 N base. It need not be determined on every sample, for it is independent of aluminum concentration, and proportional to the amount of potassium oxalate used. For precise work, however, it should be determined for each batch of potassium oxalate used.]

This procedure applies only to aluminum nitrate solutions containing an excess of acid. (If the aluminum nitrate contains an excess of base—i.e., basic salts—a measured excess of standard acid should be added to the sample. The excess may then be determined by addition of oxalate and titration with standard base according to the above procedure.)

ANALYSIS OF KNOWN SAMPLES

In order to test the accuracy of the procedure under routine conditions, 100-ml. samples were prepared by one person by mixing known volumes of the aluminum nitrate–nitric acid stock solution used in the previous studies together with standard sodium hydroxide or nitric acid and making up to volume in a volumetric flask. A second person analyzed these samples without prior knowledge of their compositions. For each sample, a 25-ml. portion was first saturated with potassium oxalate and the pH measured to determine whether the sample contained excess acid or base. Then a single 50-ml. portion was analyzed as described in the section on procedure.

The results given in Table II show it possible to determine routinely the excess acid or base normality with an average error of 0.001 in solutions containing up to 2 M aluminum nitrate.

Table II. Titration of Excess Acid (or Base) in Aluminum Nitrate[a]

Sample No.	Aluminum Molarity	Nitric Acid Molarity of Sample		
		Correct	Found	Error
1	1.12	0.019	0.018	−0.001
2	0.47	0.017	0.016	−0.001
3	0.57	0.024	0.025	+0.001
4	0.85	0.063	0.064	+0.001
5	1.02	0.111	0.111	0.000
6	0.65	0.010	0.009	−0.001
7	0.60	0.040	0.039	−0.001
8	1.08	0.090	0.091	+0.001
9	0.72	0.071	0.071	0.000
10[b]	0.63	−0.004	−0.006	−0.002
11[b]	0.86	−0.026	−0.026	0.000
12	1.55	0.093	0.094	+0.001
13	2.02	0.121	0.123	+0.002

[a] 50.00 ml. of each sample analyzed as described in section on procedure.
[b] Samples contained excess base instead of acid.

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Useful Relations for Countercurrent Distribution Computations

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Expressions have been developed for the prediction and evaluation of results from countercurrent distribution experiments. Included is a method for determining the number of transfers required for a given "degree of separation" and pair of partition coefficients. An approximate relation is proposed for determining the number of transfers required to resolve composite peaks.

RECENTLY Craig (*1, 2*) has introduced several ingenious devices for conducting a series of liquid-liquid distributions between immiscible solvent pairs. The use of these new multiple distribution techniques, which Craig has termed "countercurrent distribution," is becoming increasingly popular as a means of separating, purifying, and identifying compounds. It has also been used as an analytical means of determining purity, inasmuch as many substances have essentially linear partition isotherms in a variety of solvent combinations and when this is true it is possible to estimate accurately the amount to be expected in a certain tube for a given partition coefficient.

The calculation of theoretical distribution curves has been given an excellent treatment by Williamson and Craig (*7*). Calculations of the distribution curves for experiments involving a large number of transfers by the methods suggested are still somewhat time-consuming, however, and it requires considerable familiarity with them to make even a rough approximation as to whether the method would be applicable to certain problems. It has been the author's experience that the possible utility of the method is grasped more readily when one has available an equation relating the known partition coefficients and desired degree of separation to the number of transfers required. With a relation of this type it is at the same time possible to gain an idea of the relative efficiency of the Craig method as compared with continuous multiple extraction processes exemplified by paper and partition chromatography and countercurrent extraction. The manner in which such a comparison could be made is contained in the work of Mayer and Tompkins (*6*) on the theory of exchange resin column separations. Their treatment of the distribution of substances on an ion exchange column can be shown to be essentially mathematically equivalent to Williamson and Craig's (*7*) treatment of distribution of substances in a Craig apparatus. Mayer and Tompkins also give a graphical method for the determination of degree of separation which could be applied to countercurrent distributions. The present treatment is particularly suitable for distributions within a Craig apparatus. However, its application to column separations is also possible within the limitations already discussed by Mayer and Tompkins.

In addition to deriving equations of the above-mentioned type, a number of other useful approximate relations are given to assist in rapid computations. Included are an accurate method for determining the areas under the tails of distribution curves by means of probability function tables, and a simple approximate method for determining how many transfers are required to resolve the peaks of distribution curves when the partition coefficients are known or can be estimated. The derived equations will apply to those distributions obtained by analyzing both phases which Craig (*2*) has termed the "fundamental" operation. A complete discussion of the various operations and types of distribution apparatus is given by Craig and Post (*2*).

EQUATIONS FOR INTERSECTION POINTS AND MAXIMA

Attention is first centered on obtaining expressions for intersection points and maxima of the distribution curves of a system of two components, *a* and *b*, where the fractional amounts of *a* and *b* in the mixture are expressed by F_a and F_b, respectively.

Consider an experiment in which the upper phase migrates while the lower phase remains stationary. The tubes are numbered 0, 1, 2, 3, . . ., *r*. The lower layers of each tube are filled, the sample is placed in tube 0, equilibration of the substance between layers is effected, and the top layer of tube 0 is transferred to tube 1. The same process is repeated *n* times, each time all top layers being transferred to the next highest tube in number. The binomial expansion, Equation 1, then gives the fractional amount of the mixture as represented by substance *a*, $T_{n,r}^a$ to be found in tube *r* after *n* transfers when the partition coefficient is K_a. A similar relation holds for substance *b*. The fractional amount of the mixture in tube *r* after *n* transfers would be the sum

$$T_{n,r}^a = \frac{n!}{(n-r)!\,r!}\left(\frac{1}{1+K_a}\right)^n K_a^r F_a \tag{1}$$

of the fractions represented by substances *a* and *b*. The intersection point of the distribution curves for substances *a* and *b* is found by equating $T_{n,r}^a$ and $T_{n,r}^b$ and is shown in Equation 2. The quantity $\log F_a/F_b$ is readily seen to be negligibly small

$$r_i = n\left[\frac{\log\left(\frac{1+K_b}{1+K_a}\right)}{\log K_b/K_a}\right] - \frac{\log F_b/F_a}{\log K_b/K_a} \tag{2}$$

except when F_a and F_b are considerably different. In deriving approximate relations for the intersection point, therefore, we shall neglect the effect of this term.

Williamson and Craig (*7*) proposed the use of the normal probability function as a means of approximating the amount of material in a given tube when the number of transfers is large, and in line with their use of this function Equation 3 gives an approximate expression for $T_{n,r}^a$. The quantity r_{ma} in Equation 3 is the tube at which the maximum amount of substance *a* is located after *n* transfers. The intersection point of the distribution curves for two substances, *a* and *b*, would then be given by Equation 4.

$$T_{n,r}^a = \frac{F_a}{\sqrt{2\pi n\dfrac{K_a}{(1+K_a)^2}}}\, e^{-\dfrac{(r-r_{ma})^2}{2n\dfrac{K_a}{(1+K_a)^2}}} \tag{3}$$

$$r_i = \frac{nK_aK_b - \sqrt{n^2 K_a K_b - 4\beta K_a K_b + 4\beta}}{K_a K_b - 1} \tag{4}$$

where $\beta = 2.303 \log \dfrac{F_b\sqrt{2\pi n K_a/(1+K_a)^2}}{F_a\sqrt{2\pi n K_b/(1+K_b)^2}}$

It can be demonstrated that term β in Equation 4 is small in most cases and Equation 5, in which this term has been neglected, will serve as a good approximation for practical application—i.e., *n* is greater than 20, K's are between 0.1 and 10, and F_a and F_b are not greatly different. It is interesting to note that the first term on the right-hand side of Equation 2 is approximately equal over

$$r_i = n\left(\frac{K_a K_b - \sqrt{K_a K_b}}{K_a K_b - 1}\right) \tag{5}$$

the complete range of values of K_a and K_b to the right-hand side of Equation 5.

Another approximate relation for the intersection point between the curves of two substances a and b is shown in Equation 6. This equation is deduced by assuming the intersection point is halfway between the maxima of the two distribution curves where the position of the maxima are located by Equation 7, discussed in the following paragraph. This formula is particularly good when the partition coefficients (and F_a and F_b) are not greatly different.

$$r_i = \frac{n}{2}\left(\frac{K_a}{1 + K_a} + \frac{K_b}{1 + K_b}\right) \quad (6)$$

It will now be in line with our ultimate objective to obtain an expression for r_{ma}. Craig (1) proposed the approximate relation (Equation 7) from empirical considerations.

$$r_{ma} = n\left(\frac{K_a}{1 + K_a}\right) \quad (7)$$

The derivation of this equation is given here in order to acquaint one better with the degree of approximation involved. It is as follows: Differentiate Equation 1 with respect to n after using Stirling's approximation. Set the derivative equal to zero and the expression (Equation 8) is obtained after simplification. When n is large with respect to r, the first and third terms cancel, which leads to Equation 7, where r equals r_{ma} in this case.

$$\frac{n + \frac{1}{2}}{n} + \ln\frac{n}{n - r} - \frac{n - r + \frac{1}{2}}{n - r} + \ln\frac{1}{K + 1} = 0 \quad (8)$$

USE OF PROBABILITY FUNCTION TABLES

As previously stated, Equation 3 is the normal probability distribution curve of unit area in which the standard deviation σ is assigned the value $\sqrt{nK}/(1 + K)$. The area (A_t^a) under the tail of the distribution curve for substance a (see shaded area in Figure 1) can be defined as

$$\int_{-\infty}^{-t_0} \frac{1}{\sqrt{2\pi}}\, e^{-t^2/2}\, dt$$

FIG. 1 24 TRANSFER DISTRIBUTION
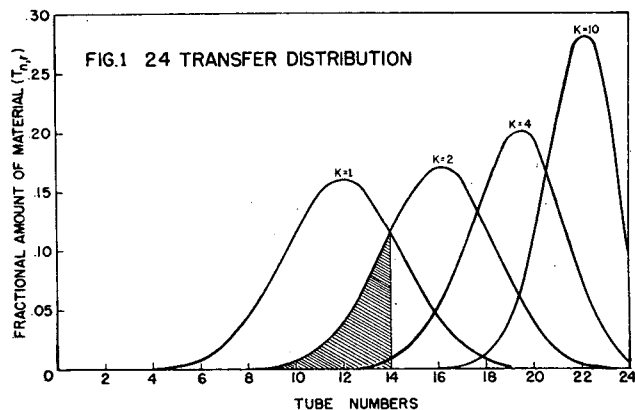
where t is equal to $(r - r_{ma})$ divided by σ_a. The limit of integration is designated as t_0 and variable of integration as t. This distinction, although mathematically precise, is not always made. However, it is particularly desirable in the present treatment.

Accordingly, multiplication of this area by the fraction, F_a, of a substance a gives the corresponding fractional amount of the total mixture as represented by substance a. The above integral is not commonly found in tables; therefore Equations 9 and 10 are given where the integral in Equation 9 can be found in Lange's handbook (4) and the integral in Equation 10 is tabulated in Hodgman's handbook (3). It will be useful to remember that for values of t equal to 1, 2, and 3, the corresponding areas under the tail are $A_1 = 0.159$, $A_2 = 0.0227$, and $A_3 = 0.0013$.

$$A_t = 1.0 - \int_{-\infty}^{t_0} \frac{1}{\sqrt{2\pi}}\, e^{-t^2/2}\, dt \quad (9)$$

Table I. Comparison of Areas under Tails of Distribution Curves as Calculated by Equations 10 with 11 and 14 and Binomial Expansion

K	n	$r_i - r_m$	Area[a] (Eq. 11)	Area[a] (Eq. 14)	Area (B.E.)[b]
1	24	6	0.012	0.007	0.0112
1	24	5	0.032	0.021	0.0318
1	24	4	0.076	0.051	0.0757
1	24	3	0.154	0.110	0.1536
1	24	2	0.271	0.207	0.2705
2	24	5	0.026	0.015	0.0191
2	24	4	0.064	0.042	0.0586
2	24	3	0.140	0.097	0.1375
2	24	2	0.258	0.193	0.2624
4	24	3	0.101	0.063	0.1145
10	24	2	0.144	0.078	0.1016
1	48	8	0.015	0.010	0.0139
1	48	4	0.155	0.124	0.1552

[a] Areas calculated on basis of unit amounts of each substance.
[b] Areas in last column are under those tails which point toward higher tube numbers. When partition coefficients differ greatly from 1, this specification is particularly necessary.

$$A_t = \frac{1}{2} - \int^{t_0} \frac{1}{\sqrt{2\pi}}\, e^{-t^2/2}\, dt \quad (10)$$

For a reasonably accurate application of the equations for a continuous distribution to a discrete distribution as actually encountered, the value of $(r_i - r_{ma})$ used in calculating t_0 can be replaced by $(r_i - r_{ma} - 0.5)$. This arises from the nature of the discrete and continuous curves. This adjustment is particularly necessary when the number of transfers is comparatively small.

The use of Equations 10 and 11 in calculating areas under the tails of distribution curves is compared with results from the binomial expansion as shown in Table I.

$$\frac{r_i - r_{ma} - 0.5}{\sigma} = t_0 \quad (11)$$

ESTIMATION OF THE AMOUNT OF SEPARATION

With a means for estimating areas under the distribution curves, it is now possible to formulate a method for determining the degree of separation to be expected for two substances of partition coefficients K_a and K_b after a given number of transfers. As a measure of the amount of separation we use the area under the tail of the distribution curve of the substance of lowest partition coefficient from the point where the two curves intersect. The t value corresponding to this area will be called the degree of separation. Martin and Synge (5) have used t values in a similar sense in their theory of partition chromatography. Mayer and Tompkins (6) have defined and used t in an analogous manner in their theoretical analysis of exchange resin column separations.

The use of Equations 11, 5, and 7 leads to the following equations, where $K_b > K_a$.

$$nf - 0.5 = \sqrt{n}\left(\frac{\sqrt{K_a}}{1 + K_a}\right) t_0 \quad (12)$$

where

$$= \frac{K_a K_b - \sqrt{K_a K_b}}{K_a K_b - 1} - \frac{K_a}{K_a + 1}$$

$$t_0 = \left(\frac{1 + K_a}{\sqrt{K_a}}\right)\left(\frac{nf - 0.5}{\sqrt{n}}\right) \quad (13)$$

When the factor 0.5 is omitted from Equation 11 we get Equation 14, which gives a rough estimation of the area which improves as n increases.

$$\frac{r_i - r_{ma}}{\sigma} = t_0 \quad (14)$$

Using Equations 12, 5, and 7, Equation 14 can be put in a more convenient form, as shown in Equation 15.

$$n = St_0^2 \quad (15)$$

where $\qquad S = \left[\dfrac{K_a K_b - 1}{(K_b + 1)\sqrt{K_a} - (K_a + 1)\sqrt{K_b}} \right]^2.$

We now have two expressions for estimating the degree of separation for given partition coefficients and a given number of transfers. Equation 13 is necessary where one deals with a limited number of transfers and intermediate degrees of separation and Equation 15 is desirable for large numbers of transfers and high values of t_0.

Comparable agreement to that previously shown in Table I for calculated areas under tails of distribution curves can be expected using Equation 12, providing we round off the $(r_i - r_{ma})$ values to the nearest whole numbers, as must necessarily be the case in actual operation. Although Equation 15 gives a rough estimate as compared with Equation 12, its convenient form makes it useful as a quick means for determining the fractionating power of the method once two partition coefficients are known. Therefore, in Figure 2 the separation factor is plotted against the higher partition coefficient. If it is desired to know the number of transfers required for practically complete separation, multiplication by 3^2 gives the answer immediately. Different curves correspond to various combinations of K_a and K_b. In deriving the expression for S it must be remembered that we have adhered to the convention that K_b is greater than K_a; therefore the abscissa in the plot corresponds to different values of K_b compared with values of K_a which have been denoted by placing the latter as subscripts to S for a given curve. The curve approaches the value of K_a asymptotically. Results of calculations from Equations 13 and 15 are more exact the nearer the partition coefficients are to unity.

One point of interest arising in connection with the separation factor S is the following. It is tempting to measure the degree of separation by the ratio of the partition coefficients or a function of the ratio of the partition coefficients—e.g., Martin and Synge (5) used a procedure of this sort in their theory of partition chromatography. The ambiguity in such a procedure as applied to countercurrent distribution studies is clearly brought out in Table II, where the factor S is shown for different values of K_a and K_b corresponding to the ratio $K_a/K_b = 1.5$.

RESOLUTION OF PEAKS

Formulas are now available for answering another question concerning multiple distribution separations. Suppose we have two substances and their partition coefficients are known or can be estimated in some way. How many transfers would be required before the composite distribution curve would show two peaks?

It can be demonstrated that the appearance of two peaks is observable when the quantity δ as defined in Equation 16 is large enough to be experimentally detectable. We are assuming F_a and F_b to be equal, which gives a minimum value for our answer. The

$$\delta = (T_{n,r_{ma}}^{a} + T_{n,r_{mb}}^{b} - 2T_{n,r_i}^{a}) =$$

$$\frac{1}{\sqrt{2\pi}\sigma_a} + \frac{1}{\sqrt{2\pi}\sigma_b} \, e^{\frac{-(r_{ma} - r_{mb})^2}{2\sigma_b^2}} - \frac{2}{\sqrt{2\pi}\sigma_a} \, e^{\frac{-(r_i - r_{ma})^2}{2\sigma_a^2}}$$

$$(16)$$

second term on the right-hand side of Equation 16 can be rearranged with the help of Equation 17 to give

$$e^{\frac{-n(K_a - K_b)^2}{2(1 + K_a)^2 K_b}}$$

For even moderately different partition coefficients and large n this term is small enough to be neglected and the simple Equation 17 will suffice.

$$\delta = (T_{n,r_{ma}}^{a} - 2T_{n,r_i}) = \frac{1}{\sqrt{2\pi}\sigma_a} \left(1 - 2e^{\frac{-(r_i - r_{ma})^2}{2\sigma_a^2}} \right) \quad (17)$$

The quantity δ is approximately 5% of $T_{n,r_{ma}}^{a}$ when $r_i - r_{ma} = 1.22\sigma_a$, and this difference should be experimentally detectable.

$$d = 2 (r_i - r_{ma}) = \frac{(K_b - K_a) n}{(1 + K_a)(1 + K_b)} \quad (18)$$

FIG. 2
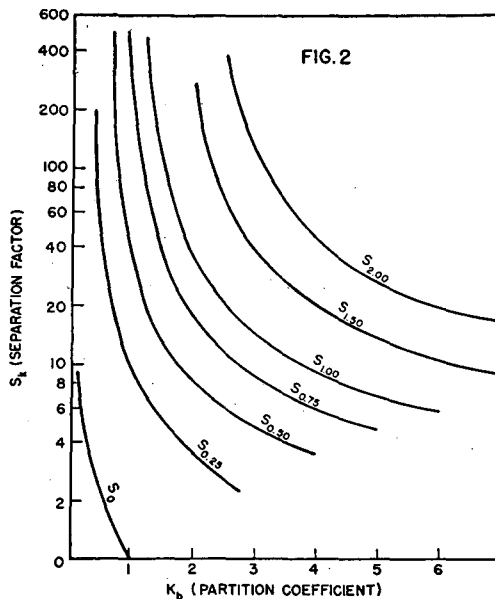
It is now worth while to observe that $r_i - r_{ma}$ is one half the distance d (number of tubes) between the peaks as shown in Equation 18 where Formulas 5 and 7 were used. The above condition expressed in terms of n and the partition coefficients is shown in Equation 19.

$$n = \left[\frac{2.44 \sqrt{K_a} (1 + K_b)}{K_b - K_a} \right]^2 \quad (19)$$

Therefore, Equation 19 gives us the number of transfers required to resolve a composite peak in terms of K_a and K_b.

Another helpful relation when dealing with composite peaks is shown in Equation 20. In this equation P_0 corresponds to the number of the tube at the peak or minimum between the peaks of a composite curve and P_e is where the peaks would be if $F_a = F_b$. Combined with $F_a + F_b = 1$, Equation 20 can be used in estimating the relative amounts of substances a and b where the

$$\frac{F_a}{F_b} = \left(\frac{K_a}{K_b} \right)^{P_0 - P_e} \quad (20)$$

partition coefficients can be estimated from the tails of the distribution curves.

Table II. Separation Factors for Partition Coefficients Corresponding to a Definite Ratio

K_a	K_b	K_a/K_b	S
0.6	0.4	1.5	110
0.9	0.6	1.5	99
1.5	1.0	1.5	98
6.0	4.0	1.5	172
9.0	6.0	1.5	230

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Rapid Methods for Determining Fluoride in Waters

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A dilute solution of the aluminum lake of eriochromecyanine is used as a reagent for the rapid determination of fluoride. Small volumes of samples are required. The method should be useful for the field determination of low, optimum, and excess fluoride in potable waters. A rapid method for the distillation of fluoride is described. The results obtained directly and upon the distillate agree well.

BECAUSE the fluoride content of potable water has a direct relationship to dental health, a rapid and simple method for determining fluoride is desirable. The method described below requires only a 10-ml. sample and a short time of standing before color comparisons can be made, whereas in the generally used official method, Sanchis' (4) modified by Scott (6) and Lamar (3), 100-ml. samples and 1-hour standing are required.

In the colorimetric determination of fluoride in waters, those given above and those of Araujo (2) and Tageeva (7), the alizarin red lake of zirconium is used as reagent. Because the fluoride ion also destroys the color of the aluminum lake of eriochromecyanine, it was expected that a buffered preparation would make a good reagent for the fluoride ion. Eriochromecyanine has also been used by Saylor and Larkin (5) as an indicator in the titration of a fluosilicic acid distillate with aluminum chloride.

REAGENTS AND APPARATUS

Matched test tubes or specimen vials about 125 × 15 mm. were used.

Standard sodium fluoride solutions contained 0.1 to 1.2 p.p.m. of fluoride with differences of 0.1 or even 0.05 p.p.m. and 1 to 6 p.p.m. with differences of 0.5 or even 0.25 p.p.m.

Eriochromecyanine solution, 0.3% aqueous on the basis of a 36% ash, was prepared and purified as previously (8) reported. A preparation under the name of Eriochromecyanine R.C. obtained from Geigy & Co., Inc., 89 Barclay St., New York, N. Y., yielded 61% ash. A 0.5% solution of this was found satisfactory. A preparation under the name of Alizarol Cyanine R.C., from the National Aniline Division of the Allied Chemical & Dye Corporation, yielded 59% ash and gave good results when a 0.5% solution was used.

Aluminum chloride solution was prepared by dissolving 0.447 gram of the hexahydrate to make 1 liter of solution containing 0.01 mg. of aluminum per ml.

Buffer solution was prepared by dissolving 50.0 grams of ammonium acetate in 100 ml. of water and 1.0 gram of ammonium benzoate and then adding 3 ml. of glacial acetic acid. One milliliter of this diluted to 20 should have a pH between 5.4 and 5.6.

Composite reagent was prepared by mixing 3 volumes of the dye solution, 2 volumes of the buffer, and 1 volume of 0.1% gum arabic solution.

Stock lake solution was prepared by mixing 50 ml. of the composite reagent, 50 ml. of the aluminum chloride solution, and 5 ml. of water and warming to 65° to 70° for 10 minutes with constant stirring before allowing to cool. It keeps for at least 4 months.

Dilute lake solution was prepared by mixing 10 ml. of the stock lake solution with 90 ml. of water and 10 ml. of the buffer solution.

PROCEDURE, DIRECT METHOD

Because the reaction is affected by pH, all very alkaline samples should be made slightly acid with a few drops of dilute hydrochloric acid. To determine whether the buffer is adequate, 2 ml. of the dilute lake solution are added to a 10-ml. sample. The mixture is tested with a paper and compared with a test on a dilute buffer solution. One or two drops of buffer may adjust the pH.

For a range of 0.1 to 1.1 p.p.m. of fluoride, 10 ml. of the sample water and 10 ml. of standard solutions are pipetted into the matched test tubes or specimen tubes. Then 2 ml. of the dilute lake solution are added. Comparisons are made 10 to 15 minutes after mixing.

For a range of 1 to 6 p.p.m. of fluoride a 5-ml. sample and 5 ml. of standard solutions are pipetted into matched tubes. Then 5 ml. of the dilute lake solution are added, mixed, and compared 10 to 15 minutes later. The two ranges overlap.

Discussion The rate of color decrease varies with the temperature. Therefore more accurate results are obtained if the sample, standard solutions, and reagent are at the same temperature.

As the amount of fluoride increases, the color changes from a red purple to red, cherry red, peach pink, and orange. In the lower range color differences corresponding to 0.05 p.p.m. can easily be distinguished, and standards with 0.05 p.p.m. differences in fluoride may be desirable. A piece of paper wrapped around each of two tubes that are held against each other facilitates comparison. Thus a blank determination is easily distinguished from a standard containing 0.025 p.p.m. of fluoride, but differences between standards of 0.025, 0.05, and 0.075 and 0.10 can be less easily distinguished. The color of the blank determinations remains constant. Thus a freshly prepared blank compared with blanks 15 and 30 minutes old showed no differences in color. For the higher range, standards of 0.25 p.p.m. difference may be used; it is better to view the tubes from above against a white background. Because the approximate fluoride content can be determined with two or three standards after standing 3 to 5 minutes, it is suggested that the operation be repeated with standard solutions narrowed to the proper range.

In the upper range the color changes continue to occur when more than 6 p.p.m. of fluoride are present, but the deep orange colors are not so easily distinguished.

Because the color change is rapid in the beginning, a time interval is required for the contents of the tubes to which the reagent was added later to catch up with the first tube. The change after 30 minutes is slow, and in standard solutions the color after 15 minutes is almost that of a solution which has stood 30 minutes. A special preliminary treatment of a hydrogen sulfide water consisted in shaking it thoroughly with air, allowing the sulfur precipitate to settle, or allowing the sulfur to redissolve.

Interferences. Bicarbonate does not interfere except as it affects the pH. If the pH of reacting solutions are too high, the color will remain too deep and give low results. Phosphate up to 5 p.p.m. does not interfere but at 10 p.p.m. low results are obtained. Chloride and nitrate at 1000 p.p.m. do not interfere. Sulfate at 760 p.p.m. does not interfere. Above 1 p.p.m., iron begins to give high results. Added aluminum up to 1 p.p.m. does not interfere. Added silicate as silica up to 6 p.p.m. does not interfere. Calcium at 168 p.p.m. as calcium carbonate gives results that are high by 0.7 p.p.m. of fluoride; at 124 p.p.m., 0.4 p.p.m. too high; at 106 p.p.m., 0.1 p.p.m. too high. Magnesium as calcium carbonate at 120 p.p.m. gives results that are high by 0.2 p.p.m.; at 60 to 100 p.p.m., 0.1 p.p.m. high; at 40 p.p.m. there is no interference.

Because of the greater dilution by the reagent in the upper range procedure, the limits of interference should be about 1.67 times as great and were so found experimentally.

It was found that sodium salt solutions of 9000 and 5000 p.p.m. of chloride, nitrate, and sulfate lower the color of the aluminum lake. This is probably a salt effect and suggests that very hard or briny waters be diluted before the direct method is used. This also has the advantage of decreasing the amount of interfering substances.

DISTILLATION METHOD

Water samples are distilled (*1*) when an excess of interfering substances is present or to eliminate unsuspected interferences. The standard (*6*) method, a modification of the Willard and Winter (*9*) procedure, required preliminary evaporation, and the distillation requires 1 hour. The procedure given below requires much less time and coupled with the above procedure requires less than an hour for a determination.

Distillation Apparatus. A 300-ml. Kjeldahl flask is fitted with a two-hole rubber stopper. A bent glass tube is inserted through one hole, so that one end reaches nearly to the bottom of the flask. The flask is connected with a shallow inverted U to an upright West type of condenser having a jacket 50 cm. long. The outlet should be slightly constricted. The U-tube should be 8 mm. in diameter and about 15 cm. wide, having one arm about 8 cm. long and the other 12 cm. long. The short arm is inserted flush with the stopper in the distillation flask. The longer arm is inserted through a rubber stopper, so that it reaches the constricted part of the condenser tube. The apparatus is supported with clamps on a tall ringstand. The flask is supported on an asbestos board having a hole of 7-cm. diameter. The heating is carried out with a Meker type of burner. The compressed air is led to the Kjeldahl flask through a 500-ml. gas-washing bottle containing water.

A condenser having a 25-cm. jacket and a 40-cm. tube gives good results, but the condensate is much warmer.

For a quicker operation a 100-ml. Kjeldahl flask may be arranged using 6-mm. tubing to connect it to a shorter condenser. The asbestos board supporting the flask should have a hole of 5-cm. diameter. A smaller burner is used.

Distillation Procedure. A sample of 100 ml. of the water and 10 ml. of distilled water are pipetted into the 300-ml. Kjeldahl flask and 0.2 to 0.3 gram of silver sulfate and about 10 glass beads are added. Then 40 ml. of concentrated sulfuric acid are poured down the neck with a minimum of mixing. The water is turned on to run rapidly through the condenser. The air supply and the condenser are connected to the flask. The outlet of the condenser tube is dipped into water. A 100-ml. graduate is placed under the outlet. The air supply is turned on to give high turbulence. About 30 seconds later a large flame is applied from a Meker type of burner and distillation is carried on at a rapid

Table I. Comparison of Results

Source of Sample	Direct Method, P.P.M. F	Distillation Method, P.P.M. F	Remarks
Aurora, Ill.	0.7	0.7	Hardness 322 p.p.m. Diluted for direct method
Aurora, fluoride added equivalent to 1 p.p.m.	1.55	1.65	
Aurora, fluoride added equivalent to 20 p.p.m.	20.0−	20.0+	Distilled undiluted; distillate and sample diluted 10 to 100
Frankfort, Ind.	1+	1+	Municipal from wells
Florida well	0.7+	0.7	100-ft. well, 200 feet from an East Central Florida beach
Hebron, Ind.	0.3	0.3	Well
Valparaiso, Ind.	0.1	0.1	From lake, hardness 80 p.p.m.
Sheboygan, Wis.	1.1−	1.1+	Lake Michigan water, fluoride added at plant. 1.15 reported by official method
Grand Rapids, Mich.	1.1−	1.1	Municipal, fluoride added at plant. 1.09 reported by official method. Al 1.4 p.p.m.
Strongbow well	0.2	0.2	60-foot well 1 mile East of Valparaiso, Ind.
Lowell, Ind.			
Diluted 1 + 3	4.4+	4.4+	Well 200 feet, diluted 1 + 3.
Undiluted	4.5	4.5−	Slight H₂S odor
Small scale	..	4.5	
Lowell well	0.3−	0.3+	60-foot well, 1 mile east of Lowell. Very slight smell of H₂S
Salt Lake, Utah	4.5	4.5	Diluted 5 to 100 ml.
By weight	3.2	3.2	
Small scale	..	4.2	
Dunn's Bridge flowing well S.E. of Kouts, Ind.	2.3	2.25	Shaken until S ppt. was dissolved. Contains H₂S

rate until 90 ml. have been collected. The gas is turned off and the air allowed to go through for a few seconds longer. The condenser is disconnected and rinsed with about 3 ml. of water from a pipet into the graduate. One or two drops of a concentrated ammonium carbonate solution are added to the distillate, and it is allowed to cool to room temperature. About 0.5 ml. of the buffer solution is added and then the distillate is diluted to 100 ml. It is mixed and the fluoride determined as given above. The actual time for distillation is about 14 minutes.

The operation on a smaller scale requires a 35-ml. sample, 5 ml. of water, and 15 to 16 ml. of sulfuric acid in a 100-ml. Kjeldahl flask; 35 ml. are distilled into a 50-ml. cylinder. After neutralizing and cooling, it is made up to 40 ml., and mixed and the fluoride is determined as above. The actual time for distillation is about 7.5 minutes. The parts per million of fluoride determined are multiplied by 1.14 to get the parts per million in the original.

Discussion. Known added amounts of fluoride were added to several water samples and recovered in the distillate. The rapid addition of air causing great turbulence and the application of a large flame are essential. With smaller flames and slower distillation, the recovery is low, especially when the fluoride content is above 0.5 p.p.m. During the distillation some steam escapes. There is no increase in recovery of fluoride when the bottom of the condenser tube is immersed in water, and some steam escapes just the same. In the outlet of the condenser tube there is always some distillate hanging by capillary attraction, through which the vapors are blown. The addition of silver sulfate makes the distillation smoother and possibly retains sulfide in water containing a trace of it and some chloride. The extra water is added to give the distillate a larger volume and to collect less hydrogen chloride. A standard solution containing 10 p.p.m. of fluoride as sodium fluoride was distilled and the distillate made up to 100 ml. One volume of this was made up to 10 volumes and compared with a 1 p.p.m. standard which it matched. Blank determinations using distilled water, 0.3 gram of silver sulfate, and ten 5-mm. soft glass beads gave results that showed negligible fluoride content; the maximum was equivalent possibly to 0.001 p.p.m.

RESULTS

The results by both methods on a variety of waters are given in Table I. In two cases they are compared with the standard

method. There is excellent agreement between the two methods within the precision that can be expected. The precision in the lower range is less than 0.05 p.p.m., and in the upper range less than 0.25 p.p.m. Such precision is adequate for all health purposes.

The presence of aluminum ions should deepen the color of the lake, and silicate ions (8) should destroy its color. Therefore, it is reasonable to assume that the aluminum and the silicate ions are tied up in natural waters and are not freed to any extent at pH 5.4 to 5.6 in 15 minutes.

The escape of some steam during the rapid distillation is disconcerting, but the results in recovering added fluoride (as sodium fluoride) justify confidence in the method.

For both methods Great Salt Lake water was diluted 1 to 10 before the determination was made.

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Punched Card Catalog of Mass Spectra Useful in Qualitative Analysis

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A method for indicating the prominent features of a mass spectrum on punched cards and the way these cards can be used as an aid to qualitative analysis with the mass spectrometer are described in detail. Further aids for the identification of peaks observed on the mass spectrometer are the measurement of mass defects and correlation of relative peak heights with known isotopic distribution.

PUNCH cards of the Keysort variety (Keysort cards manufactured by McBee Company, Athens, Ohio; Rocket cards manufactured by Charles R. Hadley Company, Los Angeles, Calif.) have been used in many chemical applications (*2, 4–7*) particularly in bibliographies, but other kinds of information can also be put on punched cards. An isotope file (*10*), for instance, is coded to permit sorting out the cards for isotopes having some particular property. Wright (*15*) introduced the use of punched cards for the presentation of infrared data, and infrared charts can now be obtained (Samuel P. Sadtler & Son Co., Philadelphia, Pa.) printed on punched cards which indicate the absorption bands by means of a direct index.

During the past two years the author has used a punched card system for cataloging mass spectra. Besides being a convenient method for filing, these cards have been useful in the identification of mixtures of compounds.

Several hundred spectra of compounds of special interest have been put on these cards, and, in addition, mass spectra reported in the literature have been incorporated in the file. The mass spectra given in A.P.I. Project 44 publications (*1*), for example, have been included.

Although the finer details of a spectrum will differ from one instrument to another, the main features are similar, and hence data obtained on other kinds of spectrometers are useful for qualitative and rough quantitative work.

DESCRIPTION OF CARDS

The cards used for this catalog of mass spectra are the 5 × 8 inch McBee Keysort cards with single rows of holes at the sides and double rows at the top and bottom (Figure 1).

A card for a given compound includes a copy of the spectrum as recorded on the General Electric photoelectric recorder, pasted directly on the card if the spectrum was obtained in this laboratory, or a transcribed record of peak heights if from the litera-

ture. Other recorded data are sensitivity (peak height ratio of an arbitrary prominent peak per unit pressure on the leak to the peak height per unit pressure for some peak of a reference substance under identical conditions), references to more detailed data on the spectrum of the compound, a description of the conditions under which the spectrum was obtained, a designation of the five or six highest peaks, and any other pertinent data. The spectra are generally obtained at a single attenuation setting of the amplifier, so that the highest peak will be nearly full scale. In this way, the various features of the spectrum retain their proper perspective.

In comparing the spectra obtained on different spectrometers, the relative peak heights for adjacent ions are more likely to be similar than comparisons of peak heights far apart in mass. This is due to the fact that the focusing may not be equally effective at the various parts of the spectrum, particularly if magnetic scanning is used, whereas with voltage scanning the sensitivity varies with the accelerating voltage. For most of this work magnetic scanning with a single setting of the focus was used, giving the best focus at mass 44, the geometric mean of the range 12 to 160. This range will include a majority of the compounds cataloged. The attenuation due to focusing at the extremes of this range was about 2.

The cards are punched under two headings (Figure 1). First, a means is provided for sorting the card of a desired compound. The molecular weight of the compound is used as the basis for this classification and the hundreds (below 7), tens, and units holes on the left side of the card are reserved for it. The convention has been adopted of using the nearest integral weight of the most abundant natural isotope—i.e., $Cl = 35$, $Br = 79$, $Ge = 74$. By this convention all cards of a given molecular weight can be quickly separated and hand sorting of the few cards so separated gives the desired compound. Isomers, of course, fall into a common group. Although this method of
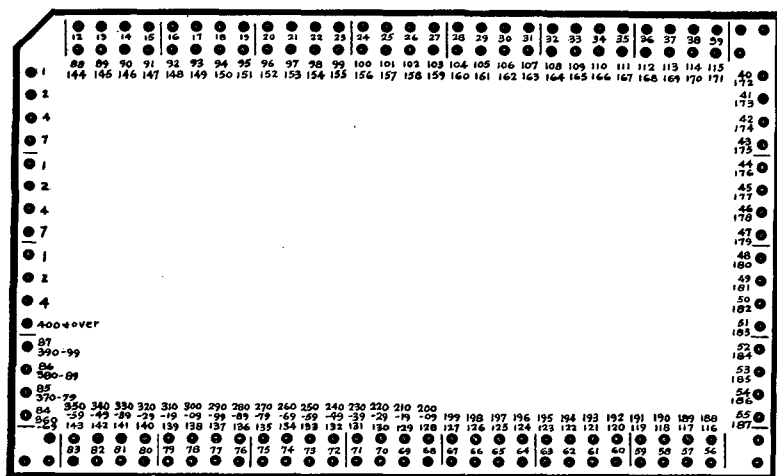
Figure 1.   Card Showing Punching Code

Upper left.   Molecular weight of compound.   Other spaces.   Principal peaks

classification has proved satisfactory, an additional classification designating the elements (other than carbon and hydrogen) contained in each compound may be convenient. A field of five or six holes corresponding to as many groups of elements would be sufficient.
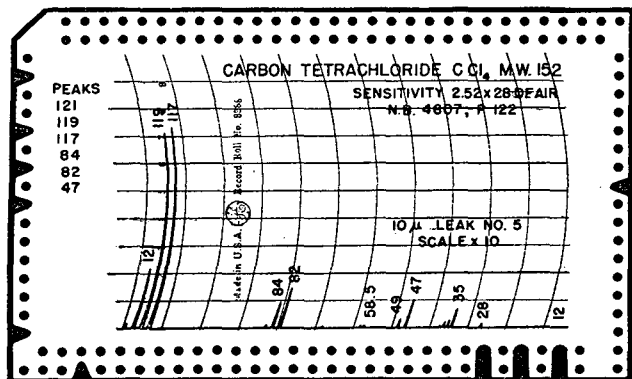

Figure 2.   Completed Card of Carbon Tetrachloride

The rest of the spaces, with the exception of the corner spaces, are used in a direct index for several of the more prominent peaks in the mass spectrum. After trying several different systems, the spaces were assigned seriatim starting at mass 12. By duplicate assignments on the sides and for the deep punches 208 spaces are provided. Starting with mass 200 each space is assigned 10 mass units—i.e., 200–209, 210–219, etc. For masses of 400 and above, the 700 space of the molecular weight field is reserved. (The author does not contemplate getting mass spectra of compounds of molecular weight higher than 700.) A completed card is shown in Figure 2. Only the five or six most prominent peaks are punched. This number has been found to be adequate. A larger number would be confusing.

USE OF CARDS FOR ANALYSIS

This classification is used for identification of unknown mixtures by their spectrum by noting the prominent peaks, and sorting out the cards containing them, starting with the peak of highest mass. A somewhat similar method has been developed for infrared spectra (15).

After the spectrum of the unknown is compared with the spectra sorted out in this way, one of the components can gener-

ally be identified, and its spectrum subtracted, and the process repeated on the residual peaks. By using the sensitivity, the amounts can then be estimated in the usual fashion (14).

This method of identifying compounds can be used only if all the compounds likely to be encountered in a mixture have previously been cataloged. If one is working in restricted fields this is possible. Obviously, the value of the catalog is limited unless it includes a large number of compounds in all groups likely to be encountered.

Several alternative sorting methods have been tried or considered. One of these was to indicate not only the six highest peaks but also their height (sensitivity). This proved too complicated and the additional information so punched was not useful. Indirect codes for punching the highest peaks, although more economical of space, make sorting inconvenient.

Other methods of indicating a particular compound than by the molecular weight may be more specific, but they are also more complicated. So the simplicity of the method used again recommends it.

The small charts pasted onto the card do not give detailed and accurate peak height relationship for all the peaks, in particular, the smaller one. But this graphic presentation shows the important points in the spectrum better than a more detailed table. The detailed table can be easily found by a reference, or if desired, written on the back of the card.

Most of the data which are on the cards were obtained on a General Electric analytical mass spectrometer, using a General Electric photoelectric recorder with the full scale response time of 0.3 second. The convenience of the smaller tape and rapidity with which spectra could be obtained compared with the larger (10 inch) strip chart recorder (4 seconds full scale) usually used with this instrument recommends the small chart for this work.
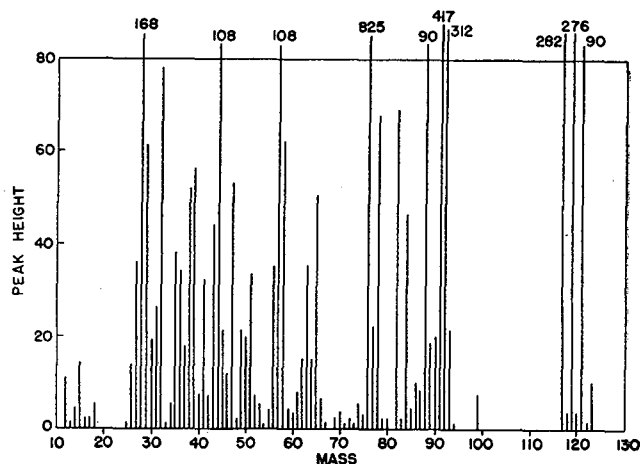

Figure 3.   Mass Spectrum of Carbon Tetrachloride, Carbon Disulfide, Dioxane, Toluene, and 2,2,4-Trimethylpentane Mixture

A spectrum can be obtained in 5 or 6 minutes from mass 12 to 160, and the peak height measured to 1% of full scale. These spectra can be very conveniently filed, or pasted directly on the Keysort cards. The larger recorder is used for more detailed spectra. If the spectrum of the compound has peaks higher than 160, the sweep speed can be increased to allow the entire spectrum to be recorded on a strip that will fit the card.

To demonstrate how the system works, and to indicate some other aids to qualitative analysis, a mixture of several com-

ponents was made, and the spectrum shown in Figure 3 was obtained for it.

Because the prominent peaks of higher mass are more apt to be specific, the cards were first sorted for peak 119. Of the eight cards so obtained, hand sorting indicates that the group of peaks 117 to 123 had the correct ratios for the isotopic distribution obtained from $CCl_3{}^+$. Comparing the spectrum of the mixture with spectra for compounds having the 119 peak indicated that all the peaks of carbon tetrachloride were present in the mixture, with proper ratios, or higher (other ions contributing); but that some of the ions which would be required by other compounds having the 119 peak were lacking. Thus, carbon tetrachloride was established as a probable component of the mixture. Repeating the procedure with the next prominent peak (92) led to the conclusion that toluene was a component. The 99 peak was not sorted at this time, because it may have been due to a minor component, and its identification would have been difficult at this point. Peak 88 gave dioxane and 76 carbon disulfide. In the high mass region there remained the small peak at 99, a large one at 57, and some other smaller peaks. When cards with peak 57 were separated from the file many were removed, but if peak 99 were chosen, only a few cards dropped out, and the next component was identified as 2,2,4-trimethylpentane. This last component had been accidentally included in the mixture and its presence was not suspected until the procedure outlined above had been followed. After each peak had been examined in detail, it was found that there were no significant residuals except for background.

ISOTOPIC DISTRIBUTION

It was mentioned that the group of peaks 117 to 123 were typical of the ion $CCl_3{}^+$. The natural isotopic distribution is often an aid in the identification of a substance. If, for instance, an ion contains a single chlorine, the peaks due to Cl^{35} and Cl^{37} will have a ratio of about 3 to 1 (provided isotopes of other elements with which it is combined do not interfere with that ratio). With two chlorines, the ratio is about 1:6:9 for alternate peaks, starting with the peak of highest mass. In the case of ions containing a single carbon, the C^{13}-containing ion gives a peak one unit higher in mass and theoretically about 1.1% (9) as high as the peak due to C^{12}. With two carbons, the next higher peak is 2.2%, etc.; in the mixture used the 93 peak was about 6.7% (theory 7.8%) as great as the 92.

It has been found after an examination of the spectra of some 40 or 50 compounds that better results are obtained by the use of 1.04 as the percentage of C^{13} in carbon. The individual values are considerably scattered beyond the probable error in measurement and indicate that all compounds may not respond alike to changes in isotopic composition. If the value 1.04 is used for toluene, one would expect the 93 peak to be 7.3% of the 92. The value observed, 6.7%, is actually the poorest correlation with the expected value of the compounds measured and an example of the extreme scattering. The deficiency of the C^{13} peaks may be due to a lower probability of ionization (3, 13) rather than to a lower isotopic ratio, but the average behavior is as if the amount were 1.04%. The 76, 77, and 78 peak height distribution is typical of two sulfur atoms in an ion, with some C^{13} contribution in addition on the 77 peak. In general, the distribution of a polyisotopic ion is given by $(a + b + c + \ldots .)^n$ where a, b, c, are isotopic fractions and n is the number of atoms of the element in the ion; if there are several polyisotopic elements present (carbon and sulfur in carbon disulfide), their distribution can be calculated independently in a similar fashion and then ions of equal mass combined. Norton has given a detailed calculation (11) for B_2H_6.

MEASUREMENT OF MASS DEFECTS

Another means of identification that is sometimes useful is the measurement of mass defects (12). In the example given (Figure 4), the doubly ionized $CCl_3{}^{++}$ peaks at mass 58.470, 59.469, and 60.469 calculated from the values (9) for C^{12}, Cl^{35}, and Cl^{37} give known reference points for measuring the masses of the peaks at 57, 58, 59, and 60. By scanning this part of the spectrum at a very low speed, the peaks can be spread far apart, and the values of m/e measured to about $1/100$ part of a mass unit if known reference peaks are available. Figure 4 gives the assumed ions, their mass, and the measured mass for the corresponding peak.

Because the values agree to within the experimental error, one can conclude that the assignments are correct. The ac-

NOMINAL MASS	ION	ISOTOPIC MASS	MEASURED MASS*
57	$C_4^{12}H_9^{\cdot}$	57.088	57.08
58	$C_3^{12}H_6O^+$	58.060	58.06
58.5	$C^{12}Cl_3^{35++}$	58.470	—
59	$C_2^{12}C^{13}H_6O^+$	59.064	59.06
59.5	$C^{12}Cl_2^{35}Cl^{37++}$	59.469	—
60	C_5^{12+}	60.023	60.02
60.5	$C^{12}Cl^{35}Cl_2^{37++}$	60.469	—

* USING C Cl₃⁺ IONS AS REFERENCE POINTS, AND MEASURING THE DISTANCE BETWEEN PEAKS
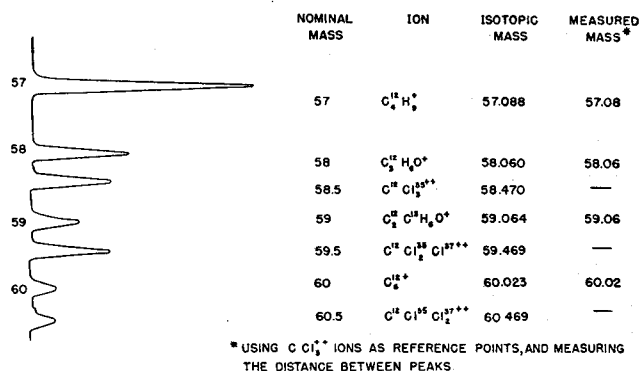
Figure 4. Mass Spectrometer Trace

Used to illustrate verification of assignments of ion peaks by measurement of mass defects

curate measurement of the 58 peak in this case would distinguish between the ion actually found, $C_3{}^{12}H_6O$, whose mass is 58.060, and the parent peak of butane, for instance, with mass 58.096. Each hydrogen adds about 0.01 mass unit to the accumulated mass defect. If this method is to be successfully applied up to mass 100, the spectrometer should have sufficient resolution and stability to distinguish a difference in the value of m/e to $1/10,000$.

This means of identification must be used with caution, however, for the apparent value of m/e may occasionally differ from the true value because of excess kinetic energy of the ions (8). The design of the spectrometer and source will to some extent determine how frequently they will be observed. Ion peaks displaced because of excess kinetic energy usually give unsymmetrical envelopes, and their shape can be modified by varying the drawing out potential. Although the occurrence of such peaks may not be predicted, they can be detected and due allowance made for them.

Using the known isotopic distribution data and measuring the mass defects are useful aids in identifying the ions produced, but do not in themselves suffice for identification of a compound. For this, the mass spectrum of the compound must be available; hence analysis with the mass spectrometer depends ultimately on an adequate library of reference spectra, for there exists at present no adequate theory for predicting these spectra.

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Identification of Esters of Monobasic Acids by the Use of Ethanolamine

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THE successful use of ethanolamine for the identification of esters of dibasic acids has been reported (2). It has now been found possible to apply the procedure to esters of monobasic acids. These esters undergo rapid ammonolysis on refluxing with ethanolamine. From the reaction mixture the alcohol or phenol can be distilled in a state of purity satisfactory for identification purposes or, if the alcohol or phenol boils close to or above the boiling point of ethanolamine (172° C.), it can be extracted with ether. The ether extract is washed with a small amount of water to remove traces of the alkanolamine which would otherwise interfere with the refractive index of the alcohol or phenol to be identified. During the distillation it is possible to make an adequate check on the boiling point of the alcohol or phenol. In the case of a solid alcohol, distillation might not be advisable, but it can be isolated by filtration and identified in the usual way. A determination of refractive index and the preparation of a typical derivative complete the identification of this fragment from the ester.

In some cases the acid from the ester appears as an insoluble solid N-β-hydroxyethyl amide when the reaction mixture is cooled, after removal of the alcohol or phenol. This amide serves as a derivative for characterizing the acid. In most cases investigated, however, a solid amide was not obtained. In this circumstance the reaction mixture is acidified with hydrochloric acid and refluxed a short time to hydrolyze the soluble amide. The liberated organic acid may be in solution, or may appear as an insoluble liquid or solid. Solid acids are removed by filtration; otherwise the acid is removed by ether extractions. Formic and hydroxy aliphatic acids could not be recovered by extractions. The acid is subsequently identified through the boiling or melting point, index of refraction, and a typical derivative.

Results obtained by the use of the above procedures with a variety of esters are given in Table I. All melting and boiling points are corrected. The N-β-hydroxyethyl amides of cinnamic acid and salicylic acid were found to have the correct nitrogen analyses.

MATERIALS

Ethanolamine was redistilled commercial grade. The esters examined were Eastman Kodak white label products or products of comparable purity.

Table I. Identification of Esters

Ester	Alcohol or Phenol B.P., °C Found	Lit.	n_D^{20} Found	Lit.	M.P. of 3,5-Dinitrobenzoate, °C Found	Lit.	Acid B.P. or M.P., °C Found	Lit.	n_D^{20} Found	Lit.	M.P. of p-Bromophenacyl Ester, °C Found	Lit.
Isoamyl formate	128–132	132	1.4109	1.4075	...	...	...	...	...	...	...	...
Methyl acetate	64–66.5	64.7	1.3276	1.3288	105–106	107	...	...	...	...	...	...
n-Octyl acetate	..	..	...	...	58.0–58.5	61	...	...	...	...	...	...
Ethyl propionate	77–79.5	78.3	1.3616	1.3610	90.8–92.5	93	...	...	...	...	...	...
Isoamyl propionate	129–134	132	1.4091	1.4075	58.3–59.0	61.8	135–142	141.4	1.3885	1.3868	61.9–62.4	63.4
Ethyl n-butyrate	75–79	78.3	1.3608	1.3610	...	...	156–164	164	1.3921	1.3979	62.1–62.8	63
Ethyl n-caproate	76–79	78.3	1.3604	1.3610	...	...	197–204	205.4	1.4171	1.4163	...	...
Methyl n-caprylate	63–65	64.7	1.3275	1.3288	103.9–104.4	107	235–240	239.3	1.4301	1.4268	67.0–67.8	67.4
Methyl pelargonate	64–68	64.7	1.3348	1.3288	105.2–106.8	107	...	...	...	...	69.6–70.5a	...
Methyl palmitate	63–64	64.7	1.3354	1.3288	...	...	...	...	...	...	87.2–88.0a	...
Methyl stearate	63–68	64.7	1.3354	1.3288	...	...	...	...	...	...	93.3–94.2a	...
Ethyl α-hydroxybutyrate	76–78	78.3	1.3602	1.3610	...	...	210–212	212	...	...	...	...
Ethyl lactate	77–79	78.3	1.3607	1.3610	...	...	b	...	...	...	...	...
Di-n-butyl tartrate	115–120	118	1.3993	1.3991	...	...	b	...	...	...	...	...
Triethyl citrate	76–78	78.3	1.3618	1.3610	...	...	b	...	...	...	...	...
Ethyl benzoate	78–80	78.3	1.3598	1.3610	...	...	120.8–121.4	121.7	...	...	...	...
Isopropyl benzoate	80–84	82.4	1.3771	1.3793	120.7–121.3	122	121.0–121.4	121.7	...	...	...	...
Benzyl benzoate	197–205	205.5	1.5390	1.5396	121.1–121.4c	121.7	121.0–121.4	121.7	...	...	...	...
Methyl salicylate	63.5–64.3	64.7	1.3283	1.3288	...	...	...	...	...	...	112.3–114.2a	...
n-Butyl p-hydroxybenzoate	113–119	118	1.3986	1.3991	...	...	...	...	...	..	150.6–151.5a	...
Methyl o-chlorobenzoate	63.6–64.0	64.7	1.3310	1.3288	...	...	138.8–140.1	141	...	...	...	...
Methyl anthranilate	63.1–64.3	64.7	1.3292	1.3288	...	...	140.2–141.0	144	...	...	...	...
Methyl p-aminobenzoate	63.0–64.1	64.7	1.3311	1.3288	...	...	...	...	...	...	163.3–164.2a	...
Methyl p-toluate	64–67	64.7	1.3305	1.3288	...	...	176.5–177.2	178	...	...	...	...
Methyl p-anisate	63.3–64.2	64.7	1.3346	1.3288	...	...	183.8–184.3	184.2	...	...	...	...
Ethyl o-benzoylbenzoate	76.2–78.2	78.3	1.3615	1.3610	...	...	90.3–93.5	93–94	...	...	...	...
Methyl cinnamate	63.4–64.1	64.7	1.3290	1.3288	...	...	130.3–130.7	133	...	...	100.0–100.2a	...
Ethyl cinnamate	77.5–79	78.3	1.3602	1.3610	...	...	...	...	...	...	100.3–101.0a	...
Ethyl phenylacetate	76.1–77.2	78.3	1.3652	1.3610	...	...	75.8–76.5	76.5	...	...	...	...
Isopropyl phthalate	81–83.5	82.4	1.3770	1.3793	120–121	122	...	...	...	...	127.5–128.5d	126–127d
Di-n-butyl phthalate	115–117	118	1.3989	1.3991	63.5–64.0	64	...	...	...	...	127–128d	126–127d
Cyclohexyl acetate	158–160	161.1	...	...	...	...	...	...	...	...	78.2–78.6e	78
Phenyl acetate	179–180	182	...	...	...	...	...	...	...	...	...	...
o-Cresyl acetate	190–191	190.8	...	...	...	...	...	...	...	...	...	...
1-Naphthyl acetate	94.3–95.2f	94f	...	...	...	...	...	...	...	...	...	...
2-Naphthyl benzoate	121.9–122.3f	123f	...	...	...	...	120.1–121.3	121.7	...	...	...	...
2-Naphthyl salicylate	120.9–121.5f	122.2f	...	...	...	...	158.2–158.6	158	...	...	...	...
Cellosolve acetate	135–140	134.8	1.4190	...	...	...	...	...	...	...	...	...
Benzyl acetate	198–204.2	205.5	1.5396	1.5396	110.5–111.5	112	...	...	...	...	...	...

a N-β-hydroxyethyl amide.
b Isolation of acid unsuccessful.
c Benzoic acid by oxidation of alcohol.
d N-β-hydroxyethyl phthalimide.
e p-Nitrobenzyl ester.
f M.P.

APPARATUS

For the reflux step acetylation flasks of 50-ml. capacity with a short water condenser were employed. A short Vigreux column replaced the condenser during distillation. All pieces of equipment were provided with 〒 joints. Melting points were determined in a Hershberg outfit (1). A Bausch & Lomb Abbe refractometer was used for the determinations of index of refraction.

PROCEDURE

Alcohol Esters. Approximately 5 grams of ester and 15 ml. of ethanolamine are refluxed for 30 minutes (15 minutes are sufficient for esters of aliphatic acids). The flask and contents are cooled and the condenser is replaced by the short Vigreux column. The alcohol or phenol is slowly fractionated from the mixture and the boiling range is noted. If the alcohol boils close to or above the boiling point of ethanolamine, distillation is impractical. In this case the reaction mixture is cooled and extracted with three 25-ml. portions of ether in a small separatory funnel. The ether solution is washed with a small amount of water and dried, and the ether is evaporated to obtain the alcohol. A solid alcohol which is insoluble in the cooled reaction mixture may be removed by filtration. Without further purification index of refraction is measured and a typical derivative is prepared from the alcohol.

The reaction mixture after the removal of the alcohol is cooled to room temperature. In some cases (see Table I) a solid N-β-hydroxyethyl amide separates, is removed by filtration, and is recrystallized from alcohol-water before the melting point is determined.

If no solid separates the mixture is acidified with 20% hydrochloric acid, while cooling. In some cases this leads to a separation of an amide which is handled as above. If no solid separates, a further 25-ml. portion of 20% hydrochloric acid is added and the mixture is refluxed for 20 minutes to hydrolyze the amide. On cooling, the acid may be soluble or separate as a liquid or solid. Solid acids are removed by filtration and soluble and/or liquid acids are removed by extraction with three 25-ml. portions of ether. After the ether solution is dried and the ether evaporated, the acid is identified by means of the boiling point, index of refraction, and a derivative. Extraction failed to remove the acid from formate esters or esters of aliphatic hydroxy acids.

Phenol Esters. In the case of phenol ester the phenol is obtained most conveniently by ether extraction of the acidified reaction mixture at the end of the reflux step.

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Determination of Oxygen in Metal Oxides and Sulfides

By Reaction with Sulfur Vapor

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The usual methods for determination of oxygen in inorganic compounds become complicated when metal sulfides are present. von Wartenberg suggested a means of analysis free from this interference, based on the reaction of the sample with sulfur vapor at high temperature. Oxygen is liberated as sulfur dioxide, which is determined iodometrically. Application of this procedure to molybdenum, tungsten (wolfram), and nickel oxides, and to samples containing both oxygen and sulfur combined with these metals is here described. Oxygen contents from 0.1% upward were determined with samples of less than 0.1 gram. Water was found to interfere in the analysis. Other probable interfering materials include organic compounds and inorganic hydrides and carbides.

A METHOD was desired for determination of oxygen in solid samples containing oxygen and sulfur combined with molybdenum, tungsten, or nickel. The usual schemes, employing reduction with carbon (1, 6) or hydrogen (5, 7, 9) are complicated by reaction of the sulfur with the reducing agent. von Wartenberg suggested that this difficulty could be avoided by allowing the oxide-sulfide mixture to react with sulfur, and measuring the sulfur dioxide evolved (8). He gave a single illustration of the method in a determination of the oxygen content of zinc oxide. Sulfur vapor in a stream of pure nitrogen was passed over the oxide at 900° to 1000° C., and the sulfur dioxide formed was determined iodometrically. von Wartenberg concluded from the literature on conversion of oxides to sulfides, and from approximate equilibrium calculations, that oxide-sulfide mixtures of a large number of metals could be analyzed in this way.

The von Wartenberg method was adopted for the present work, and a detailed procedure was first developed for determination of oxygen in the oxides of molybdenum, tungsten, and nickel. The procedure was then applied to the determination of oxygen in samples containing oxygen and sulfur combined with one of the three metals listed.

EXPERIMENTAL

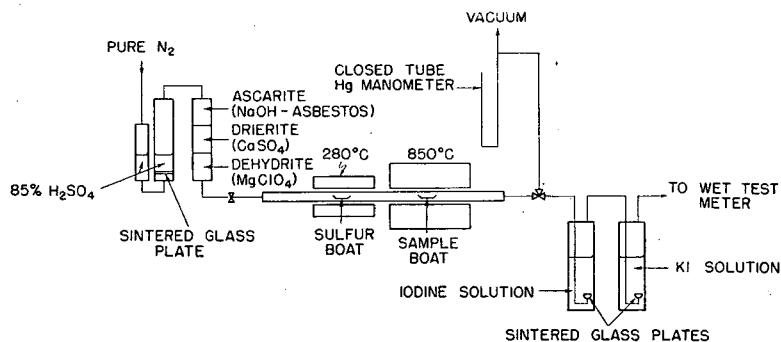A schematic drawing of the apparatus is given in Figure 1.

Figure 1. Apparatus for Oxygen Analysis

Scale, 1 inch = 8 inches

Table I. Reaction of Metal Oxides with Sulfur

Metal Oxide	Sample No.	Sample Weight, Mg.	% of Theoretical Oxygen Reacted after Successive 1-Hour Treatments		
			450° C.	600–650° C.	800–850° C.
MoO₃	1	6.8	54	91	..
MoO₂	2	4.4	0	101	..
	3	21.8	..	..	101
WO₃	4	5.9	11	45	107
NiO	5	20.8	80	..	..
	6	5.5	..	96	101

A silica reaction tube of 1.2 cm. inside diameter is employed. Connecting lines are of 6-mm. glass tubing. Ground-glass joints lubricated with Apiezon N stopcock grease connect the various parts of the apparatus. Pure nitrogen, the carrying gas for the sulfur vapor, passes through the drying and carbon dioxide absorption system shown in the diagram, then enters a silica tube, and passes over a small boat containing sulfur heated to 270° to 290° C. Further along the tube the sulfur-laden gas passes over the sample to be analyzed, which is heated to a higher temperature. Temperatures as high as 850° C. were usually employed to ensure complete reaction, although in most cases lower temperatures would have been adequate. Excess sulfur condenses in the cool exit portion of the reaction tube. No difficulty was encountered from plugging of the tube or connecting lines. Sulfur dioxide in the exit gas is absorbed by a solution containing a known amount of iodine; iodine evaporating from this solution (usually a negligible amount) is absorbed by a solution of potassium iodide. The total unreacted iodine is determined by titration with standard sodium thiosulfate.

Materials. SULFUR. One or 2 grams of powdered stick sulfur (Merck & Co. "fused stick" sulfur), contained in a small porcelain boat, served as the source of sulfur. Sulfur in the boat was replenished before each determination.

NITROGEN. Commercial "prepurified" nitrogen (Air Reduction Sales Company) was found satisfactory without further reduction in oxygen content. In most of the cylinders tested, the oxygen content, as determined in a blank run, was only 30 to 60 micrograms per liter of nitrogen; this is equivalent to 0.1 to 0.2 ml. of 0.02 N iodine solution.

SODIUM THIOSULFATE AND POTASSIUM IODATE. Two standard solutions of each, approximately 0.02 N and 0.10 N, were employed.

ABSORPTION SOLUTIONS. The first absorption bottle contained 50 to 75 ml. of distilled water, 1 to 2 grams of potassium iodide, and 0.5 gram of sodium bicarbonate (3). Between 5 and 25 ml. of one of the above solutions of potassium iodate were then added, depending upon the estimated oxygen content of the sample. Finally 10 ml. of 3 N hydrochloric acid were added just before the absorption bottle was put into place.

The second bottle contained 1 to 2 grams of potassium iodide in 50 ml. of water.

MOLYBDENUM TRIOXIDE. Molybdic acid (J. T. Baker Chemical Company, 99.9% molybdenum trioxide) was dried overnight in air at 110° to 120° C.

MOLYBDENUM DIOXIDE, prepared according to the method of Chaudron (2). Molybdenum trioxide (above) was reduced by treatment with an equimolar mixture of hydrogen and steam at 700° C. for 6 hours. Analysis: per cent molybdenum, 76.6 (theoretical, 75.0%).

TUNGSTEN TRIOXIDE. Tungstic acid (J. T. Baker Chemical Company, "purified powder") was dried for 2 hours at 500° to 550° C.

NICKEL OXIDE, prepared by heating nickel carbonate (J. T. Baker Chemical Company) in air for 2 hours at 800° to 850° C. (4).

METAL SULFIDES. A number of metal sulfides and partially oxidized sulfides, having unknown oxygen contents, were employed in this study. These preparations were made with reagent grade chemicals and were therefore expected to contain only the metal in question, sulfur, and oxygen.

Procedure for Routine Analysis. The sulfur boat and the boat containing finely powdered sample (10 to 100 mg.) were placed in a clean, flamed silica tube. Air was removed by evacuation of the tube (laboratory vacuum, approximately 200 mm. of mercury), followed by filling with pure nitrogen; this operation was repeated three times. The furnace surrounding the sulfur was heated to about 280° C. (sulfur vapor pressure about 30 mm. of mercury) while the system was flushed with pure nitrogen, and after that temperature was attained, 1 liter of nitrogen was passed through the system in order to eliminate volatile impurities that may be present in the sulfur.

The nitrogen flow was interrupted, the absorption bottles were put in place, and the flow was resumed at the rate of about 2 liters per hour during heating of the sample furnace according to the following schedule: from room temperature to 500° C. in about 20 minutes; from 500° to 800° C. in about 20 minutes; at 800° to 850° C. for 20 minutes.

When it was desired to continue the reaction and test for complete conversion to sulfide, the flow of nitrogen was interrupted, fresh absorbing solutions were put in place, and the flow of nitrogen was again started. The reaction at 850° C. was continued in this manner for as many additional half-hour periods as desired.

At the end of each reaction period the iodine remaining in the absorption bottles was titrated with standard thiosulfate and the quantity of oxygen equivalent to the iodine reduced was calculated. A correction for the value of the blank was made in each case.

Two reactor tubes in parallel were employed, and four determinations were ordinarily made in 8 hours.

RESULTS

Metal Oxides. Molybdenum trioxide (MoO₃), molybdenum dioxide (MoO₂), tungsten oxide (WO₃), and nickel oxide (NiO) were first tested in an exploratory manner for reactivity with sulfur vapor in order to determine the minimum temperature necessary for complete reaction. The results of these tests are given in Table I. Nickel oxide reacted the most readily, 1 hour at 450° C. being nearly sufficient for complete reaction, while tungsten trioxide was the most refractory of the oxides tested.

Table II. Determination of Oxygen in Pure Metal Oxides

Metal Oxide	Sample No.	Sample Weight, Mg.	Total Reaction Time, Hours[a]	Oxygen Content Found, %
MoO₃, % O (theor.) = 33.3	7	25.1	1	32.5
		14.9	1	32.6
			1.5	34.2
		27.5	1	34.2
			1.5	34.8
WO₃, % O (theor.) = 20.7	8	15.8	1	18.1
			1.5	19.3
			2.0	20.3
			2.5	20.3
		25.0	1	12.2
			1.5	18.2
			2.0	19.2
NiO, % O (theor.) = 21.4	9	22.5	1	21.0
		52.5	1	21.4
			1.5	21.4

[a] Heating schedule. From room temperature to 500° C. in 20 min.; from 500° to 800° C. in 20 min.; at 800° to 850° C. for 20 min. Longer heating times represent prolongation of final temperature.

The results of these preliminary tests indicated that a temperature of 800° to 850° C. was sufficiently high for complete conversion of molybdenum dioxide, molybdenum trioxide, tungsten oxide, and nickel oxide to the sulfides. Accordingly, a series of analyses was made of all these oxides except molybdenum dioxide. The results are shown in Table II. In order to test for completeness of reaction at the temperature used, 850° C., one or two experiments with each oxide were continued for successive half-hour periods beyond the usual reaction time of 1 hour. Additional amounts of oxygen reacting with the sulfur are shown in Table II.

Molybdenum and nickel oxides reacted completely in 1 hour with the temperature schedule shown in the footnote to Table II, and the oxygen contents found were close to the theoretical values. Tungsten trioxide reacted less easily; with the larger sample the reaction was not quite complete even after 2 hours. This difficulty was not experienced with the tungsten oxide–sulfide samples analyzed, 1 hour being adequate for complete reaction (see below).

Metal Oxide–Sulfides. After a suitable procedure had been developed for the oxides, the same method was tested with molybdenum, tungsten, and nickel sulfide preparations of widely different oxygen contents. Determinations were also made of metal and sulfur; a summation of the elemental analyses close

Table III. Analysis of Molybdenum, Tungsten, and Nickel Oxide-Sulfides

Sulfide or Oxide-Sulfide	Sample No.	Analysis			
		Metal	S	O	Summation
		%	%	%	%
Molybdenum	10	59.7	40.5	0.1 0.0 Av. 0.1	100.3
	11	59.0	39.6	0.88 0.92 Av. 0.9	99.4
	12	54.5	42.9	1.60 1.69 Av. 1.6	99.0
	13	58.7	33.7	8.0	100.4
	14	67.6	12.5	19.2 18.7 Av. 19.0	99.1
Tungsten	15	72.5	24.5	2.65 2.77 Av. 2.7	99.7
	16	71.7	25.5	2.82 2.74 Av. 2.8	100.0
	17	73.6	19.9	7.22 6.62 Av. 6.9	100.4
Nickel	18	69.0	31.4	0.42 0.40 Av. 0.4	100.8
	19	..	..	0.86 0.96 Av. 0.9	...

to 100% is then good evidence of satisfactory oxygen determination. Results of these experiments are given in Table III. The samples employed were laboratory preparations of either (1) metal sulfides which were intended to be fairly pure, or (2) partially oxidized sulfides, termed "oxide-sulfides" here, which were made by careful oxidation of the corresponding sulfides. The oxygen analyses of Table III were carried out at a final reaction temperature of 850° C. with the 1-hour heating schedule shown in Table II; longer periods were not found necessary. At least one preparation containing each metal was tested for complete reaction with sulfur by continuing the reaction for an additional half hour at 850° C.; no further reaction was observed. Sample weights were from 20 to 100 mg. The procedure was otherwise as described in the experimental section. Sulfur was determined gravimetrically as barium sulfate. Molybdenum was analyzed by reduction to trivalent molybdenum with zinc and titration with standard permanganate. Tungsten was determined gravimetrically as tungstic oxide, and nickel gravimetrically as nickel dimethylglyoxime. Metal and sulfur were determined in duplicate.

The analytical results in Table III show good agreement in duplicate analyses for oxygen over a range of oxygen contents from 0.1 to 19%. All summations were near 100%. Many similar preparations have been analyzed with equally good results.

To illustrate the data obtained in a typical oxygen analysis, one set of results for sample 16, an oxide-sulfide of tungsten, is given below. A 62.5-mg. sample was employed, and the absorption bottle initially contained 10.00 ml. of 0.01995 N potassium iodate solution.

Equivalent Ml. of 0.02006 N Thiosulfate

In Absorption Bottle			
Before reaction, (a)	After reaction, (b)	Blank, (c)	SO₂ Liberated, (a) − (b) − (c)
9.96	4.25 ·	0.23	5.48

Oxygen in sample = (5.48) × (0.02006) × (16) = 1.76 mg.

$$\text{Per cent oxygen} = \frac{1.76}{62.5} \times 100 = 2.82$$

DISCUSSION

Water interferes in the above analysis by reaction with sulfur to form sulfur dioxide and hydrogen sulfide; each of the latter substances reduces iodine in the absorbing solution and leads to an incorrect, high oxygen content. (Results of control experiments with small amounts of water as an impurity indicate that this reaction proceeds practically to completion under the conditions of the analysis, probably because an excess of sulfur is present.) Hydrogen sulfide formation is readily detected by the appearance of a turbid sulfur sol in the iodine solution.

Samples were therefore dried thoroughly in a stream of inert gas before analysis. Some preparations of molybdenum sulfide and tungsten sulfide had to be dried in place before analysis in order to avoid absorption of atmospheric moisture during transfer to the reaction tube. A trace of water invariably causes a turbid absorption solution, with high results, as mentioned above. Experience with blank determinations indicated that as little as 0.02 mg. of water (equivalent to 0.2 ml. of 0.02 N thiosulfate) will produce turbidity; on the other hand, a perfectly clear or faintly turbid solution is good evidence that no significant error arises from interfering water.

Other possible interferences were not studied, but interference would be expected, for example, (1) from carbon, which may react with oxygen in the sample, resulting in an incorrect, low oxygen content, and (2) from hydrocarbons, which would affect the analysis in a rather complicated manner depending on the products formed by reaction with sulfur and with oxygen in the sample.

The above method of analysis is probably applicable to many other metal oxides and sulfides as well as those of molybdenum, tungsten, and nickel. Other types of compounds containing oxygen and/or sulfur, such as metal sulfates and sulfites, might also be included among the substances to which the method can be applied. The present method is doubtless unsuitable for oxides having unfavorable equilibria for reaction with sulfur, or reacting slowly with sulfur at elevated temperatures, such as beryllium oxide, magnesium oxide, boron oxide, aluminum oxide, titanium oxide, and silica (8).

Because the reaction between sulfur and some metal oxides occurs with difficulty, it would appear feasible to apply the method of analysis to metal oxides reactive with sulfur, supported on unreactive oxides. An attempt was made to determine oxygen in the oxides of molybdenum and nickel supported on activated alumina. By selection of proper conditions for pre-drying the samples and for reaction with sulfur, interference from residual water was apparently eliminated (no sulfur sol formation in the absorbing solution). However, good accuracy was not obtained with either supported oxide. With molybdenum oxide supported on alumina, reaction with sulfur continued slowly beyond the expected end point. The reason for this high result has not been established. With nickel oxide on alumina, the results were lower than theoretical, probably because of formation of a relatively unreactive compound between nickel oxide and the support during the necessary drying operation before analysis.

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Determination of Small Amounts of Silicon in Cathode Nickel

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A method is described for the separation of small amounts of silicon from the major component and interfering elements in cathode nickel by using perchloric acid. The final determination is made by the heteropoly blue procedure recently discussed by Boltz and Mellon.

B ECAUSE the determination of small amounts of silicon in cathode nickel by gravimetric procedures seems to require very large samples, a spectrophotometric procedure in which a much smaller sample is used has been desired. A number of colorimetric procedures had been investigated but did not seem to give consistently reliable results in the hands of different analysts. The "heteropoly blue" procedure of Boltz and Mellon (1) has given consistently reliable results in this laboratory, when used under carefully controlled conditions.

DISCUSSION

Colorimetric methods were first tried, in which no separation of other elements was made. However, because it was noted that as the sample size was increased the percentage of silicon decreased, it was felt that some of the silicon was present in a form that was not acid-soluble. It was found by experiment that some of the elements present in cathode nickel tend to increase and others decrease the sensitivity of the color reaction. Therefore, the determination of silicon in the presence of the major component and other elements was abandoned.

Separation of the silicon from the major component and interfering elements was then tried by dehydration with hydrochloric, sulfuric, and perchloric acids, respectively. But in dealing with such small amounts of silicon, the loss entailed due to necessary washing made the error too high.

The method that finally gave consistently reliable results was to dehydrate the silica with perchloric acid in a platinum dish, filter through a small hydrofluoric acid-treated filter paper, and wash just once with a small amount of 1 to 99 hydrochloric acid. The small amount of other elements left is so small as to be entirely without effect. The filter paper containing the silica is then put back in the platinum dish, oxidized with a small amount of nitric and perchloric acid, evaporated to dryness, and gently ignited. The residue is fused with a small amount of anhydrous sodium bicarbonate, the fusion is taken up in water, the pH is properly adjusted, the solution is diluted to volume, and suitable aliquots are taken for the final determination.

In working with such small amounts of silica, a rather large error was sometimes caused by contamination from glassware. Therefore, all operations were carried out in platinum ware and polyethylene beakers, with exception of the final color development, which was of such short duration that no error was encountered.

APPARATUS AND REAGENTS

Instruments. Beckman spectrophotometer Model DU and pH meter.

Standard. Dissolve 2.5 grams of sodium metasilicate ($Na_2SiO_3.9H_2O$) in water in a stainless steel or polyethylene beaker, dilute to 500 ml., and store in a polyethylene or wax-lined bottle. This stock solution must be standardized by gravimetric determination. Calculate the required amount to make 1000 ml. of solution containing 0.01 mg. of silicon per ml., dilute to nearly

1000 ml. with water, add a small amount of 6 N sulfuric acid to make the solution faintly acid, about pH 6.0, then dilute to 1000 ml., and store in wax-lined or polyethylene bottles.

Ammonium Molybdate. Dissolve 18.8 grams of ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in water containing 23 ml. of concentrated sulfuric acid and dilute to 250 ml.

Reductant. Solution A. Dissolve 2 grams of anhydrous sodium sulfite in 25 ml. of water and add 0.4 gram of 1-amino-2-naphthol-4-sulfonic acid. Solution B. Dissolve 25 grams of sodium bisulfite in 200 ml. of water. Add solution A to solution B and dilute to 250 ml.

Specially Prepared Filter Paper. Immerse Whatman No. 42, 7.0-cm. filter papers or paper of similar quality in 1 to 1 hydrofluoric acid for 15 to 20 minutes and then wash thoroughly.

Polyethylene Beakers. The polyethylene bottles used for hydrofluoric acid have been found very satisfactory after the tops have been removed.

Other Reagents. All other reagents were of reagent grade. Sodium bicarbonate is used for the fusion because it can generally be obtained with higher purity than sodium carbonate and hence results in a lower blank.

PROCEDURE

Calibration Curve. Transfer suitable aliquots of the standard solution containing from 0.01 to 0.06 mg. of silicon to 100-ml. volumetric borosilicate glass flasks, dilute to about 95 ml., and add 1 ml. of 7.5% ammonium molybdate solution. After 5 minutes add 4 ml. of 10% tartaric acid and mix (2). Add 1 ml. of reductant and dilute to the mark. After 20 minutes make transmittancy measurements at 820 mμ, using a blank of the same quantities of reagents in the reference cell. The color is stable for at least 12 hours (1). Plot the transmittancy values obtained against milligrams of silicon per 100 ml. of solution.

Table I. Accuracy of Method

Sample No.	Weight of Sample, Gram	% Si	% Si by Other Laboratories
E-39-45	1.0	0.029, 0.029	0.026-0.040
H-1400	1.0	0.017, 0.017	0.012-0.020
63	0.5	0.022, 0.020	0.03
66	0.5	0.020, 0.022	0.03
71	0.5	0.026, 0.026	0.03
72	0.5	0.022, 0.023	0.03
73	0.5	0.023, 0.025	0.024
74	0.5	0.089, 0.087	0.091
R	1.0	0.22, 0.22	0.22
N.B.S. Al alloy	0.4	0.108	0.108-0.12
80	1.0	0.020, 0.019, 0.019	0.015
81	1.0	0.021, 0.019, 0.019	0.020

Analysis of Unknown. To 1 gram of sample in a platinum dish add about 5 ml. of concentrated nitric acid, cover with a borosilicate cover glass, and heat gently to dissolve. When dissolution is complete, carefully wash down the sides of the dish with a small amount of water, then add about 4 ml. of perchloric acid, replace cover on dish, and evaporate to copious fumes and to as small a volume as possible without allowing the contents of the dish to become solid; if this occurs the separation of silica is always incomplete (3). Cool slightly, until crystallization starts, then quickly dilute with 1 to 99 hydrochloric acid, bringing the volume to a total of 25 to 30 ml. Add a small pinch of the

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specially prepared filter paper pulp to help collect the silica, filter immediately through one of the specially prepared filter papers, and wash once with 1 to 99 hydrochloric acid. Put the paper containing the silica back in the platinum dish, add 5 ml. of concentrated nitric acid and 3 ml. of perchloric acid, cover with the cover glass, and heat gently to oxidize the paper.

After oxidation is complete, wash down the cover and sides of the dish carefully with a small amount of water, continue the evaporation to dryness, and then ignite gently. Fuse the residue with 2 grams of anhydrous sodium bicarbonate, allow to cool, take up fusion with water, and then neutralize and adjust to pH 4.5 to 5.0 with a pH meter, using 6 N sulfuric acid. Keep dish covered while neutralizing, in order to avoid loss from spattering. It was found by experiment that this pH will result in the optimum pH of 1.6 at the point of formation of molybdisilicic acid (1). It will be necessary to have some silica-free ammonium hydroxide on hand to help in adjusting the pH at 4.5 to 5.0. Heat the solution to remove carbon dioxide, cool, and then dilute to 100 ml. The oxides of nickel that will be present soon settle and a clear solution can be pipetted off the top, or if desired, the solution can be filtered through one of the specially prepared filter papers and then diluted to volume. Suitable aliquots are treated as in the preparation of the calibration curve, and transmittancy measurements are made at 820 mμ after 20 minutes. Values are obtained from the calibration curve.

Data. Table I indicates the accuracy of the method; the results are compared to those reported by other laboratories.

SUMMARY

Although to date this method has been used only for determining silicon in cathode nickel and a National Bureau of Standards sample of aluminum alloy, it should be applicable to the determination of silicon in almost any metal or material that is acid-soluble, unless the major component is an element that interferes seriously with the color development. In that case, it would be necessary to wash the filter more thoroughly, determine the loss of silica for the necessary number of washings, and apply a correction in subsequent similar analyses.

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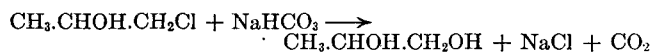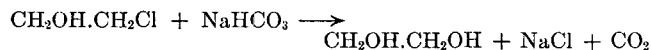# Simultaneous Determination of Ethylene and Propylene Chlorohydrins

W. A. CANNON
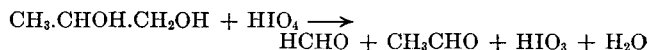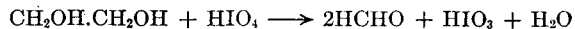
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Ethylene and propylene chlorohydrins are determined simultaneously with an average error of 1.9% for ethylene chlorohydrin and 2.0% for propylene chlorohydrin. The mixed chlorohydrins are hydrolyzed to glycols by heating with sodium bicarbonate in sealed bottles. The glycols are oxidized with periodic acid and the acetaldehyde and formaldehyde are determined polarographically after a simple distillation. The method is applicable to mixtures of ethylene and propylene chlorohydrins in water solution or water-soluble solvents. The principal limitation to the method is that there must not be present or formed any volatile substances polarographically reducible at the same potential range as the aldehydes. The presence of monohydric alcohols or moderate concentrations of hydrochloric acid, aliphatic dichlorides, or dichloro ethers does not interfere with the determination.

ALTHOUGH several methods have been described for the quantitative determination of chlorohydrins, none is applicable to a quantitative determination of ethylene and propylene chlorohydrins in the presence of each other. Trafelet (4) determined total water-soluble chlorohydrins by selective hydrolysis with sodium bicarbonate and titration of the chloride ions liberated. Other methods mentioned in the literature, such as Uhrig's (5) method for determination of ethylene chlorohydrin, cannot be used to distinguish between ethylene and propylene chlorohydrins in mixtures. The method described in this paper consists essentially of hydrolyzing the chlorohydrin mixture with sodium bicarbonate to the corresponding glycols.

$$CH_2OH.CH_2Cl + NaHCO_3 \longrightarrow CH_2OH.CH_2OH + NaCl + CO_2$$

$$CH_3.CHOH.CH_2Cl + NaHCO_3 \longrightarrow CH_3.CHOH.CH_2OH + NaCl + CO_2$$

After neutralization, the glycol mixture is oxidized with periodic acid to give formaldehyde and acetaldehyde according to the following equations:

$$CH_2OH.CH_2OH + HIO_4 \longrightarrow 2HCHO + HIO_3 + H_2O$$

$$CH_3.CHOH.CH_2OH + HIO_4 \longrightarrow HCHO + CH_3CHO + HIO_3 + H_2O$$

The aldehydes produced are removed by distillation and determined polarographically according to the procedure described by Warshowsky and Elving (6) and Whitnack and Moshier (7).

The acetaldehyde produced by periodic acid oxidation is a measure of the propylene chlorohydrin concentration of the mixture before hydrolysis. The ethylene chlorohydrin can be estimated by deducting the formaldehyde produced by the oxidation of propylene glycol from the total formaldehyde produced.

MATERIALS AND APPARATUS

Periodic Acid, 0.5 N. A solution is prepared by dissolving 11 grams of periodic acid (G. Frederick Smith Chemical Company) in distilled water and diluting to 100 ml. This solution should be stored in a dark, glass-stoppered bottle.

Lithium Base Solution. This consists of a solution 1 N with respect to lithium hydroxide and 0.1 N with respect to lithium chloride.

Ethylene and Propylene Chlorohydrins. Eastman Kodak chlorohydrins were used without further purification. By total chlorine analysis each assayed over 98% chlorohydrin.

Polarograph. A Sargent Model XXI polarograph was used for all determinations. Measurements were made at a sensitivity of 0.1 μa. per mm. with damping control off. The polarographic cell was of 25-ml. capacity and immersed in a constant temperature water bath thermostatically controlled at 25° ± 0.1° C.

Distilling Apparatus. The distilling apparatus used consisted of a 100-ml. Kjeldahl flask, spray trap, vertical condenser, and water bath for cooling the receiver.

Citrate of Magnesia Bottles, 350-ml. capacity.

PROCEDURE

Chlorohydrin Hydrolysis. An aliquot of the water, or water-soluble, solution of the sample containing approximately 0.25 gram of total chlorohydrins is pipetted into a 350-ml. citrate of magnesia bottle. Two grams of sodium bicarbonate are added and the solution is diluted to approximately 150 ml. with distilled water. The bottle is sealed and immersed up to the neck in boiling water for 2 hours. The operator should guard against accidental explosion of the bottle when it is heated above room temperature. The bottle is removed from the water bath and cooled gradually to slightly below room temperature.

The contents of the bottle are transferred to a 250-ml. volumetric flask. Concentrated hydrochloric acid is added drop by drop, while the flask is shaken to expel carbon dioxide, until the sodium bicarbonate is neutralized and the solution has a pH of 5 to 7 when tested with pH paper. The solution is then diluted to the mark with distilled water.

Periodic Acid Oxidation. A 50-ml. aliquot of the solution is pipetted into a 100-ml. Kjeldahl flask. Several glass beads, 10 ml. of water, and 3.5 to 4.0 ml. of 0.5 N periodic acid solution are added, and the flask is immediately connected to the trap of the distilling unit.

A 45 × 190 mm. borosilicate glass test tube containing 75 ml. of distilled water is used as a receiver to absorb the aldehydes. The tip of the condenser should extend below the surface of the water at all times during the distillation except for the last 5 to 10 ml. In order to minimize loss of aldehydes, the receiver should be placed in a bath of ice water during the distillation. ·

The contents of the Kjeldahl flask are distilled at the rate of 3 to 5 ml. per minute until about 5 ml. remain in the flask. Near the end of the distillation the receiver is lowered until the tip of the condenser is above the liquid in the receiver. At the conclusion of the distillation the tip of the condenser is rinsed into the receiver with distilled water. The distillate is transferred to a 250-ml. volumetric flask. The polarographic analysis of the aldehyde solution should be carried out without delay.

Polarographic Analysis. Immediately prior to the polarographic determination of aldehydes 25 ml. of the lithium base solution are added to the distillate in the volumetric flask and the contents are diluted to the mark with distilled water. The polarographic cell is rinsed and filled with the solution and allowed to come to constant temperature in the water bath maintained at 25° C. After 10 minutes have elapsed from the time of addition of the supporting electrolyte, the currents at applied voltages of −1.40, −1.61, and −1.89 (dropping mercury electrode versus the mercury pool) are recorded. The wave height produced by the formaldehyde is the difference in current reading between the first and second applied voltages and the wave height due to acetaldehyde is the difference in current reading between the second and third applied voltages.

The wave heights are then compared with the values obtained by carrying through the analytical procedure a sample of known concentration of pure mixed ethylene and propylene chlorohydrins. The relative concentration of ethylene and propylene chlorohydrins in the latter should be approximately the same as in the solution being analyzed.

CALCULATIONS

Propylene Chlorohydrin.

$$Weight \ in \ sample, \ mg. \ = \ Wp \ = \ \frac{Ha \times Wp'}{Ha'}$$

where Ha = wave height produced by acetaldehyde in sample
Ha' = wave height produced by acetaldehyde in standard
Wp' = milligrams of propylene chlorohydrin in standard

% by weight = $100 \ Wp/S$

where S = weight of sample in milligrams

Ethylene Chlorohydrin. Weight in sample, mg. =

$$We = \frac{Hf(We' + 0.4259Wp')}{Hf'} - 0.4259Wp$$

where Hf = wave height produced by formaldehyde in sample
Hf' = wave height produced by formaldehyde in standard
We' = milligrams of ethylene chlorohydrin in standard
Wp' = milligrams of propylene chlorohydrin in standard
Wp = milligrams of propylene chlorohydrin in sample

% by weight = $100 \ We/S$

where S = weight of sample in milligrams

DISCUSSION

Representative data on the analysis of mixtures of ethylene chlorohydrin and propylene chlorohydrin are given in Table I. Using synthetic mixtures of chlorohydrins, the average error was 1.9% for ethylene chlorohydrin and 2.0% for propylene chlorohydrin.

Table I. Simultaneous Determination of Ethylene Chlorohydrin and Propylene Chlorohydrin in Mixtures

Ethylene Chlorohydrin			Propylene Chlorohydrin		
Present	Found	Error	Present	Found	Error
Mg.	Mg.	%	Mg.	Mg.	%
175.8	177.9	+1.2	71.4	70.2	−1.7
175.8	175.6	−0.1	71.4	71.3	−0.1
165.4	170.0	+2.8	81.6	78.8	−3.4
165.4	160.1	−3.2	81.6	84.5	+3.5
162.2	163.0	+0.5	118.5	121.9	+2.9
162.2	166.0	+2.3	118.5	119.0	+0.5
140.4	136.6	−2.7	108.0	103.3	−4.3
140.4	137.4	−2.1	108.0	107.0	−0.9
108.1	112.1	+3.7	118.5	119.0	+0.5
108.1	107.5	−0.6	118.5	123.7	+4.4
103.4	102.4	−1.0	142.8	144.2	+1.0
103.4	101.9	+1.5	142.8	146.0	+2.2
82.6	86.0	+4.1	163.2	162.8	−0.2
82.6	83.2	+0.7	163.2	166.1	+1.8
	Av.	±1.9			±2.0

The lithium base solution is added to the sample just prior to the polarographic analysis in order to minimize the condensation of aldehydes in the presence of the strong base. Constant temperature control is advisable, because it has been shown that the formaldehyde wave height increases approximately 6.5% for each 1° C. rise in temperature (1, 2). The acetaldehyde wave height increases approximately 1.5 to 2.0% per degree rise in temperature (3).

The presence of hydrochloric acid in the sample up to a molar concentration equal to that of the chlorohydrins does not interfere with the determination. The following aliphatic chlorides and chloro ethers have been checked for interference and found not to hydrolyze under the conditions used in this determination: dichloroisopropyl ether, dichloroethyl ether, propylene dichloride, and ethylene dichloride. The presence of these materials in moderate amounts therefore does not affect the chlorohydrin analysis. The sample must not contain or produce on periodic acid oxidation any volatile substance polarographically reducible at the same potential range as formaldehyde and acetaldehyde.

This method has been found applicable for analyses of chlorohydrins in aqueous solutions or water-soluble solvents such as alcohol, but not to analyses of chlorohydrins in water-insoluble solvents. For such solutions the solvent must be removed by distillation or the chlorohydrin extracted by water.

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Determination of Surface-Active Substances in Refined Sugar

Classification by the Polarographic Method

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The polarographic method, owing to its great sensitivity, makes it possible to determine the surface-active substances in refined sugar. These substances represent organic nonsugars in the sample under investigation. It has been ascertained by means of about 850 analyses that the content of surface-active substances, expressed numerically in special units, is a very important constant of the sample and consequently it forms a new and suitable basis for the classification of refined sugars.

THE analysis of refined sugar has been the subject of a large number of studies and publications which have led to exact and convenient methods. Considerably less attention has been paid to the determination of surface-active substances in refined sugars, though this subject has proved of great importance, especially in studies of the surface tension of sugar solutions, and in the sugar-consuming industries.

Because of the very low content of surface-active substances in refined sugars, only highly specific and sensitive methods may be used for their determination. Heyrovský's polarographic method (1), used for the first time in sugar analysis by Šandera and Zimmermann (3), proved most suitable for this purpose.
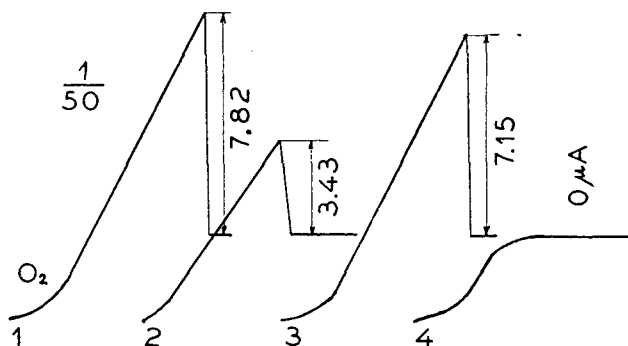
Figure 1. Current-Voltage Curves

Under certain conditions, polarographic current-voltage curves with so-called maxima (Figure 1) are encountered, which are most readily suppressed by the surface-active substances. This occurs to an extent such that it is usually possible to detect them in concentrations as low as 10^{-6} molarity. It has been found that the formation of polarographic maxima and their suppression by the surface-active substances are essentially an adsorption phenomenon (1).

The original method has been improved and extended by the author, and the polarographically determined content of the surface-active substances in refined sugar—i.e., the "polarographic purity"—has been made the basis for its classification. About 850 analyses made with individual samples during 7 years have proved that this polarographic purity is a very important property of refined sugars. It is an excellent characteristic of these sugars, especially in connection with the ash content of any individual sample.

Table I. Conditions for Polarographic Analysis

Concentration of sugar in solution, g./100 ml.	26.0 ± 0.05 or 6.5 ± 0.01
Electrolyte	0.002 N K₂SO₄
Diameter of capillary, mm.	0.08 ± 0.001
Drop time, t, sec.	3.30 ± 0.05
Temperature, ° C.	20.0 ± 0.3

EXPERIMENTAL

A solution of 26.0 grams of the sugar in 100 ml. of 0.002 N potassium sulfate solution is prepared with distilled water of highest purity, and is analyzed with free access of air, from 0 to −1.0 volt. The potassium sulfate electrolyte forms a very pronounced oxygen maximum, which is readily suppressed by the surface-active substances in the sample, lowered by the increased viscosity of the solution, and therefore varies inversely with the content of surface-active substances in the sugar. By analyzing under uniform conditions, it is possible to determine the content of the surface-active substances through comparison of the heights of the maxima, h. Comparable precision of these determinations is not attainable by any other method (5). The value of h is measured from the highest point of the curve to the upper part of the teeth of the oxygen diffusion current, and expressed in microamperes (see Figure 1).

The height of the polarographic maximum, h, often depends very much on the conditions of the analysis. In order to be able to compare the results directly, it is necessary to carry out the analysis under uniform conditions. The conditions which gave the best results are summarized in Table I.

The drop time, t, has to be determined in the solution under investigation, without the application of external e.m.f. The lower concentration (6.5 grams) is used if the maximum in a 26-gram solution is lower than about 5 mm.

The polarographic method is extraordinarily sensitive. Special attention must therefore be paid to the occasional presence of minute traces of surface-active substances, introduced during the preparation of the solution for analysis and therefore not present in the sample under investigation, which may affect the results. It is necessary to use only purest analytical reagents for the preparation of the electrolyte, to keep the equipment scrupulously clean, and to work only with mercury of highest purity and with a clean surface. It is advisable to analyze a special standard sugar of exactly known height of oxygen maximum for the first curve of a series of samples, to make sure that the results are perfectly reliable. If all the described conditions are maintained with care (the change in the value of h due to variations in the atmospheric

pressure may usually be neglected), the variation in h does not exceed ± 2 mm.

For the classification of refined sugars by the polarographic method, the content of surface-active substances must be known as exactly as possible. Consequently, it is necessary to have a polarographic zero standard sugar which is practically free of surface-active substances. In the first series of experiments a refined sugar of the highest technical purity was used. It had a higher polarographic purity than any one of the 850 analyzed samples, but in order to have a still more reliable basis for the numerical classification, a sample of purest sucrose was prepared. This sample did not contain any surface-active substances, within the limits of the sensitivity of the polarographic method, because special care had been taken to ensure their complete removal. This zero standard sugar was prepared by making use of the adsorptive properties of specially purified active carbon (carboraffin), followed by recrystallization from ethyl alcohol and ether (4).

It seemed most appropriate for the numerical expression of the surface-active substances in refined sugars to work out a uniform scale of suppressive effects of some surface-active substances under uniform conditions (Table I). Such a scale may be worked out readily by adding increasing quantities of such a contaminant substance to the solution of the polarographic zero standard sugar. The dependence of h on the concentration of the suppressive agent in the solution can best be demonstrated graphically, and the equations of the curves can be calculated, or often deduced from Langmuir's adsorption isotherm (4). By measuring the h of the solution under investigation, and by comparing it with the standard scale, it is possible to determine easily the amount of surface-active substances in the refined or other sugars, in terms of the standard scale.

A standard beet sugar molasses has been used as the suppressive agent. The results for the sugar in solution were expressed either as milligrams per cent of molasses (referring to the standard technical refined sugar), or as milligrams per cent of corrected molasses (referring to the polarographic zero standard sugar) (5). Because of the somewhat different effects exhibited by different beet molasses, two "model" scales have been proposed. These make it possible to express the results, if desired, in special units which are practically independent of the different suppressive effects of molasses. The results may thus be related easily to a new basis and compared with those obtained with the standard molasses.

The first model scale is based on methyl orange (Merck), the results being expressed in mg. % × 100 of methyl orange on the zero standard sugar in solution (conditions as in Table I). The second model scale is completely independent of any suppressive agent. The amount of surface-active substances in the zero standard sugar is here set equal to 0, and the amount of these substances in a sample completely suppressing the maximum (conditions as in Table I) is set equal to 100. The relation between h and the amount of the surface-active substances in the solution is assumed to be linear, to simplify the evaluation of the results. The polarographic test (P.T.) of the sugar may then be calculated by means of the expression:

$$P.T. = \frac{(h_s - h) \times 100}{h_s}$$

where h_s is the height of the maximum of the polarographic zero standard sugar ($h_s = 14.23$ microamperes).

The molasses scale is very comprehensive, and is preferred by the author. The model scales should be used only for comparing accidental discrepancies in the results.

The numerical values, in terms of the standard corrected molasses scale together with some values in terms of the model scales for comparison, are shown in Table II (conditions as in Table I).

In order to simplify the procedure for expressing the results in

Table II. Scales for Polarographic Analyses

(Using 26 grams of sugar in 100 ml. of 0.002 N K_2SO_4)

h, μa.	Corrected Molasses, Mg. %	Methyl Orange, Mg. % × 100	P.T.
14.23	0	0	0
11.58	10	15	19
8.82	30	34	38
7.72	50	43	46
5.67	100	65	60
3.53	150	98	75
1.51	200	172	89
0.00	235	350	100

Table III. Polarographic Analyses of Sugars from Different Liquors

Sugars Equivalent to Purity of Refined Sugars from		Corrected Molasses, Mg. %	Ash, Mg. %
I	Liquor	<80	<8
II	Liquor	50–110	8–12
I + II	Liquor	<110	<12
III	Liquor	100–130	12–16
II	Liquor + thick juice	130–180	14–20
	Thick juice alone	>180	>20

some of the above-mentioned units, it is advisable to make an exact graph of the values summarized in Table II. To express h in microamperes, it is necessary to know the full sensitivity of the galvanometer, because the height of the maximum on the polarogram can be directly measured usually only in units of length, and not in microamperes. The following example may clarify the method of calculation:

The full sensitivity of the author's galvanometer was 2.52 × 10^{-9} ampere per 1 mm. on the polarogram. A sample of refined sugar had under standard conditions (see Table I), using $^1/_{50}$ of the full sensitivity, the height of the oxygen maximum, h, equal to 45 mm. This equals $2.52 \times 10^{-9} \times 50 \times 45 = 5.67$ microamperes. Comparing this result with Table II, we find the following content of surface-active substances in the sugar under investigation: 100 mg. % corrected molasses, 0.65 mg. % methyl orange, or P.T. equal to 60. Using the above equation, we have:

$$P.T. = \frac{(14.23 - 5.67) \times 100}{14.23} = 60$$

in good agreement with Table II.

Table III presents the averages of about 250 analyses of refined sugars from the years 1940 to 1942. "Ash" means conductometrically determined content of inorganic salts (2).

The average ratio, f, between the polarographic purity and the ash content—i.e., the approximate ratio between the "molasses content" and the inorganic salts—is in normal samples, as expected, between 8 and 12 (average 9.83). The calculation of f seems to be very suitable for judging the normal course and the unusual interferences during the production of the sample under investigation.

The lower the polarographic purity of the sugar—i.e., the higher the milligrams per cent of corrected molasses—the worse is the quality of the sample, and vice versa. The differences in the average results for the various classes of sugar in Table III are comparatively great. They are in good agreement with the quality of the raw materials used for the production of the various types of sugar, and demonstrate the practical value of the above-described classification.

As little as 1.3 grams of sugar may be sufficient for the polarographic analysis. Each analysis, with the development of the polarogram, takes about 15 minutes, and the results are precise to about ±4%.

A characteristic polarogram of four different refined sugars, at a concentration of 26 grams in 100 ml., is shown in Figure 1 (conditions as in Table I), depicting the following results:

	Curve h, μa.	Corrected Molasses, Mg. %	Ash, Mg. %	f	Quality
1	7.82	49	5	9.8	I
2	3.43	153	15	10.2	III
3	7.15	64	6	10.6	II
4	0.00	>235	28	>8.4	IV

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Determination of Cerium

Photometric Method with Radiometric Correction

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A rapid method has been developed for the estimation of small amounts of cerium in mixtures of rare earths and other elements, based upon a separation of part of the cerium in pure form, followed by a spectrophotometric determination of the cerium and a measurement of the efficiency of the recovery process with a radioactive tracer. The procedure takes about 4 hours, and under the conditions used is accurate to about 1.8%. A method of counting radioactive liquid samples with an end-window Geiger tube to a reproducibility of better than 0.5% is reported. Applicability of the combined photometric-radiometric technique as a general method for determination of trace amounts is discussed.

THE direct determination of a constituent in complex mixtures is often not possible because other substances which are present interfere in the measurement. At the same time, the quantitative separation of the element to be analyzed may be prohibitively difficult. Long procedures and many repeated steps are sometimes necessary to ensure complete recovery of a small amount of an element from macroquantities of other materials. However, it is frequently possible to separate part of the substance in very pure form in only a few steps. If some independent method is available for determining the efficiency of the separation procedure, a short-cut method may be developed which will greatly reduce the time necessary for a complete analysis. Because measurements of radioactivity afford a simple indication of the efficiency of a recovery process, the availability of radioactive isotopes of many elements offers opportunities for the development of such procedures.

This technique has been used by other workers. Hevesy and Hobbie (3), for example, applied it in the determination of microgram amounts of lead in rocks, and it is used in modified form in the isotope dilution method of analysis (7). However, except in unusual circumstances, the methods available up until the present have not permitted the use of radioactive tracers in precise analytical work. It is the purpose of this paper to illustrate the potentialities of the general procedure as an analytical tool of high precision when good techniques for measuring the radioactivities are employed.

The present paper describes the determination of small amounts of cerium in mixtures containing rare earths and other elements with which cerium is often associated. The activity used is Ce^{144}, which decays according to the following scheme:

$$Ce^{144} \xrightarrow[\beta- = 0.348 \text{ mev.}]{275 \text{ days}} Pr^{144} \xrightarrow[\beta- = 3.07 \text{ mev.}]{17.5 \text{ minutes}} Nd^{144}$$
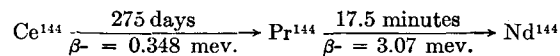
A known number of counts per minute per milliliter of active cerium are added to the cerium-containing sample, and the cerium

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is separated by precipitation as ceric iodate, ceric hydroxide, and perceric hydroxide, the number and order of precipitations depending upon the other constituents of the solution. The separated cerium is then determined spectrophotometrically by measuring the color of ceric ion in sulfuric acid solution. The completeness of recovery of the cerium is found by measuring the number of counts per minute per milliliter in the final solution. The radioactive isotope was available in sufficiently high specific activity so that the amount needed to give a convenient activity in the solution did not affect the spectrophotometric determination.

The over-all accuracy with which an analysis of this type can be carried out depends, of course, on the errors involved in the determination of the separated element and in the measurement of the activities. Up until the present, the limiting factor has generally been the activity determinations, because most of the techniques in common use for this purpose are accurate to only 2 to 5%. It was felt, therefore, that a necessary preliminary to the analytical work was the development of a precise and reproducible method of counting radioactive samples similar to the ones found in this study.

ACTIVITY DETERMINATIONS

Geiger Tubes. As part of the investigation of the factors influencing the determination of the radioactivity of a sample, a study was made of the characteristics, reproducibility, and stability of several commercial Geiger tubes of various designs. In order to be useful in precise analytical work, a tube must count reproducibly to within the limits of error desired for the experiment, and it should be stable during the period of the investigation. Wide variations were found among the tubes tested, and many tubes were completely unsuited for use in the present work. Some of the tubes could not reproduce the activity of a given sample to better than 5 to 10%. Most of these tubes showed a marked voltage hysteresis effect—that is, the counting rate for a given sample depended upon whether the

operating voltage of the tube was approached from above or below, and upon the time the tube was maintained at constant voltage. Photosensitivity was observed with some tubes; this was a disturbing effect even with completely shielded tubes, because light which entered when the shield was opened to change samples caused a rise in counting rate which persisted for several minutes after the shield was closed. The effect was observed regardless of whether or not the scalers connected to the Geiger tubes were operating. High humidity caused most of the tubes that were tested to count spuriously. This factor was controlled by keeping a good, dust-free drying agent in the counting shield at all times, and, on extremely moist days, by blowing a slow stream of dry air through the shield.

The tubes finally selected for use in the analytical work were models No. 100C and 200C, manufactured by the Amperex Electronic Corporation, Brooklyn, N. Y. These are end-window tubes with thin mica windows; they were used inside lead shields of standard design (2), which kept the background count at about 15 counts per minute. The tubes showed no voltage hysteresis and no photosensitivity; the humidity effect was controlled as above. Four of these tubes showed equally good characteristics. A uniform sample counted 38 times over a 2-month interval in a 200C tube gave a standard deviation of the mean of 0.1%. Hence, the Geiger tube was not the limiting factor in determining the accuracy of the experimental results. This discussion illustrates the care which should be taken in selecting a tube for use in an analytical study.

Preparation of Samples for Counting. Self-scattering and self-absorption effects made it impossible to obtain counting reproducibility of better than 2 to 5% with active samples mounted as solids, when the sample contained more than 1 or 2 mg. of material. Many different techniques were tried in order to reduce these errors to a minimum. It was found, however, that by using liquid samples, these sources of error could be avoided.

One-milliliter samples were placed in aluminum or copper cups 20 mm. in diameter and 4 mm. deep, and the liquid surfaces were covered with thin lacquer films. One lacquer which was used was Zapon 1233-D, diluted 5 times with Zapon Thinner 20, but several other commercial lacquers and thinners were found to be equally useful. Eight drops of the diluted lacquer were carefully placed on the surface of the solution and allowed to harden (about 30 minutes). The cups were then mounted on cards and placed in the conventional shelf arrangement (2) for counting with an end-window tube.

The lacquer technique cannot be used with concentrated acids or bases, but solutions of dilute acids and bases are easily handled. If the cups react with the solution to be counted, they may be coated with lacquer before use. Even though a 1-ml. sample represents an infinitely thick layer for β-particles of moderate energy, it is best to measure the volume of the solution accurately in order to be sure that the surface area and counting geometry of the sample remain constant. For β-energies greater than 0.5 m.e.v., the counting rate is not sensitive to small variations in the densities of the solutions. Carrier-free activities tend to adsorb on the bottom of the cup or on the lacquer film, and it is therefore advisable to have a few milligrams of carrier ion in the solution for the activity being counted. It is desirable that the solution counted as the "standard" in the analytical investigation have approximately the same composition as the solution being analyzed.

The method was tested with a series of β-emitting isotopes of different β-energies, and it was found that isotopes with β-energies of about 1 m.e.v. or higher could be counted with an average precision of 0.5% or better. Lower β-energies resulted in slightly poorer precision because of the greater influence of sample and film thicknesses on the counting rate. The detailed results of these experiments will be published elsewhere, but some typical results with Ce^{144} are presented in Table I (the 3.07 m.e.v. Pr^{144} β- is counted). Each group of four numbers in column 2 of this table represents an independent solution. Four samples were taken from each solution; each sample was counted three times, and the averages are shown in the table. The agreement among these four samples in each case, as shown in columns 3 and 4, indicates the reproducibility of this method of sample preparation for the activity used in this investigation. The data in Table I are the counting results which were obtained as part of one determination of cerium (run I in Table II).

The activity determinations in the analytical work were completely empirical. For each run, samples were prepared having the expected final composition of the solution to be analyzed, assuming complete recovery of the cerium. The activity of this solution was taken as the "standard" in each case and compared with the activity of the "unknown." All counting samples were prepared in triplicate or quadruplicate, each was counted three

Table I. Precision of Liquid Counting Method

Soln.	Counts/Min.	Mean Counts/Min.	% Std. Deviation
Standard	3375 3360 3363 3355	3363 ± 4	0.1
	3122 3149 3138 3112	3130 ± 8	0.3
	3051 3067 3037 3066	3055 ± 7	0.2
	3188 3191 3175 3183	3184 ± 4	0.1
4	3168 3151 3104 3128	3138 ± 14	0.4

Errors represent standard deviations of mean. Each figure in column 2 represents average of three counts on independent sample.

Table II. Determination of Cerium

Run	Cerium Taken Mg.	Cerium Found (Spectro.) Mg.	Std. Dev. %	Recov. Tracer (Radiom.) %	Std. Dev. %	Corrected Cerium Mg.	Std. Dev. %	Exptl. Error %
I A	8.026[a]	7.44 ± 0.08 7.30 ± 0.08	1.1 1.1	93.1 ± 0.3 90.9 ± 0.2	0.3 0.2	7.99 ± 0.09 8.03 ± 0.09	1.1 1.1	−0.5 0.0
I B	16.05[a]	15.11 ± 0.17 14.81 ± 0.09	1.1 0.6	94.7 ± 0.1 93.3 ± 0.2	0.1 0.2	15.96 ± 0.18 15.87 ± 0.09	1.1 0.9	−0.6 −1.1
II	0.1892[b]	0.00974 ± 0.00056 0.03432 ± 0.00058 0.0963 ± 0.0006 0.0981 ± 0.0006	5.7 1.7 0.6 0.6	5.11 ± 0.04 18.08 ± 0.07 50.13 ± 0.04 52.13 ± 0.02	0.7 0.4 0.7 0.4	0.191 ± 0.011 0.1897 ± 0.0034 0.1921 ± 0.0017 0.1884 ± 0.0013	5.7 1.8 0.9 0.7	+0.8 +0.3 +1.7 −0.4
III	1.605[c]	0.753 ± 0.015 1.046 ± 0.015 0.996 ± 0.014 0.924 ± 0.029	2.0 1.4 1.4 3.1	46.82 ± 0.02 65.99 ± 0.03 61.84 ± 0.02 57.97 ± 0.02	0.5 0.5 0.4 0.4	1.613 ± 0.034 1.588 ± 0.024 1.614 ± 0.024 1.598 ± 0.050	2.1 1.5 1.5 3.1	+0.5 −1.1 +0.6 −0.4
IV	1.605[d]	0.775 ± 0.016 0.814 ± 0.014 0.858 ± 0.015	2.0 1.7 1.7	48.42 ± 0.04 50.53 ± 0.04 53.49 ± 0.03	0.8 0.7 0.5	1.601 ± 0.035 1.610 ± 0.029 1.604 ± 0.029	2.2 1.8 1.8	−0.3 +0.3 −0.1

Errors in columns 3, 5, and 7 represent standard deviations of mean. Columns 4, 6, and 8 show corresponding percentage values. Column 9 represents percentage differences between known mg. of cerium in solutions and experimental values.

[a] Soln. contained 60 mg. La as nitrate.
[b] Soln. contained 0.6 mg. La as nitrate.
[c] Soln. contained 20 mg. Nd, 18 mg. Sm, 20 mg. Th as chlorides, plus 30 mg. La as nitrate.
[d] Soln. contained 20 mg. Fe as nitrate, 20 mg. V as NH_4VO_3, and 20 mg. Cr as $K_2Cr_2O_7$.

times, and the efficiency of the counter was checked by counting a uniform standard (radium E in equilibrium with radium D) at frequent intervals. The duration of each measurement was sufficient to give a minimum of 10,000 counts (1% standard deviation as calculated from the square root of the number of counts taken) except in the case of the first sample in run II (Table II). For this sample, about 400 counts were recorded each time. All observed values were corrected for background, coincidence errors, and variations in counter efficiency. The average percentage standard deviation of the mean for the samples counted in this work is 0.4% with a spread of 0.1 to 0.7%. The counting results are used as a ratio of two counts, representing the percentage recovery of the cerium, and the average of the percentage standard deviation of the mean for these results is 0.5% (see below for definitions of terms and methods of calculation). The individual absolute values are shown in Table II, column 5.

SPECTROPHOTOMETRIC DETERMINATION OF CERIUM

Reagents and Apparatus. Reagent grade ceric ammonium nitrate (G. Frederick Smith Chemical Co., analytical or reference purity) was precipitated three times with ammonium hydroxide and dissolved in sulfuric acid. The cerium was then precipitated as ceric iodate according to the standard procedure outlined below. The final ceric hydroxide precipitate was dissolved in 0.1 N sulfuric acid. The solution was standardized against reagent grade arsenious oxide and found to contain 8.026 $\pm$ 0.004 mg. of cerium per ml. This solution was used to prepare the standard curve for the spectrophotometric method and to make up the test solutions which were analyzed for cerium. All other reagents were c.p. grade and were used without further purification. Spectrophotometric measurements were made with a Beckman Model DU spectrophotometer, using matched silica cells of 1.002-cm. light path.

Method of Analysis. Sandell (5) lists three methods for the photometric determination of cerium, and of these, the color of ceric ion in sulfuric acid solution was found to be the most adaptable for accurate routine measurements.

The cerium solution, sufficient to give a final concentration of less than 27 p.p.m. of cerium in a volume of 10 ml., is placed in a test tube and a solution of 0.2 gram of ammonium persulfate in 1 ml. of water, 1 ml. of 10 N sulfuric acid, and 1 drop of 0.05 N silver nitrate are added. The mixture is diluted to 10.00 ml. and heated in boiling water for 10 minutes, or until all the persulfate ion is decomposed, cooled to room temperature in tap water, and transferred to the cuvette for measurement. Variations in the temperature of the tap water do not affect the optical densities of the solutions. The optical densities remain constant for several hours after the solutions are prepared.

An optical density vs. wave-length curve for ceric sulfate in 1 N sulfuric acid is shown in Figure 1. The curve shows a pronounced maximum at 315 mμ; this is in agreement with Sandell's suggestion (5) that the sensitivity of the method might be improved by working in the ultraviolet rather than the visible portion of the spectrum. The rise in the curve below 250 mμ marks the beginning of a broad absorption band characteristic of many of the rare earths, nitrate, and other common ions. Ions such as iron, dichromate, vanadate, and some of the rare earths absorb at 315 mμ and must be removed before any determination of cerium can be made at that wave length. Persulfate ion in large amounts gives a slight absorption at 315 mμ, but none of the other constituents present in the solution whose optical density is measured absorb at 315 mμ. This wave length was therefore used for all the analytical work, and the persulfate ion was destroyed before the optical density was determined in each case.

A plot of optical density vs. concentration of cerium follows Beer's law for concentrations up to at least 26 p.p.m. In Figure 2 the data are plotted according to the method of Ringbom (4) as discussed by Ayres (1). The concentration range in which the maximum accuracy can be attained in the determination is represented by the linear portion of this curve, and extends from about 6 to 19 p.p.m. of cerium. The accuracy in this region, as
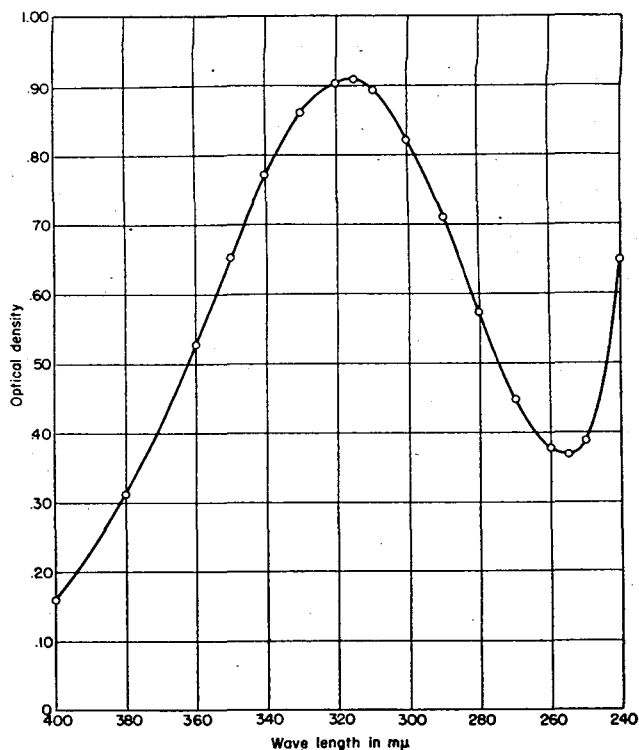

Figure 1. Absorption of Ceric Sulfate Solution

20 p.p.m. of ceric sulfate in 1 N sulfuric acid

evaluated from the slope of the curve, is 2.86% per 1% absolute photometric error. All optical density determinations on "unknown" samples which were analyzed for cerium were made in triplicate, and each sample was measured three times. The average of the percentage standard deviations of the mean of the experimental values is 0.6%, with a spread of 0.2 to 2.0%. Hence, the average percentage standard deviation of the mean for the observed concentrations of cerium as calculated from these data is 1.7%. The individual absolute standard deviations of the mean are shown in Table II, column 3.

SEPARATION OF CERIUM

The basic procedure for the separation of cerium, active and inactive, from solutions containing only other rare earths, is as follows:

To a sample volume of 1 to 5 ml. are added a known number of counts per minute of active carrier-free cerium (radiochemically pure, obtainable from the Atomic Energy Commission), 8 ml. of concentrated nitric acid, 10 drops of 1 M sodium bromate, and 20 ml. of 0.35 M iodic acid. The precipitate of ceric iodate is cooled in ice, centrifuged, washed with water, and dissolved in 1 drop of concentrated hydrochloric acid, 1 drop of 35% hydrogen peroxide, and 8 ml. of concentrated nitric acid. The precipitation of ceric iodate is repeated twice more in order to remove small amounts of rare earths which may be coprecipitated from the original solution with the ceric iodate, and the resulting nitric acid solution is diluted with water and neutralized with concentrated sodium or ammonium hydroxide. It is necessary to destroy all the hydrogen peroxide by shaking and heating the solution before the neutralization is begun, in order to prevent the precipitation of perceric hydroxide, which is difficult to redissolve. The precipitate of ceric hydroxide is washed, dissolved in dilute sulfuric acid, and reprecipitated with dilute ammonia. Finally, this precipitate is washed, dissolved in sulfuric acid, and diluted to some standard volume in 0.1 N sulfuric acid, and aliquots are taken for the spectrophotometric and radiometric determinations. The standard volume which is chosen in each case depends upon the expected concentration of the cerium and the amount of activity which is used.

Thorium acts as a carrier for ceric ion and will follow it through the procedure outlined above. Large amounts of thorium tend to make the iodate precipitates bulky and cause some interference in the spectrophotometric and radiometric determinations. In such cases, it is therefore desirable to remove the thorium.

To the original solution are added a known amount of carrier-free active cerium, 8 ml. of concentrated nitric acid, 1 drop of 35% hydrogen peroxide, and 3 ml. of 3.5 M iodic acid. The precipitate of thoric iodate is washed with a mixture of nitric and iodic acids and discarded. Two milliliters of 1 M sodium bromate and 2 ml. of 0.35 M iodic acid are added to the liquid, and the resulting precipitate of ceric iodate is treated as before.

The iodate precipitation will separate cerium from most of the di- and trivalent cations. It was found, however, that cerium is not separated from iron, dichromate, and vanadate in this way, so that a different procedure is necessary. One milliliter of potassium tartrate solution (0.3 gram per ml.) and a small amount of dilute sulfuric acid are added to the sample, and concentrated ammonium hydroxide is added dropwise until the solution is alkaline. One drop of 35% hydrogen peroxide is then added, with vigorous shaking. The precipitate of perceric hydroxide is centrifuged and washed with water until the washings are colorless and neutral. One drop of concentrated hydrochloric acid, 1 drop of 35% hydrogen peroxide, and 2 ml. of concentrated nitric acid are added to the precipitate, and 1 M sodium bromate is added dropwise with vigorous shaking until the peroxide is destroyed and the solution is clear (about 5 minutes). Ceric iodate is then precipitated by the standard method. The precipitation of perceric hydroxide from an alkaline tartrate solution affords a convenient separation of cerium from many metals.

EVALUATION OF ACCURACY

The precision of the radiometric and spectrophotometric determinations has been evaluated above in terms of the percentage standard deviations of the means of the observed results. The standard deviation of the mean of a series of data is defined by

$$\sigma = \left[\frac{\sum_{i=0}^{n} (r_i)^2}{(n)(n-1)} \right]^{1/2}$$

where r is the residual, or difference between the average value and each of the individual determinations, and n is the number of measurements. Defined in this way, σ is a measure of the reliability of a mean value calculated from a series of determinations, and hence indicates the precision with which the analysis, can be performed. The percentage recovery of the cerium and the final corrected amount of cerium in the sample are both found as quotients of two independent experimental quantities. The standard deviation of a quotient or product is defined by

$$\frac{\sigma_Q}{Q} = \left[\left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2 \right]^{1/2}$$

That is, the percentage or fractional standard deviation of a product or quotient is the square root of the sum of the squares of the individual percentage standard deviations. In Table II are presented the results of four independent determinations of cerium. The rare earths and other ions present in runs III and IV are those with which cerium is commonly associated, and which are likely to interfere in spectrophotometric estimations of cerium. The σ values for sample 1 in run II and sample 4 in run III are relatively large compared to the other results, because of the errors in the spectrophotometric measurements on these samples. By applying Chauvenet's criterion of statistical reliability, it can be shown that these results should be neglected in calculating the most reliable mean value of σ for the analytical method. The average value of the percentage standard deviation of the mean for the final results is then 1.4 $\pm$ 0.5%, and this figure may be taken as a measure of the statistical reliability of the analytical method. The deviation in this value (0.5) represents the standard deviation of the individual errors used in computing the mean value, and is calculated from the formula

$$\sigma_x = \left[\frac{\sum_{i=0}^{n} (r_i)^2}{n} \right]^{1/2}$$

Good discussions of the statistical theory involved in the above calculations may be found (2, 6).

In the last column of Table II are listed the percentage differences between the known compositions of the solutions and the experimental values. The percentage average absolute error is 0.6 $\pm$ 0.4%, and the standard deviation is calculated as described above. The individual errors are about equally distributed between positive and negative values, and the absolute error is well under 1%. The fact that the results are more accurate than could be predicted from the statistical reliability of the experimental values is probably partly fortuitous, but the precision and accuracy of the method compare favorably with other procedures for the direct determination of small amounts of cerium.

The data illustrate the great range of applicability of the method. Within the limits indicated above, the method is useful over at least a hundredfold change in concentration of cerium, and over a 90% change in percentage recovery of the cerium. All the work was done as rapidly as possible, and no special effort was made to ensure complete recovery of the cerium at any time. The time needed for a complete separation of cerium, in quadruplicate, is about 1.5 hours or less. The spectrophotometric and radiometric measurements can be done concurrently; the time needed will depend on the number of samples counted and their activities, but will in general average about 2 to 3 hours. Hence, the total time needed for a complete analysis of a cerium sample by this method may be estimated at about 4 hours. The laborious and lengthy procedure necessary to determine cerium by a conventional spectrophotometric method, ensuring complete recovery of the cerium in each sample, would require at least twice this much time.
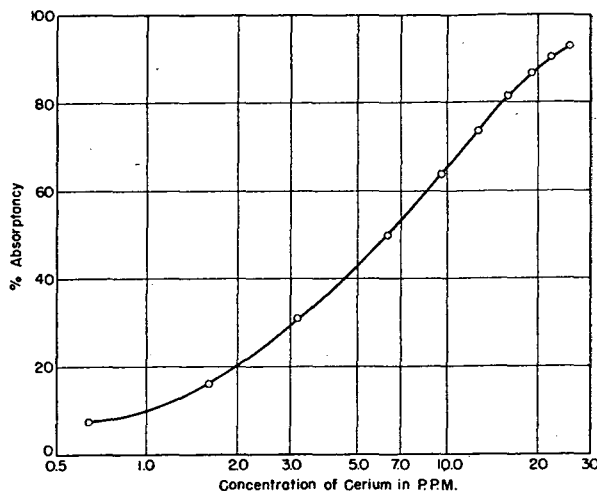

Figure 2. Calibration Curve for Ceric Sulfate Plotted According to Method of Ringbom

The radiometric correction method is a general one. It can be applied to the analysis of any element for which there are available (1) a suitable carrier-free radioactive isotope, (2) an accurate and reproducible method for measuring the activity, (3) a procedure for separating at least part of the element from substances which would interfere in its determination, and (4) an accurate method for determining the element. The counting technique described here should be very useful for precise work with

many isotopes having β-energies greater than 0.5 m.e.v., and many other counting methods are also available for both low and high energy β-emitting isotopes. If some other mounting technique is used, it is of course necessary to standardize it and determine its reproducibility, which for many commonly used methods is low and would be the limiting factor in establishing the precision of the analysis. With any technique, the counting conditions must be rigidly standardized in order to ensure reliable and reproducible results.

In choosing a radioactive isotope for use in a procedure of this type, it is well to be aware of possible effects of daughter activities on the counting rate. If the isotope decays to a stable isotope or to one whose radiations are too weak to influence the measured activity of the sample, no difficulty should be encountered. If, on the other hand, the parent isotope decays to a daughter whose activity influences the total activity, the ratio of the half-lives of the two isotopes will determine the activity to be expected at any time. The relationships in such a situation may become complicated; a good discussion of the various possibilities has been given (2, Chap. V). Care must be taken to be sure that the active and inactive forms of the element that is being determined are in the same chemical state when any separation is made. If this is not the case, and complete exchange between active and inactive atoms does not occur, the isotopes may be separated during the course of the procedure, thus giving erroneous results. Another factor to be considered in choosing an activity is that if the half-life of the parent is so short that the activity decays appreciably during the time of the experiment, a suitable correction must always be made. The specific activity of the isotope must be high, so that the amount of the element that is added to the sample being analyzed does not influence the determination of the element. If the substance which is to be determined contains radioactive impurities which are carried through the separation procedure and influence the final counting rate, erratic results may be obtained. However, if the impurities can be determined independently, and their radiations characterized, appropriate corrections can be applied to the final observed activities,

or absorption techniques can be used to separate the activities due to the impurities (2).

Because there are procedures available for the determination of virtually every element in the absence of all interfering substances, the basic chemical problem involved in any analysis is the separation of the desired constituent in a mixture from other materials which would interfere in its determination. Quantitative separations of many elements, particularly in trace amounts, are often laborious and time-consuming, and in some cases, impossible. It is in such situations that the radiometric correction method of analysis should find its greatest application, for it is usually possible to separate part of the desired element in pure form in a few steps. With the aid of the radiometric correction, it is thus possible to do a complete analysis in much less time than would be required if a quantitative recovery of the element were necessary, and often, when proper techniques are used, the analysis can be carried out with a degree of precision and accuracy greater than can be easily attained by most standard procedures for trace analysis.

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Color Reaction between Beryllium and Aurin Tricarboxylic Acid

Quantitative Studies

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PREVIOUS studies have shown that quinizarin-2-sulfonic acid (1) and quinizarin (3) as organic reagents for the microanalysis of beryllium leave much to be desired. Numerous substances interfere and operating conditions must be rigorously controlled. As part of a search for a more suitable reagent, quantitative studies of the color reaction between beryllium and aurin tricarboxylic acid (aluminon) were instituted. Yoe and Hill (4) were the first to note that aluminon formed red-colored complex with beryllium similar to that formed with aluminum. Rothstein and Meier (2) reported that the color reaction was given by very small quantities of beryllium. The effect of pH, temperature, time, dye concentration, and interfering substances on the color reaction were studied spectrophotometrically. Based on the results obtained, a procedure was developed for determining beryllium in the range of 1 to 10 micrograms with a standard error of 12%.

Though aluminon may serve as a quantitative reagent for beryllium, it offers no advantage over those previously studied.

APPARATUS

Color intensities were measured by means of either a Model DU Beckman spectrophotometer or a Klett-Summerson colorimeter. pH was determined with a Beckman laboratory model pH meter.

REAGENTS

Aluminon (aurin tricarboxylic acid, ammonium salt) was obtained as a practical grade reagent from Eastman Kodak Company. It is soluble in water, giving a dark red solution. In most studies reported below, a 0.2% aqueous solution was used. Later, it was found that a lower concentration could be employed.

Standard solutions of beryllium were prepared by dissolving pure (99.9%) metal in concentrated hydrochloric acid. Aliquots

Quantitative studies of the color reaction between beryllium and aurin tricarboxylic acid (aluminon) were conducted to determine the optimal conditions of pH, temperature, time, and dye concentration. Based on the results obtained, a procedure was developed for determining beryllium (1 to 10 micrograms) with a standard error of 12%. The effect of interfering substances is described and the procedure is compared with other micromethods for beryllium.
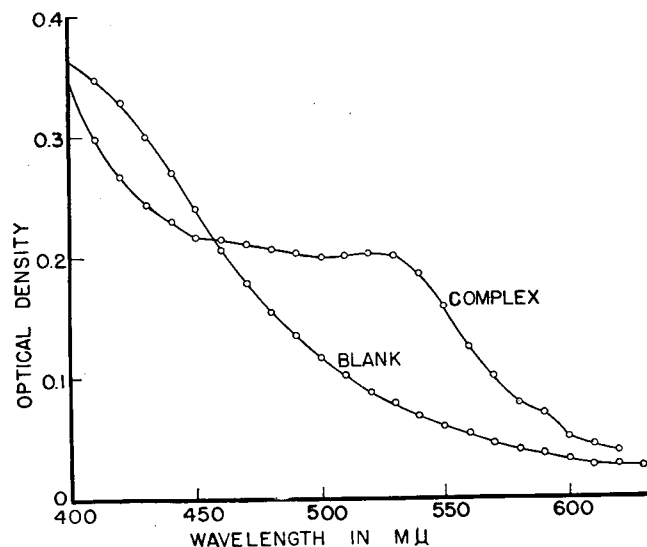

Figure 1. Absorption Spectra of Blank and Colored Complex Formed in Presence of Beryllium

of this filtered solution were ignited to beryllium oxide after addition of sulfuric acid and the beryllium content was determined gravimetrically. Dilutions of this acid stock solution to the microgram range were freshly prepared frequently to minimize the possibility of changes due to adsorption, base exchange with the glass container, etc. With this technique, no measurable losses were incurred, as evidenced by complete recoveries of radioactive Be[7] added to the stock solution.

ABSORPTION SPECTRA

Absorption spectra of the aluminon reagent and the complex formed with beryllium are presented in Figure 1. These curves were obtained with unbuffered solutions, pH 8.3 to 9.0, by mixing 9 ml. of 0.01% aluminon with 1 ml. of water for the blank and with 1 ml. of beryllium chloride (10 micrograms of beryllium) solution for the complex. The solutions were heated for 10 minutes at 80° to 90° C. and cooled to room temperature before reading. Inspection of the curves shows that a wave length of approximately 535 mμ gives the greatest difference in intensity between the blank and the complex.

EFFECT OF pH

A series of solutions containing 1 ml. of beryllium chloride (10 micrograms of beryllium), 0.5 ml. of 0.2% aluminon, and 8.5 ml. of 0.1 M buffer was prepared. For pH's below 7.0, the acetic acid–sodium acetate system was used and for pH's above 7.0, ammonium chloride–ammonia served as the buffer. The ratio of salt to acid (or base) was varied in a systematic manner, giving solutions covering the entire pH range from 3.2 to 10.5. The order of addition of reagents was kept the same in all cases and appropriate blanks (no beryllium) were also prepared. All solutions were heated in a boiling water bath for 10 minutes and cooled to 20° C., prior to the determination and subsequent measurement of optical density at 535 mμ.

The results are given in Figure 2. Although the maximal difference in color intensity between blanks and beryllium samples occurred at pH 4.2, the blanks at this pH were much too colored

and results on beryllium samples were, as a result, somewhat erratic. As a compromise, pH 7.5 to 7.7 was chosen as the optimal range for further study. Regardless of the final choice, it is important that all solutions be buffered because of the variation in color intensity with changes in pH.

EFFECT OF TEMPERATURE

It was noted early in the course of these investigations that the color developed slowly, if at all, unless the solutions of beryllium and aluminon were heated for a short time. Furthermore, it was evident that considerable fading occurred when these heated solutions were cooled to room temperature. Consequently, the effect of temperature on the color intensity was studied.
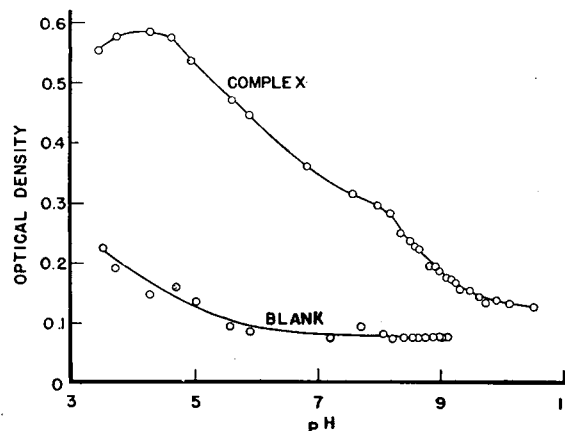

Figure 2. Effect of pH on Absorption of Blank and Colored Complex Formed in Presence of Beryllium

One milliliter of beryllium chloride solution (10 micrograms of beryllium), 0.5 ml. of 0.2% aluminon, and 8.5 ml. of 0.1 M ammonia–ammonium chloride buffer at pH 7.5 were mixed, heated in a boiling water bath for 10 minutes, and, while still hot, transferred to a Klett-Summerson colorimeter tube. Temperature measurements were taken before and after colorimeter readings and the mean of these two values was assumed to be the temperature at the time of color estimation. Klett filter No. 54 (500 to 570 mμ) was used.

As indicated in Figure 3, the color intensity was found to be dependent on the temperature. Because of this it is necessary that all intensity measurements be made at constant temperature, and all subsequent readings were made at 20° C.

After heating and cooling, the color intensity was stable; no detectable changes occurred over several hours.

EFFECT OF DYE CONCENTRATION

To determine the proper amount of dye for optimal results, two dilute solutions of aluminon were prepared (1.11 × 10⁻³ M and 2.22 × 10⁻⁴ M). Two series of solutions were then made up as follows: 8.5 ml. of 0.1 M ammonium chloride buffer at pH 7.6

1 ml. of beryllium chloride (containing from 0 to 10 micrograms of beryllium), and 0.5 ml. of either of the dye solutions. All samples were heated 10 minutes in a boiling water bath, cooled, and read on the spectrophotometer. The results are given in Figure 4.
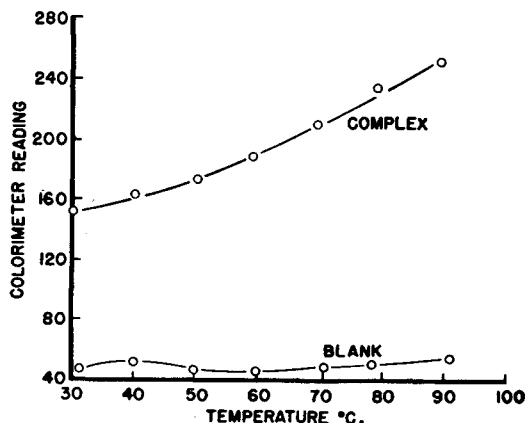

Figure 3. Effect of Temperature on Absorption of Blank and Colored Complex Formed in Presence of Beryllium

The smaller quantity of dye was insufficient to give full color development. However, with a final dye concentration of only $5.5 \times 10^{-5} M$, a curve approaching linearity was obtained. This amount gave a ratio of dye to beryllium of only 1 to 2 at the highest beryllium concentrations. Although it might seem advisable to use an even larger quantity of dye to ensure an excess of reagents, tests showed this to be impractical. Larger amounts of aluminon resulted in inordinately high and variable blank readings.

Table I. Interference of Common Ions with Beryllium-Aluminon Reaction

Ion Studied	Ratio: $\dfrac{\gamma \text{ Ion Studied}}{\gamma \text{ Be}}$		
	100:1	10:1	1:1
F $^-$	—	—	0
PO$_4$ $^{---}$	—	—	0
Cl $^-$	0	0	0
NO$_3$ $^-$	0	0	0
SO$_4$ $^{--}$	0	0	0
HCO$_3$ $^-$	0	0	0
CH$_3$COO $^-$	0	0	0
Fe $^{++}$	+	+	+
Al $^{+++}$	+	+	+
Pb $^{++}$	Ppt.	+	+
Ca $^{++}$	+	+	+
Cu $^{++}$	Ppt.	Ppt.	+
Mn $^{++}$	+	+	+
Na $^+$	0	0	0
Mg $^{++}$	0	0	0

0   = no interference
+   = color enhancement
—   = color inhibition
Ppt. = precipitate

INTERFERING SUBSTANCES

To determine the effect of added inorganic substances, a series of solutions was prepared as follows: 0.5 ml. of $1.11 \times 10^{-3} M$ aluminon, 8.5 ml. of 0.1 M ammonium chloride buffer at pH 7.6, 0.5 ml. of beryllium chloride (5 micrograms of beryllium), and 0.5 ml. of the solution containing the ion being tested for interference. Three types of interference were observed: inhibition of color development, color enhancement (possibly due to complex formation between test ion and aluminon), and precipitation of the dye. The results are summarized in Table I.

It is clear that aluminon is not specific for aluminum or beryllium. All the divalent cations tested with the exception of mag-

nesium gave increased color intensities; although most anions did not materially affect color development, fluoride and, to a lesser extent, phosphate reduced the color intensity, probably by competing with aluminon for beryllium.

PROCEDURE

To decrease the volume of buffer employed, 1 M ammonium chloride–ammonium hydroxide 19 to 1, pH 7.6, containing aluminon, $2.8 \times 10^{-3} M$, was prepared. Two milliliters of this reagent, 0 to 8 ml. (1 to 10 micrograms) of the beryllium solution to
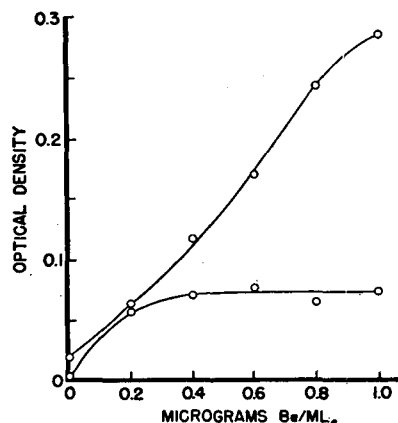

Figure 4. Effect of Dye Concentration on Colorimetric Response

Upper curve, dye concentration 5.5×10^{-5} M; lower curve, $2.25 \times 10^{-5} M$

be analyzed, and sufficient water to make a total volume of 10 ml. were mixed, heated in boiling water for 10 minutes, and cooled under running water to 20° C. and the intensity of the resultant color was determined by means of a spectrophotometer at 535 mμ. Beryllium content was read from a standard curve obtained by treating known solutions of beryllium in the same manner.

ACCURACY

Thirty-three "unknown" solutions of pure beryllium chloride were prepared by a disinterested person and analyzed by the procedure outlined above. The results are given in Table II. In terms of beryllium, the average error was 0.38 microgram. In per cent, the standard deviation was approximately ±12.

DISCUSSION

Because of the intense coloration of aluminon itself, only a small excess of the dye can be employed. This results in a dissocia-
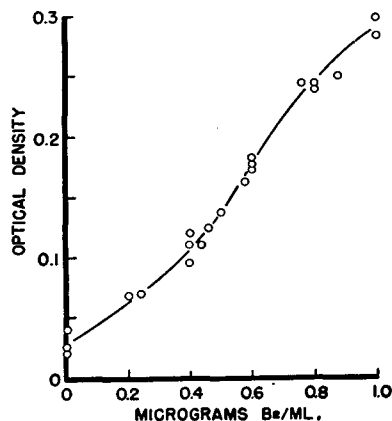

Figure 5. Lack of Linearity between Beryllium Concentration and Optical Density

Table II. Recovery of Known Quantities of Beryllium

Present γ	Found γ	Present γ	Found γ
2.0	2.3, 2.2	5.8	5.7
2.4	2.2	6.0	6.4, 6.1, 6.2, 6.4
2.8	4.2	6.2	6.3
3.4	3.7	6.4	6.8
4.0	3.7, 3.3, 4.1, 4.5, 4.2	7.6	7.3, 8.7
4.4	3.8	8.0	8.6, 8.5, 8.3, 8.3
4.6	4.2, 5.0	8.8	8.8, 8.3
5.0	4.8	10.0	10.6, 10.0, 9.0, 10.8

tion of the beryllium-dye complex such that the relation between beryllium content and color intensity plotted graphically is non-linear, but S-shaped as indicated in Figure 5. Undoubtedly this dissociation accounts in a large measure for the lack of reproducibility of the method (standard deviation approximately 12%). This situation also favors interference by competing anions and may account for the sensitivity to small amounts of fluoride and phosphate. Several sets of data have been analyzed statistically and the probability of obtaining the observed results is considerably less than 0.05 if the true relation were linear. In fact, when plotted as probit of 100 times optical density versus the square root of beryllium concentration, a linear curve is obtained.

Although aluminon may serve as a quantitative reagent for small amounts of beryllium, it offers little or no advantage over quinizarin-2-sulfonic acid (1) and quinizarin (3).

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Instrumental Improvements for Microdetermination of Protein-Bound Iodine in Blood

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A photoelectric recording colorimeter, with a very stable light source, is described. Provision is made for thermostatic control of the solutions being measured. The colorimeter was specifically designed for measurement of trace quantities of iodine (0.001 to 0.5 microgram in 5 ml. of solution). The types of records given by interfering substances are shown.

THE determination of iodine in the concentrations in which it occurs in blood is a difficult microchemical problem which has occupied the attention of many because of its practical importance in relation to thyroid status.

Particularly when only small quantities of blood are available, the iodine available may be only a few hundredths of a microgram for quantitative determination. One of the most sensitive reactions of iodine is its catalytic effect on the oxidation reduction pair of ceric-arsenite solutions (7), and it was shown about 9 years ago that this could be used for an accurate quantitative measure of iodide concentration (2).

Since that time, the use of this reaction has been adopted by a number of others, including Taurog and Chaikoff (9), Salter (8), Barker (1), Connor and associates (3), and most recently, for 1-ml. quantities of serum, by Man, Siegfried, and Peters (5).

In the absence of iodide or other catalyst the reduction of cerate or ceric sulfate by arsenite proceeds at a very slow rate, but at very low concentrations of iodide of the order of 10^{-7} molar the reaction proceeds at a rate which can be measured in a period of 5 to 30 minutes by the rate of fading of the yellow cerate solution. Generally, this has been done by making a series of readings in a photoelectric colorimeter at intervals of 5, 10, and 20 minutes and comparing the readings obtained with those of suitable standards.

It is obvious that a continuously recording colorimeter would be advantageous for these measurements, both in improved accuracy and from the saving of time.

A recording system was first tried out over 3 years ago, and has undergone a series of modifications designed to improve its performance. The author is greatly indebted to Evelyn Man and associates for an extensive trial of several of these modifications, and assisting in improving its accuracy, so that it could meet the severe requirements imposed on it for measuring the iodine content of 1 ml. of serum.

By suitable choice of conditions, the resultant record may be obtained as a straight sloping line, and the slope is a direct function of iodine concentration over the useful range. The linear record obtained is essentially the ratio of two exponential functions, the rate of decrease of ceric ion with time (2), and the optical density of the yellow ceric solution as a function of its concentration.

DESIGN OF COLORIMETER

The essential features of the colorimeter are shown in cross section in Figure 1.

The light from the 24-volt bulb, after passing through lenses L_1 and L_2 and a blue filter, is brought to a secondary focus at the center of the test tube containing the cerate solution and then passes to the phototube. The output of the phototube is recorded on the Micromax strip chart after passing through the impedance changer or amplifier tube.

The aluminum block which houses the test tube and phototube is drilled to hold several additional test tubes, and is provided with a heater and thermostat to maintain constant temperature during the recording of color change.

A vacuum-type phototube (929) is used instead of the barrier layer cell, as ordinarily used in commercial filter photometers. This contributes greatly to the stability of performance of the instrument and its spectral response is much better for the measurement of yellow solutions, as has been noted (6).

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In order to provide a very stable light source and direct current amplifier, an electronically regulated power supply is used. The output supplies current for the 24-volt lamp bulb and also for heating the filaments of the amplifier tubes of the colorimeter and of the power supply itself. A schematic circuit of the power supply and amplifier is given in Figure 2. The output of the power supply is 30 to 36 volts at 150 ma. and is constant to about 0.01% over the range of 100 to 125 volts line voltage. A general view of the complete apparatus is shown in Figure 3.
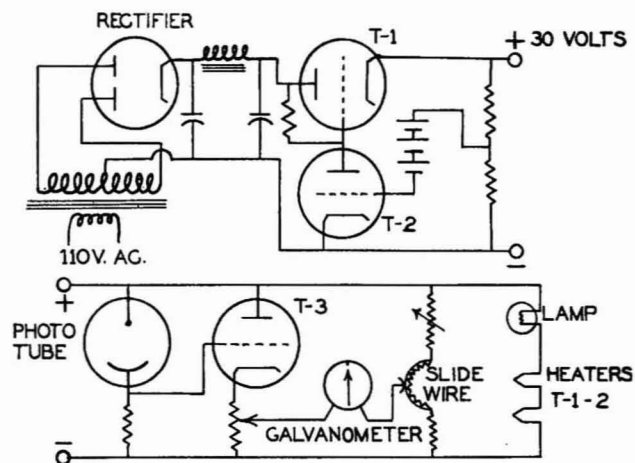

Figure 2. Schematic Circuit of Power Supply and Amplifier

initial concentration of cerate solution, which together control the starting point of the record

The temperature of the block
The acidity of the solution
The concentration of other interfering ions in the solution

Provision is made for controlling the position and length of the scale (adjusting knobs on the right of the thermostated block). A thickness of filter (about $^1/_8$ inch of Corning No. 554) is selected which gives an initial transmittance of about 25 to 30% with 0.01 N ceric sulfate in the selected test tubes. With this combination, records which are essentially straight lines are produced over the range of 25 to 70% transmittance, permitting measurement of the angle to 0.2° or 0.3°.

For convenience in calculation, it is advantageous to have a simple relation between the cotangent of the angle and the concentration of iodine in the solution. For example, using a scale length of about 90% of the width of the Micromax strip chart, a temperature of approximately 32° C., and the blue filter as described above, the iodine concentration in micrograms per mil-

Figure 1. Cross Section of Colorimeter

The general principles of electronically regulated power supplies have been well described (4). However, most of the circuits described have an output voltage which is considerably higher than is desirable for this application, and do not have the requisite stability. The use of a 22.5-volt dry battery as the voltage reference element in place of the usual gaseous discharge tube permitted a low voltage output, together with an improvement in stability. Residual drift in the present circuit is due mainly to changes in the ambient temperature of the reference battery, which could be thermostated if necessary. Because no current is drawn from it, it needs a replacement only at intervals of a year or more.

Although this colorimeter was designed to meet a specific need, it can be used to advantage for recording other reactions where changing colors occur or where a record is an advantage. In particular, it has been found useful for cholesterol determinations (using a Type 930 phototube and a filter with a maximum transmittance at 625 millimicrons) in measuring the time interval for maximum color development.

Typical records obtained by varying quantities of iodine are reproduced photographically in Figure 4. The iodine solution in these tests is similar to distillates in composition. The iodide is present in 4 ml. of 0.08% sodium hydroxide, to which are added 0.5 ml. each of 0.15 N arsenious acid and 0.1 N ceric sulfate. Selected test tubes, 13 by 100 mm., are used for the determination.

The reagent blank is shown at the bottom, followed by duplicate records of 0.033, 0.067, and 0.10 microgram of iodine in ascending sequence. The angles and the cotangent of the angles are tabulated to the right of the chart. The rate of reduction as measured by the cotangent of the angle is closely proportional to the iodine contents of the solution.

The angle produced by the recorded line is controlled by the following factors:

The scale of the Micromax strip chart—that is, the length of line between 0% light transmittance and 100% transmittance
The rate of chart movement (usually 6 inches, 15 cm., per hour)
The transmittance characteristics of the blue filter and the
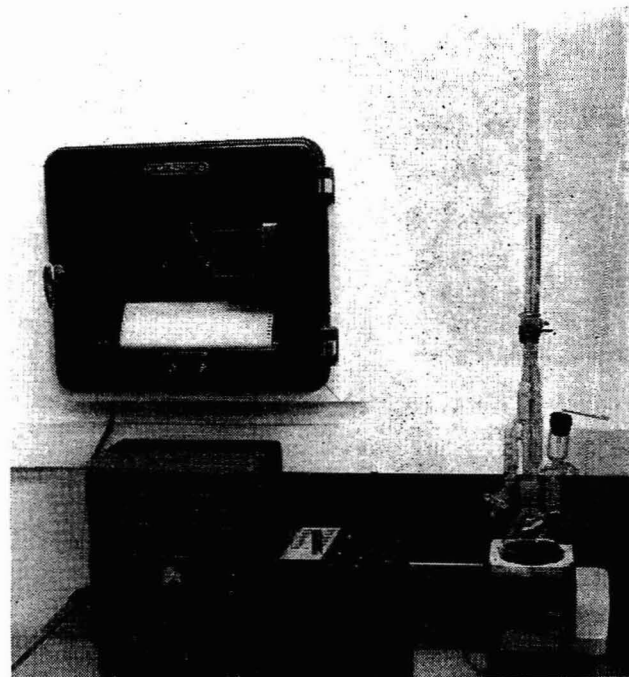

Figure 3. Complete Apparatus

liliter will be about 1/100 of the cotangent of the angle, and the conversion factor can be adjusted to this value by means of the scale adjuster or, less conveniently, the temperature of the block. Thus, a record having an inclination of 30° to the horizontal would correspond to an iodine concentration of cot 30°/100 or 0.017 microgram per ml. of final solution.

By using suitable standards freshly prepared from potassium iodide solutions, this factor may be used routinely, and any variations due to slow changes in the thermostat, or to possible variations from batch to batch of reagents, may be compensated for by adjustment of scale length to give the correct angles for standards.
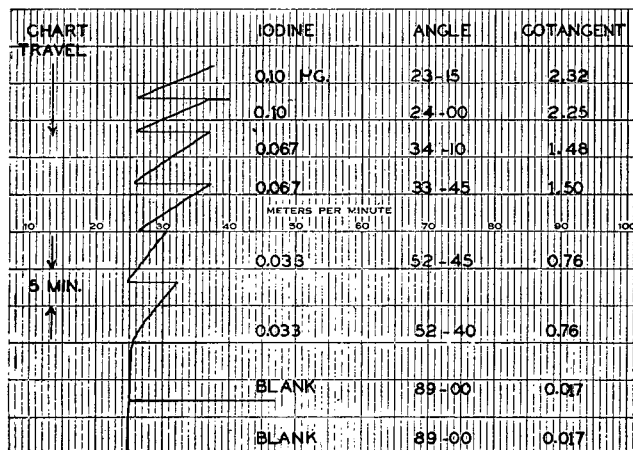
Figure 4. Typical Records for Iodine

Close control of temperature is essential, as a rise of 10° C. approximately doubles the catalytic effect. Accordingly, the temperature should be controlled to at least 0.5° C. and preferably to within 0.2° C. As long as the volume is held constant, minor variations in concentration of reagents or acidity do not appear to affect the reaction rate. The final acidity of the test solution should be at least 0.5 to 0.6 N in sulfuric acid in order to prevent precipitation of reduced cerium salts.

The state of oxidation of iodine is of importance. Thus, if the reagents are mixed first and iodine is then added as iodate, no catalytic effect occurs; this shows that iodide or perhaps free iodine is the catalyst.

EFFECT OF INTERFERING IONS

The effect of interfering ions of various types is shown in Figure 5. The presence of relatively large quantities of chloride or bromide has relatively little effect unless iodate is simultaneously present. Such a combination gives a characteristically curved record with an increasing rate. The effect of cyanide and thiocyanate ion is opposite to that of the halides, producing a record which is curved in the other direction. Either mercury or silver in trace quantities interferes by reducing the concentration of iodide ion, and this interference is proportional to the amount present. Some reducing ions such as oxalate, sulfite, or hydrazine reduce the initial concentration of cerate ion, but do not affect the slope of the subsequent line unless the reducing agent acts very slowly, in which case curved records are produced. These various abnormal records indicating the presence of interfering ions are much more readily detected with the continuous recording colorimeter than by two or more successive transmittance measurements at definite time intervals, as has been the usual procedure heretofore. An additional advantage of the continuous record is that minor scratches on test tubes or other factors which introduce errors in transmittance measurements

Table I. Effect of Acidity on Reaction Rate

Concentration of H_2SO_4, N	Cotangent of Angle	% of Initial Value
0.5	3.45	100
1.2	3.50	101
1.85	3.75	109
2.5	4.75	138
3.2	5.15	148
3.9	5.00	145
4.5	4.50	130
5.2	3.75	109
6.1	3.38	98
7.5	1.72	50

Table II. Effect of Sodium Ion on Reaction Rate

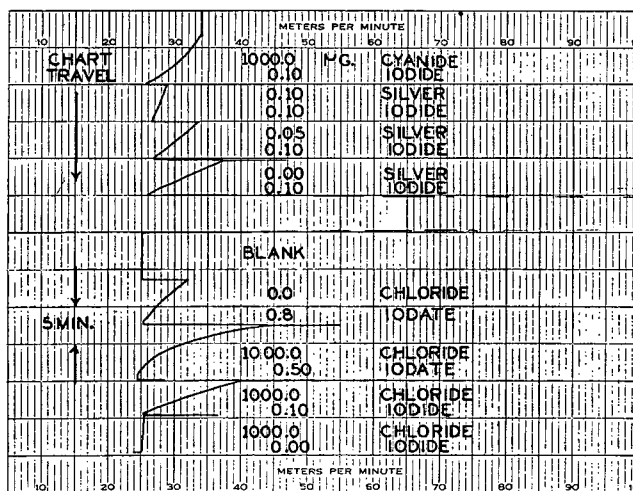| Molar Concentration of Na_2SO_4	Cotangent of Angle	% of Initial Value
0	3.40	100
0.18	2.37	70
0.35	1.85	54
0.53	1.23	36
0.70	0.97	28

Figure 5. Effect of Interfering Ions

when made successively do not affect the slope of the continuous record, because the tube remains in a fixed position throughout the measurement.

The effect of increasing the acidity by increased sulfuric acid is shown in Table I. The iodine concentration was kept constant at about 0.035 microgram per ml., and the results are expressed in terms of the cotangent of the resultant angle and also as a percentage of the value obtained at an acidity of 0.5 N.

When sodium sulfate was added, the results in Table II were obtained, the iodine concentration being 0.035 microgram per ml. and the acidity 0.5 N.

Small variations in acidity are of insignificant effect, but moderate concentrations of sodium ion greatly decrease the sensitivity of the reaction.

In regard to purity of reagents, it will probably be necessary to recrystallize arsenious acid to obtain a satisfactory blank. This is readily done from a hot solution that contains about 5% arsenic trioxide and is 0.5 molar in sulfuric acid.

Ceric sulfate is prepared from the hydrated ceric oxide. Sodium hydroxide, if used for absorbing iodine, should be low in chloride and bromide as well as iodide. With proper care, it is not difficult to obtain a blank that gives a vertical record for at least 10 minutes on these reagents alone.

The ultimate sensitivity of this recording method of measurement is of the order of 0.0002 microgram per ml. of final solution,

or 0.001 microgram of iodine if 5 ml. are used. If desired, half quantities of solution and reagents may be used without modification of the apparatus. This sensitivity corresponds to a difference of 1° in slope between the tests and the blanks. In the average range of 0.05 to 0.10 microgram, the reproducibility of replicate determinations is of the order of 1° in slope or ±0.001 microgram in 5 ml. of test solution.

This apparatus has been extensively used for the final determination of protein-bound iodine in serum by two different procedures. In the author's laboratory, following protein precipitation, the chromic acid digestion and distillation previously described (2, 9) are routinely used, while Man and associates (5) have used it following a permanganate digestion and distillation.

In the chromic acid procedure, proteins have been precipitated by the use of tungstic acid. This reagent has the disadvantage of producing a precipitate of tungstic acid in the digestion flasks, but has been satisfactory in other respects.

CHOICE OF REDUCING AGENTS

The problems connected with the choice of reducing agents for the digest have not been completely solved.

In addition to preparing all reagents with a suitable low blank, the reduction of iodic acid and the simultaneous distillation of iodine are probably the most critical step. A suitable reducing reagent must have the right oxidation-reduction potential for both chromic acid and iodic acid. It should not dilute the steam with noncondensable gases and should be nonvolatile itself.

Phosphorous acid, which has been most used as a reducing agent, is by itself not entirely suitable, probably because of its slow rate of reduction of iodic acid, and perhaps because of reduction to the iodide rather than free iodine.

Recent work indicates that the use of both phosphorous and

arsenious acids may be considerably superior. It is possible that metallic catalysts may be required for the most satisfactory reducing combination. Hydrazine has some desirable characteristics as a reducing reagent, but has given erratic results in recovery experiments. The combination of reducing agents originally recommended was phosphorous acid followed by hydrogen peroxide, which probably increased the amount of iodine present in the free state, and thus influenced the rate of distillation.

Further work on the factors involved in this stage of the procedure is currently being carried on.

With proper attention to the meticulous technique required and the proper purification of reagents, a consistent 90 to 95% over-all recovery of iodine by the methods described here has been obtained.

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Determination of Milligram Quantities of Vanadium in the Presence of Uranium

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An improved method for the determination of milligram quantities of vanadium in the presence of uranium is described. Use of a modified dead-stop procedure and a weight microburet increases the sensitivity and precision of the method. Results are given in the range of 0.10 to 4.0 mg. of vanadium.

VANADIUM in macro amounts has been determined volumetrically by a number of methods. It has frequently been separated from sexivalent uranium by a cupferron precipitation (7, 15). Numerous spectrophotometric methods are available for determination of vanadium on a micro scale. Important among these methods are those depending upon color development as phosphovanadotungstic acid (3, 18) and as the peroxidized vanadium complex (19).

The usual methods for volumetric determination of vanadium depend upon either a selective oxidation of the vanadium as in the presence of chromium or upon a complete oxidation followed by a selective reduction of the vanadium to the vanadyl state. Willard and Young (17) determined vanadium in steel by oxidation of the sample with perchloric acid. A measured quantity of ferrous ion was added and the excess titrated with permanganate at room temperature. Willard and Gibson (16) oxidized chromium and vanadium in ores and alloys with boiling 70% perchloric acid; the oxidizing action of the excess perchloric acid was

terminated by dilution with water. Decret (4) determined both chromium and vanadium in a single sample by a double titration with ferrous sulfate, depending upon a selective oxidation with permanganate. These volumetric titrations have been carried out potentiometrically and with internal indicators; a recent electrometric determination is that of Claassen and Corbey (2). However, in the presence of a large excess of uranium, the colorimetric end points are somewhat difficult to determine, and the conventional potentiometric titration does not yield an extremely sharp inflection point when only 1 or 2 mg. of vanadium are present. Although vanadium is not usually determined gravimetrically, because of interferences, a microgravimetric procedure for the separation of vanadium and uranium has recently been reported by Kroupa (10).

A rapid method for the direct determination of milligram quantities of vanadium in the presence of a large excess of uranium utilizes the reduction of quinquevalent vanadium to the vandyl ion by ferrous ammonium sulfate (8, 11). The accurate

and precise determination of the equivalence point in this titration is made possible by utilization of a modified dead-stop titration apparatus (5) and a weight microburet (1).

The method that has been developed is suitable for the determination of trace amounts of vanadium in the presence of uranium with possible presence of traces of iron, titanium, and chromium. Although the titration of vanadyl ion with permanganate in the presence of iron and chromium is possible at room temperature (9), the end point is poor when determined colorimetrically and potentiometrically. The vanadyl ion may be titrated with ceric sulfate in sulfuric acid solution (6); however, the end point is difficult to ascertain in the uranium solution.

FIGURE 1
TYPICAL TITRATION CURVE
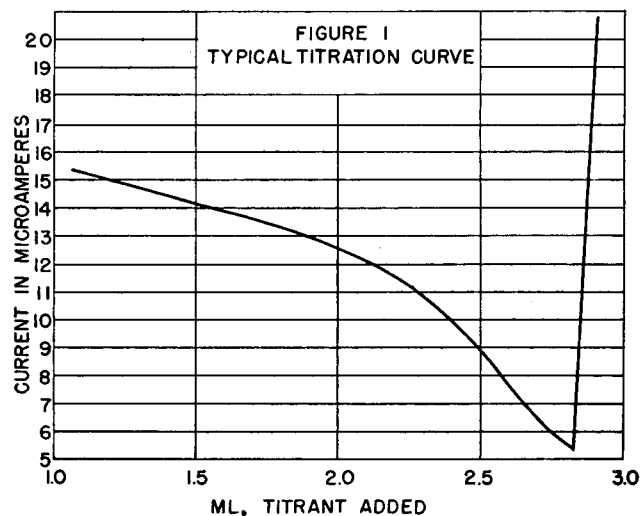
The selective reduction of quinquevalent vanadium with standard ferrous ammonium sulfate appeared to offer the best possibilities for a direct determination. Interference from chromium may be prevented through control of the initial oxidation. Any iron present will appear in the ferric state and does not interfere in moderate amounts with the ferrous ion titration. The titration was initially carried out with a Beckman pH meter as a potentiometer, using calomel and platinum electrodes. Although a usable curve is obtained in this manner, the point of deflection is not well defined even when 0.05 N ferrous sulfate solution is used. The precision of this titration is ±0.02 ml. as read from the titration curve, representing a possible deviation of ±0.05 mg. of vanadium. This deviation was larger than desired, especially in the region of 0.6 to 2 mg.

Because excellent results have been obtained in the Karl Fischer water determination with the dead-stop type of titration, it was decided to investigate this apparatus for the vanadium titration. The phenomena of the dead-stop titration have been fully discussed by several authors (12, 14).

The apparatus used is a typical arrangement, except that the usual galvanometer is replaced by a microammeter measuring 20 microamperes at full-scale deflection. The two platinum electrodes are kept in chromic acid when not in use and are occasionally sensitized by immersing them in hot chromic acid. The titrating reagent, either 0.01 or 0.025 N ferrous ion, is added from a weight microburet.

A contribution from this laboratory describing the application of the weight microburet and the techniques of its use is being prepared for publica-

tion (13). Very small increments of reagent may be added by simply touching the capillary end of the buret to the solution. Figure 1 shows a typical titration curve obtained with the dead-stop apparatus, the titrant being 0.025 N ferrous ammonium sulfate. In actual practice, the operator watches the ammeter and terminates the titration at the first permanent deflection in the direction of current increase. The precision attained in this titration is dependent upon the sensitivity of the measuring instrument, inasmuch as the amount of titrant added may be closely controlled with the weight microburet.

PROCEDURE

The sample in dilute nitric acid, containing about 1 gram of uranium and from 0.5 to 5 mg. of vanadium, is concentrated to a volume of 10 ml., 1 ml. of sulfuric acid is added, and the solution is heated until fumes of sulfur trioxide appear in order to remove nitric acid. The residue is diluted with 2 ml. of water, and the solution is refumed, cooled to room temperature, and diluted to approximately 20 ml. with water. Potassium permanganate solution is added dropwise until the solution maintains a faint pink after standing several minutes. In order to reduce the excess permanganate, a 2-ml. portion of 1% sodium azide is added and the solution is allowed to stand for 5 minutes.

The solution in a 50-ml. beaker is placed in an ice bath and cooled to 5° C. The platinum electrodes are immersed in the solution, and the initial reading on the microammeter is adjusted to 15 μa. with the variable resistance. Stirring is carried out with a magnetic stirrer. The reagent is now added dropwise from the microburet. As the reaction approaches completion, the current approaches a limiting value of about 2.5 μa. Near the end point the size of the drop being added may be sharply reduced through proper manipulation of the buret. The reagent is added until a permanent deflection of the indicator needle in the direction of increased current occurs. The product of mass of titrant by its vanadium titer gives mass of vanadium present.

DATA AND DISCUSSION

The recovery of vanadium from samples containing 1.53 mg. of vanadium in the presence of 1 to 1.59 grams of uranium by the dead-stop procedure has been compared with recoveries carried out on similar samples by gravimetric cupferron separation followed by ignition of the cupferrate to vanadium pentoxide, and with determinations made by the usual potentiometric titration of vanadium. The data for these determinations are given in Table I.

The results shown in the second column were obtained by the cupferron separation followed by ignition to vanadium pentoxide. This method tends to yield slightly low results when milligram quantities of vanadium are determined. The accuracy

Table I. Vanadium Recoveries by Gravimetric, Potentiometric, and Dead-Stop Methods

Sample	Gravimetric as V₂O₅, Mg./Ml.	Potentiometric, Mg./Ml.	Dead-Stop, Mg./Ml.
Standard solution of McKay, 99.7% V	1.53	1.53	1.54
	1.52	1.54	1.54
		1.53	1.53
Av.	1.52	1.53	1.54

Table II. Analyses of Milligram Quantities of Vanadium

		Average Vanadium Found					
Sample Source	Vanadium Present	No. of detns.	Chromium, titanium, uranium absent	No. of detns.	Chromium, titanium, uranium present[a]	Standard Deviation[b]	Maximum Deviation[b]
	Mg.		Mg.		Mg.	%	%
NH₄VO₃	0.44	8	0.44	8	0.44	3.2	4.5
	0.88	8	0.88	8	0.87	2.1	2.3
	1.32	7	1.33	8	1.32	0.87	1.5
V₂O₅	1.20	5	1.20	5	1.19	0.90	1.3
	3.58	5	3.57	5	3.59	0.35	0.56

a 10 mg. Cr, 10 mg. Ti, 100–1000 mg. U.
b Calculated on recoveries in presence of chromium, titanium, and uranium.

Table III. Vanadium Analyses in Presence and Absence of Uranium

Aliquot Soln. 1 Ml.	V Present Mg.	No. of Detns.	V Found, No Uranium Mg.	No. of Detns.	V Found, 1–1.5 Grams U Present Mg.	Standard Deviation %	Maximum Deviation %
1.00	1.78	3	1.78	3	1.78	...	...
2.00	3.56	2	3.52	2	3.52	...	...
3.00	5.34	3	5.34	3	5.33	...	...
Soln. 2					1.5 Grams U Present		
3.00	3.62	.	.	5	3.63	0.23	0.31
2.00	2.41	..	..	5	2.43	0.47	0.58
1.00	1.21	..	..	5	1.20	0.59	0.74
0.500	0.60	..	..	5	0.61	0.74	0.85
0.300	0.36	..	..	5	0.36	1.2	1.5
0.200	0.24	..	..	5	0.25	1.6	2.0
0.100	0.12	..	..	3	0.10	..	..
0.060	0.07	..	..	3	0.08	..	..

of the potentiometric method compared favorably with the dead-stop procedure; however, the rapidity and ease of the dead-stop procedure have much in their favor, especially in the presence of excess uranium.

In Table II are shown data for recoveries of vanadium in the presence of 10 mg. of chromium and 10 mg. of titanium as well as excess of uranium. These elements are two that frequently occur in samples analyzed for vanadium. It is apparent that as much as 10 mg. of chromium or titanium will not interfere in the determination of milligram quantities of vanadium.

Table III contains data for recoveries of vanadium in the range of 5 to 0.10 mg.

The largest single deviation has a value of 4.5% when 0.44 mg. of vanadium is present. In the usual sample containing approximately 2 mg. of vanadium, the maximum deviation was less than 0.6% and the average deviation in several samples will be considerably less than this amount. When this deviation is considered in terms of a sample containing an excess of uranium, the result is much better than can be utilized. The method is applicable to the usual source materials containing vanadium and uranium and to samples containing no uranium. One sample may be run several times by this method; only a reoxidation of

the vanadium is necessary, because the iron present from the initial titration does not cause difficulty.

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NOTES ON ANALYTICAL PROCEDURES . . . .

Separation and Determination of Cobalt in Presence of Nonvolatile Radicals

Use of Quaternary Ammonium Hydroxides

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COBALT may be weighed accurately as cobalt sulfate following ignition at not over 550° C. (6, 7). When only volatile or ashless ions or molecules are present, cobalt may be determined by evaporating to dryness with a little sulfuric acid and igniting (5).

When nonvolatile radicals are present, cobalt is frequently separated by precipitation with a strong base and an oxidizing agent. Because the precipitated cobaltic hydroxide always occludes some of the alkali (4) and some of the other nonvolatile components of the solution, high results are obtained if the cobaltic hydroxide, even though very thoroughly washed, is converted to cobalt sulfate for weighing. The procedures available for accurately estimating cobalt in these cases involve special equip-

ment or techniques which lack the simplicity and elegance of the sulfate method.

The purpose of this paper is to show that by substituting the readily available, strong, ashless quaternary ammonium hydroxides for the alkalies, precipitates are obtained which can be converted quantitatively to the sulfate for accurate weighing.

When nonvolatile constituents are present, the cobaltic hydroxide must be dissolved again and reprecipitated to avoid occlusion of traces of nonvolatile substances. Sodium hydroxide may be used for the first precipitation. Bromine water may not be used as the oxidizing agent in the precipitation with the quaternary ammonium hydroxide, because these reagents form orange precipitates, probably perbromides (2), when mixed.

Table I. Determination of Cobalt in [CoCl (NH₃)₅] Cl₂

(Co = 23.53% by theory)

Section	Results, %	Average, %	Method
A	23.50 23.52 23.54	23.52	Evaporating with H₂SO₄. Weighing as CoSO₄
B	23.60 23.53 23.57	23.57	In presence of an equal number of moles of K₂CrO₄ and of Na₂WO₄: precipitating Co(OH)₃ with H₂O₂ and NaOH, redissolving, and precipitating with H₂O₂ and trimethylbenzylammonium hydroxide. Weighing as CoSO₄
C	23.75 23.87 25.08	24.23	Precipitating Co(OH)₃ with H₂O₂ and NaOH. Washing with 500 ml. of hot water. Weighing as CoSO₄
D	23.53 23.56 23.59	23.56	Precipitating Co(OH)₃ with H₂O₂ and trimethylbenzylammonium hydroxide. Washing with 20 ml. of hot water. Weighing as CoSO₄

EXPERIMENTAL

Chloropentamminecobaltichloride was chosen as the source of cobalt in all the experiments described, because this compound can be prepared readily in a pure state (1). A sample of this salt, weighing approximately 0.6 gram, was used for each of the analyses listed below. This weight produces 0.37 gram of cobalt sulfate.

A. Cobalt was determined in each of three samples by the sulfate method. The results are listed in section A of Table I.

B. Each of three samples, weighed out into a 50-ml. beaker, was dissolved, with warming, in 20 ml. of water and treated as follows:

A solution (10 ml.) was added which contained the same number of moles of potassium chromate and of sodium wolframate as the number of moles of salt in the sample. (The orange colored chromate and wolframate of the cobaltammine cation were precipitated.) A little macerated Whatman's No. 42 filter paper was added as a filter aid. The liquid was heated to the boiling point, and removed from the heat source, and 1 ml. of 3% hydrogen peroxide solution was added, followed by 5 ml. of 3N sodium hydroxide solution, added cautiously beneath the watch glass from a pipet, in order to decompose the salts and precipitate cobaltic hydroxide. The mixture was stirred and, after effervescence had ceased, boiled gently on a hot plate for a short time, after which the precipitate was allowed to settle. While still warm, the mixture was filtered with gentle suction through a glass sealing tube 10 mm. in diameter containing a medium-fineness fritted-glass disk. Previous to this filtration, a suspension of macerated filter paper had been filtered through the sealing tube, so that a moderately loose mat of paper pulp, approximately 4 mm. thick, lay on top of the fritted glass. The mat was washed with a little dilute solution of the same base that was used for the precipitation (sodium hydroxide in this case) before filtration of the cobaltic hydroxide. The filtrate, acidified with hydrochloric acid and heated, was tested for cobalt with negative results.

The precipitate, which was never sucked dry until washing was complete, was washed with about 40 ml. of hot water that had first been used to rinse the beaker. After most of the water had been drained from the precipitate, the suction apparatus disconnected, and the lower parts of the sealing tube washed, the beaker was placed beneath the tube and about 2 ml. of hot concentrated hydrochloric acid were added at the top of the sealing tube. The dissolution of the cobaltic hydroxide was facilitated by cautious warming of the outside of the sealing tube with a very low flame. The resulting solution was blown through the sealing tube by gentle air pressure applied at the top, and the sealing tube was washed once with a little water. The excess hydrochloric acid was evaporated by placing the beaker on the hot plate. Toward the end of this evaporation, a watch glass was placed on the beaker and 0.5 ml. of concentrated nitric acid was added to destroy the sugar from the filter paper. When the slight effervescence had ceased, the watch glass was rinsed into the beaker and it was replaced beneath the sealing tube. The remaining traces of cobaltous chloride were washed from the tube into the beaker with small portions of hot water.

The filter paper remaining in the sealing tube was colored light yellow by a little wolfram trioxide from wolframates which had been occluded in the precipitate. A trace of this wolfram trioxide washed through into the cobaltous chloride, but was separated by the second precipitation. The filter paper remaining after this latter precipitate had been dissolved was pure white.

Macerated filter paper and hydrogen peroxide were again added exactly as before; and, after dropwise neutralization with a 2.5 N aqueous solution of trimethylbenzylammonium hydroxide (Triton B, Rohm & Haas Company), the procedure was followed exactly as previously described, except that the 2.5 N trimethylbenzylammonium hydroxide was substituted for the 3 N sodium hydroxide solution, and that it was unnecessary to fume off the excess hydrochloric acid before thoroughly washing the cobaltous chloride from the sealing tube.

When the cobaltous chloride had again been transferred to the beaker, 0.5 ml. of concentrated sulfuric acid was added, and the beaker was placed on the hot plate. The solution was evaporated to about 3 ml., and covered with a watch glass, and 1 ml. of concentrated nitric acid was added to aid again in the destruction of organic matter. After the effervescence had ceased, the solution was transferred to a 15-ml. porcelain crucible and the content evaporated, using a low flame applied to a miniature air bath made from a large crucible. The beaker and watch glass were washed with small portions of hot water and the washings were added periodically to the crucible as evaporation progressed. After a full Bunsen flame failed to produce more visible sulfur trioxide fumes, the crucible was allowed to cool, and 2 drops of water were added to aid in the expulsion of the last traces of sulfur trioxide (3). The content of the crucible was evaporated to dryness with a low flame as before and heated a short time on the air bath with full Bunsen flame. The crucible and content were ignited to constant weight (approximately 25 minutes) in an electric muffle furnace at 550° C. The residue was weighed as cobalt sulfate. The results are listed in section B of Table I.

Tetraethylammonium hydroxide was used qualitatively with every indication of equally satisfactory results. Commercially available quaternary ammonium hydroxide solutions have frequently been stored in soft-glass bottles and therefore contain appreciable quantities of silica. It is most important, in applying this method, that a little of the base be ignited to ascertain the amount of nonvolatile impurities it contains. If no ashless base is available, it may be prepared conveniently from a solution of a quaternary ammonium salt, which usually will be free from silica, by ion exchange using Amberlite IRA-400 (Rohm & Haas Company).

The following experiments were performed in order to contrast the effects of the use of sodium hydroxide and of quaternary ammonium hydroxide bases in precipitating cobaltic hydroxide.

C. Each of three samples, containing no chromate or wolframate, was precipitated once with hydrogen peroxide and 3 N sodium hydroxide solutions, filtered, washed, redissolved, evaporated, and weighed exactly as described above, except that 500 ml. of hot water were used to wash the cobaltic hydroxide instead of 40 ml. The results, all high, are listed in section C of Table I.

D. Each of three samples was treated exactly as in part C except that a 2.5 N aqueous solution of trimethylbenzylammonium hydroxide was substituted for the 3 N sodium hydroxide and only 20 ml. of wash water instead of 500 ml. were used. The results are listed in section D of Table I.

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Correction

In the article on "Rapid Routine Calculation of Multicomponent Mixtures with Punched Card Machines" [Opler, Ascher, ANAL. CHEM., 22, 559 (1950)] in the second column, step 2, the number under "3" should be 289, not 589 as printed.

Nomograph for Thermometer Temperature Correction

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IN MOST distillation work, particularly in fractional distillation, temperature readings must correspond to total immersion of the thermometer mercury and to a fixed pressure, usually 760 mm. of mercury. When partial immersion thermometers' are used, it is necessary only to correct the reading to 760 mm. For accurate work, however, thermometers graduated in 0.2° C. or less are used, and such thermometers are usually of the total immersion type. In this case it is necessary to correct both for emergent mercury stem and for pressure.

In fractional distillation work where temperature readings are taken at frequent intervals, the calculation of the correction is time-consuming and tedious. The time required is greatly reduced, and all calculations are eliminated by the use of a nomograph.

The nomograph shown here is based on the regular formulas for emergent stem correction for mercury-in-glass thermometers,

$$C = N(T - t)\, 0.000156$$

and for reducing boiling points to sea level,

$$c = C - (P - 760)\frac{dt}{dp}$$

where c = final temperature correction, ° C. (emergent stem and pressure); C = emergent stem correction only; N = length of emergent mercury stem measured, ° C.; T = temperature being corrected; t = average temperature of emergent mercury stem; P = barometer reading, mm. of mercury; and dt/dp = variation in boiling point per mm. of pressure change for particular compound being distilled. This factor can be determined experimentally or calculated from the Clausius-Clapeyron equation.

The nomograph is used as follows:

Determine $T - t$ and connect this point on A by means of a straightedge to the emergent stem in ° C. on N. Determine the point of intersection on C and connect this point with the barometric pressure in millimeters on D. The intersection on the dt/dp line for the vapor under consideration gives the final correction for T for total immersion and 760-mm. pressure.

Example. Assume in a fractional distillation at atmospheric pressure that the vapor under consideration is substantially phenol.

The temperature of the vapor is $T = 179.8°$; the average temperature of the emergent stem (determined by means of a thermometer placed near the mid-point of the emergent mercury stem) is observed to be 30° C., and the emergent mercury stem has a length of 40° C. The barometer is 750 mm. For phenol
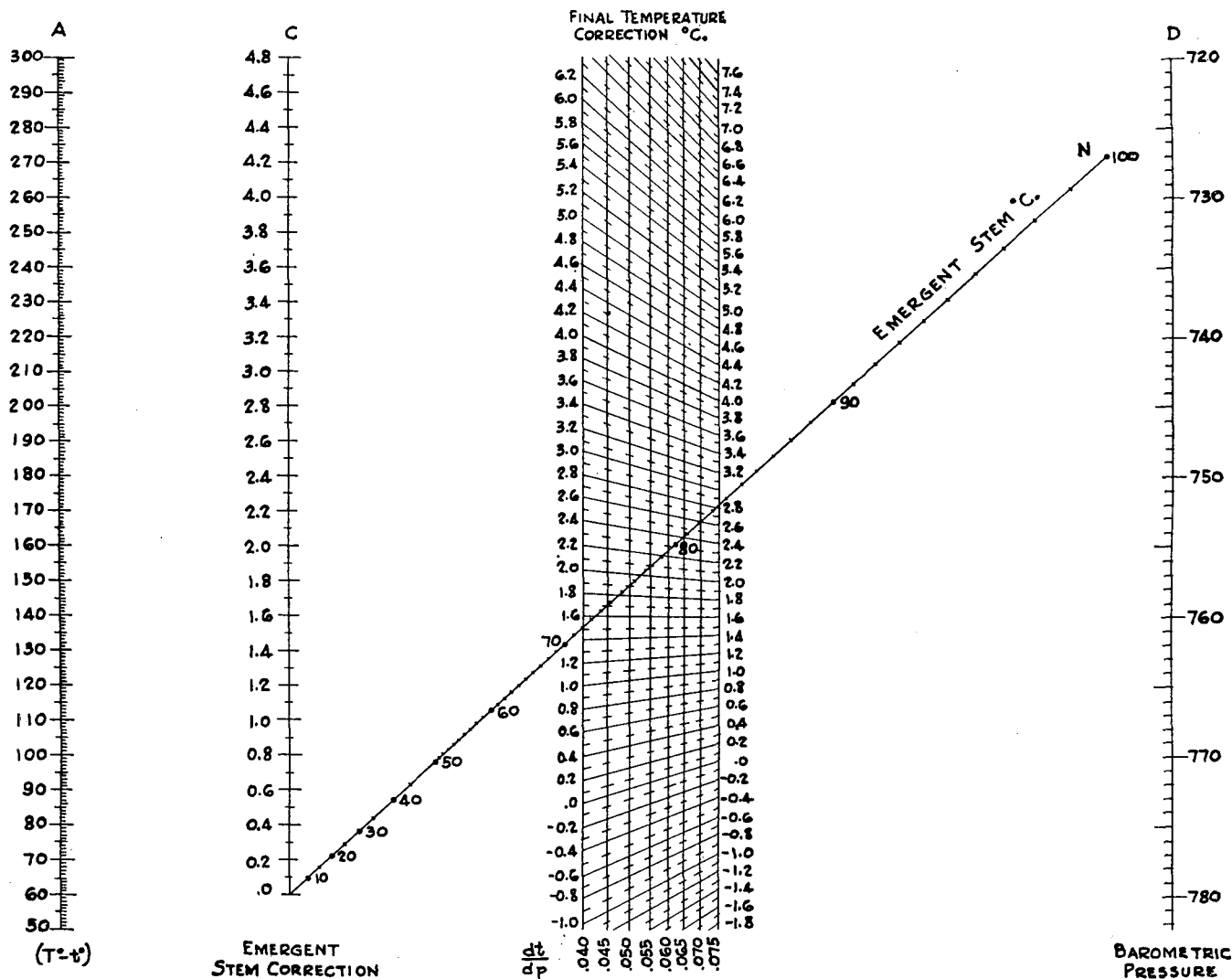

A — (T-t) scale; C — EMERGENT STEM CORRECTION; FINAL TEMPERATURE CORRECTION °C.; $\frac{dt}{dp}$; D — BAROMETRIC PRESSURE

Table I. Values of dt/dp for Various Compounds

Benzene	0.043	n-Heptane	0.045
Toluene	0.046	n-Octane	0.047
Xylenes	0.049	n-Decane	0.064
Ethylbenzene	0.049	Tetralin	0.058
Pseudocumene	0.052	Aniline	0.057
Mesitylene	0.051	o-Toluidine	0.058
Styrene	0.049	Dimethylaniline	0.058
Phenol	0.045	Carbon tetrachloride	0.045
Cresols	0.050	Ethylene dichloride	0.040
Pyridine	0.047	Chloroform	0.042
Quinoline	0.058	Acetic acid	0.069
Naphthalene	0.058		
Cyclohexane	0.044		

$dt/dp = 0.045$. Then $T - t = 149.8$. Connect 150 on A with 40 on N by means of a straightedge; the reading on C is 0.95. This is the emergent stem correction. Connect this point with 750 on D. The intersection on the $dt/dp = 0.045$ line gives the final correction of 1.4° C., or a corrected temperature of $179.8 + 1.4 = 181.2°$ C.

The nomograph is designed for correcting the temperature readings of total immersion thermometers used in distillations carried out at atmospheric pressure. For distillations at reduced pressures the use of dt/dp to correct to 760 mm. does not apply. In this case lines A and N are used to obtain the emergent stem correction on C only. It is then necessary to correct to 760 mm. by means of the integrated form of the Clausius-Clapeyron equation or experimentally determined vapor-pressure curves.

If partial immersion thermometers are used instead of total immersion, it is only necessary to correct for pressure. In this case the straightedge is used to connect the 0 of line C with the barometric pressure on D. The intersection with the proper dt/dp line gives the temperature correction for pressure.

Determination of Sulfur Dioxide in Presence of Sulfur Trioxide

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AN ACCURATE colorimetric method has been developed for determining small quantities of sulfur dioxide in gases resulting from the catalytic manufacture of sulfuric acid. The colored solution formed by combining sulfur dioxide with fuchsin-formaldehyde reagent in an acid medium follows Beer's law up to a concentration of 1 mg. of sulfur dioxide in 500 ml. of solution at $25° \pm 3°$ C.

The composition of converter exit gases encountered in sulfuric acid manufacture is of interest in studying catalytic efficiency. The sulfur dioxide content of such gases is determined by a combination of methods suggested by Haller (3) and Grant (2). Haller absorbed the sulfur dioxide and the sulfur trioxide from a gas completely with a relatively simple apparatus in 10% sodium hydroxide solution containing 5% glycerol, which effectively prevented oxidation of the sulfur dioxide. Steigman (5) used fuchsin and sulfurous acid to determine the concentration of formaldehyde by measuring the intensity of the color produced.

The method was employed with complete success in determining the sulfur dioxide of the converter exit gas in a contact sulfuric acid plant. A gas containing 8% trioxide was effectively analyzed. It was found that sulfur dioxide in concentrations up to 1 mg. in the scrubbing solution diluted to 500 ml. at room temperature followed Beer's law.

The method is adaptable for long or short tests. Results showing the average composition of the gas over fairly long periods are obtained by diluting the absorption liquor and taking an aliquot containing less than 1 mg. of sulfur dioxide.

The methods described in the literature for the determination of small quantities of sulfur dioxide in an excess of air with a comparatively high concentration of sulfur trioxide are involved and subject to error. Work was carried out with the primary object of finding a reliable method for the determination of sulfur dioxide in the gases resulting from the catalytic production of sulfuric acid.

The Reich test by Dragt and Greenan (1) was investigated thoroughly. This method is suitable for analyzing the gases entering the converter and leaving the stack. It is a very handy and rapid method for control work in commercial processes, but it is dependable only for a gas containing a negligible sulfur trioxide content; for reasons unknown to the author high results are obtained when sulfur dioxide is determined in a sulfur trioxide gas. If analysis of the converter exit gas is required for investigation purposes, the method below may prove to be valuable.

An attempt was made to eliminate the sulfur trioxide before testing for sulfur dioxide by scrubbing the gas with concentrated sulfuric acid. The sulfuric acid scrubbers were good for only a very limited period while running the Reich test. As the acid strength increased, there was a tendency to strip dissolved sulfur dioxide from the acid, giving high results.
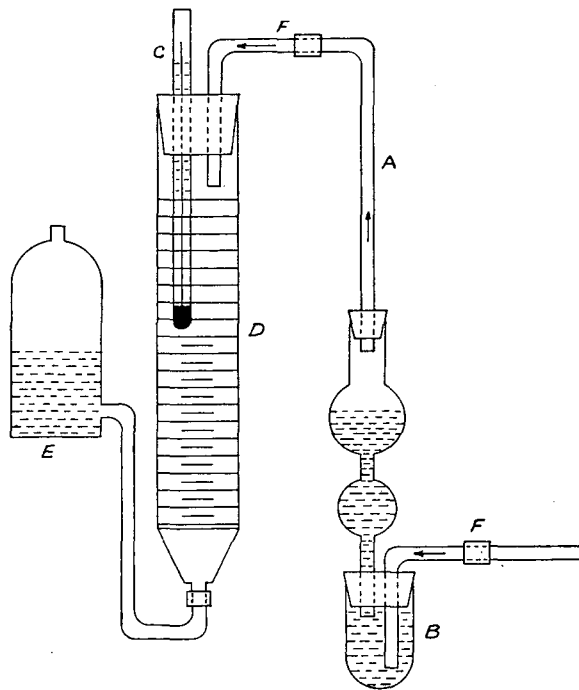

Figure 1. Absorption Apparatus

A. Calcium chloride tube
B. End of test tube, 0.75 inch in diameter and 1 inch high
C. Thermometer
D. 250-ml. buret
E. Leveling bottle
F. Pinchclamps

The Reich test has an uncertain end point, owing to the large excess of iodine mixed with the starch solution, and gives the sulfur dioxide content of the gas only at the moment the test is made.

Reis and Clark (4) absorbed the sulfur dioxide and sulfur trioxide in a gas in a sodium hydroxide solution containing stannous chloride and then titrated the strongly acidified solution with 1 N

Table I. Accuracy of Method

Test No.	SO$_2$ Determined, Mg.	SO$_2$ Added, Mg.	Total SO$_2$ Found, Mg.
1	0.105	0.200	0.304
2	0.522	0.400	0.930
3	0.390	0.100	0.488
4	0.625	0.250	0.900

Table II. Sulfur Dioxide in Gas

Test No.	Fuchsin Method, %	Reich Test, %
1	0.27	0.28
2	0.30	0.28
3	0.30	0.33
4	0.29	0.35
5	0.29	0.36
6	0.29	0.38
7	0.30	0.45

potassium iodate. Although this method is reliable, there is always danger of losing sulfur dioxide by vaporization in a strong acid solution. The titration is rather tedious for the inexperienced operator, and the end point is difficult to see and can be passed very easily.

Haller (3) used normal iodine for titrating the dissolved sulfur dioxide. There is no objection to this method if the sodium hydroxide solution containing the sulfur dioxide is used for titrating an acid solution of normal iodine, and the starch indicator is added just before the end point. This can be observed by the light amber color of the iodine solution. For very low concentrations of sulfur dioxide in a gas, such a procedure would become impracticable.

REAGENTS AND APPARATUS

Fuchsin solution is prepared by adding 15 ml. of concentrated sulfuric acid to 200 ml. of distilled water, adding 4.0 ml. of a 3% basic fuchsin solution in alcohol and 1.0 ml. of 40% formaldehyde, and diluting to 250 ml. with distilled water.

The sodium hydroxide used is a 10% solution containing 5% glycerol.

Standard sodium bisulfite solution is prepared by dissolving C.P. sodium bisulfite in water, so that 1 ml. will contain 0.1 mg. of sulfur dioxide. It is standardized by titrating iodometrically.

A Fisher electrophotometer or Beckman DU spectrophotometer is used. The absorption apparatus is shown in Figure 1.

PROCEDURE

Preparation of Standards. Prepare standards by adding 1 to 10 ml. of the standard sodium bisulfite solution to a 500-ml. volumetric flask containing 300 ml. of water, 4.0 ml. of fuchsin solution, and 2.5 ml. of concentrated sulfuric acid. Dilute to 500 ml. with distilled water and allow to stand 0.5 hour at room temperature,

$25° \pm 3°$ C., for the development of the color. Shake occasionally and measure the per cent light transmitted in the electrophotometer, using a green filter on the spectrophotometer at 580 mu with the reagent in the reference cell.

Analysis of Gas. Scrub the gas through 15 ml. of the sodium hydroxide solution in the apparatus as shown in Figure 1. (The volume of the test tube is small to allow the liquid to rise in the calcium chloride tube to facilitate efficient scrubbing.) The volume of the residual gas collected is dependent on the sulfur dioxide content of the gas. Measure between 50 and 250 ml. of residual gas in the buret by using the leveling bottle. Correct the measured volume to standard conditions (0° C. and 760 mm. of mercury), and adjust for the volume of sulfur dioxide to obtain the total volume of the gas sample. At 0° C. and 760 mm. of mercury, 1 mg. of sulfur dioxide occupies a volume of 0.34. ml.

Wash the sodium hydroxide solution into a 500-ml. volumetric flask containing 300 ml. of water, 4.0 ml. of fuchsin solution, and 2.5 ml. of concentrated sulfuric acid (an excess of 100% acid will have no appreciable effect), and proceed as directed for the preparation of the standards.

DISCUSSION

For determining the accuracy of the proposed method, known amounts of sulfur dioxide were added to aliquots of samples previously analyzed by the method and the total sulfur dioxide content was determined. Results are shown in Table I.

For comparative purposes simultaneous tests of a gas containing 8.0% sulfur trioxide using the above method and the Reich test (with sulfuric acid scrubbers) gave the sulfur dioxide content as shown in Table II.

These tests, made at 5-minute intervals, indicate the stripping of the sulfur dioxide from the concentrated sulfuric acid, giving successively higher results in the Reich test. The sulfur dioxide in the exit stack gas at the same time was 0.25%, as determined by the Reich test. In the absence of sulfur trioxide, reproducible results can be obtained with the Reich test.

Temperature has a definite effect upon the intensity of color produced at the 0.5-hour period. At 10° C. a concentration up to 2.0 mg. of sulfur trioxide in 500 ml. of solution will also follow Beer's law.

Time is also an important factor during the test. Readings should be taken within 5 minutes of the allotted time. A 15-minute variation from the 0.5-hour limit will produce approximately a 10% error.

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Purification of Ninhydrin by Crystallization

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THE use of ninhydrin (triketohydrindene hydrate) for the specific determination of alpha-amino acids in the ninhydrin–carbon dioxide method (6), for the detection of amino acids in paper chromatography (1), and for the quantitative colorimetric determination of amino acids in fractions obtained from fractionating columns (2, 4) has established it as an important reagent in amino acid chemistry. Moore and Stein (2) found a single treatment with Norit followed by crystallization from water adequate purification of their ninhydrin. However, a single crystallization from water is not adequate for commercial

ninhydrin that is orange-brown in color, has a strong odor, and contains traces of selenium. The following procedure has been found efficient and gives a good product in high yield with few crystallizations.

Crude ninhydrin (100 grams) is dissolved in 500 ml. of hot 2 N hydrochloric acid and any brown scum is removed with a spatula. Acid-washed neutral Norit (10 grams) is added, and the solution is allowed to boil gently for about 10 minutes, and then filtered hot through a medium-pore fritted disk. Hot saturated solutions of ninhydrin are somewhat orange in color, but when cool are very pale yellow. Crystallization of ninhydrin from the

filtrate is allowed to take place slowly with occasional stirring while the solution cools to room temperature. Crystallization is completed at 4° C. for 16 hours. The crystals are collected on a fritted disk, washed three times with 50-ml. portions of ice-cold 1 N hydrochloric acid, and sucked free of excess liquid. Residual water and hydrochloric acid are removed in 24 hours in an evacuated desiccator over solid potassium hydroxide. The yield is approximately 94% of the starting material. When dry, the product is stored in an amber bottle.

Pure ninhydrin is very pale yellow with a greenish tint, is completely odorless, and dissolves in water to give a clear light yellow solution. Ninhydrin purified as above turns pink at 125° C., shrinks with loss of water of hydration, becomes deep purple red at 139–140° C., and melts sharply with decomposition at 241° C. (uncorrected). Corrected for stem temperature the melting point is 247° C. Ruhemann (3) reported similar observations and found a melting point of 239–240° C. (uncorrected). Teeters and Shriner (5) recorded a value of 241–243° C. but did not state in their publication whether this was a corrected melting point.

Samples of ninhydrin have been found which contribute 50 to 60 mm. gas pressure, measured at the 0.5-ml. marked in the Van Slyke–Neill manometric apparatus (7), in excess of the normal blank analysis in the ninhydrin carbon dioxide method (6). After purification, two treatments with Norit, each followed by crystallization, a product was obtained with properties as described above and which no longer contributed to the gas pressure of the blank ninhydrin carbon dioxide analysis.

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Kjeldahl Microdetermination

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THREE improvements with respect to accuracy and convenience in the micro-Kjeldahl procedure have been made. The first modification is designed to eliminate the occasional, but extremely annoying, suck-back of material into the steam generator, or of distillate and receiving acid back into the distillation flask. This is accomplished by means of a simple, all-glass check valve on the steam generator.

In Figure 1, the valve is shown on a Kirk-type Kjeldahl apparatus (2). It consists of a solid, ground-glass ball, a ground ring seat 1 mm. in width, and four indentations placed to allow approximately a 2-mm. lift. The seat is ground in with a 45° taper brass grinding tool. This valve is applicable to steam distillation setups in general, and is particularly effective on the type in which the steam generator surrounds the distillation flask; there are numerous occasions when interruption without suck-back of a steam distillation in a Pozzi-Escot apparatus (7) may be desirable. At the completion of a Kjeldahl distillation, the flame is removed, and the distillation flask emptied in the usual way by holding a fingertip over the tip of the valve.

An investigation carried out in this laboratory into the cause of frequent, slightly low results obtained on standard samples led to the second modification of the Kirk apparatus. Willits, John, and Ross (8) obtained "slightly low nitrogen values" on pure nitrogenous compounds, using the Kjeldahl macroprocedure of the Association of Official Agricultural Chemists. These results were accounted for by assuming that all the ammonia was not caught by the trapping liquid. Subsequent use of a Goessman trap (1) on the receiver gave higher and more nearly theoretical results.

The practice in this laboratory had been to immerse the delivery tip (8 mm. in outside diameter) of a Kirk apparatus in 5 ml. of 2% boric acid in a tilted, 50-ml. Erlenmeyer flask. Distillation had been carried out with the tip immersed for 3 minutes, and then for 1 minute with the tip above the liquid (5). The slightly low results obtained with pure ammonium sulfate samples indicated incomplete absorption of ammonia. Therefore, in order to facilitate absorption of ammonia and still use the smallest possible amount of boric acid, a small bulb was blown on the delivery tip and five holes were punched therein with a hot, 1-mm. tungsten wire (Figure 2). This bulb was immersed in 5 ml. of boric acid in a 20 × 150 mm. test tube. The use of the test tube provided a greater depth of boric acid, and permitted distillation of a definite volume (appropriate marks on the test tube) rather than the indefinite amount which varied with the rate of distillation during the fixed time interval. Eight milliliters were collected with the tip immersed and 2 ml. with the tip raised. A quantitative transfer to a suitable titration flask with two 1-ml. washings brought the total volume to about 17 ml.
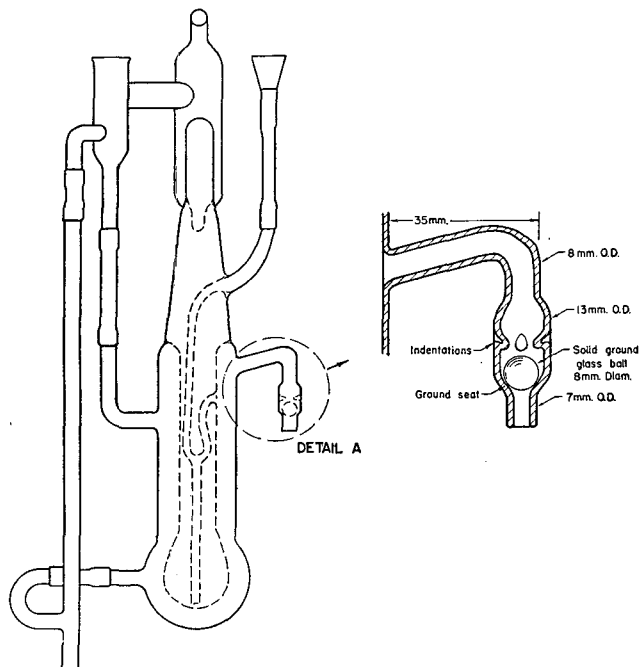

Figure 2

Figure 1   Diagram of Check Valve
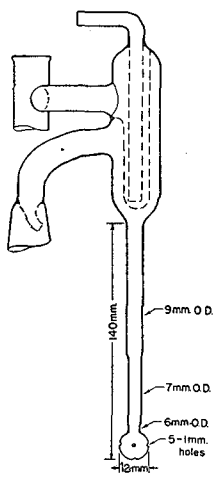
Theoretical results were obtained, thus confirming on a micro scale the observations of Willits and co-workers. Although these authors and others have reported blanks due to alkali entrainment (and considerably reduced them with a new connecting bulb), this is not a problem in micro-Kjeldahls, using either a Kirk or a Parnas and Wagner apparatus (6).

The third modification consists of a simplified titration procedure. The use of boric acid as a receiver in micro-, semimicro-, and macro-Kjeldahl procedures is widespread. Ordinarily, standard hydrochloric or sulfuric acid is used to titrate the trapped ammonia. Niederl (5) uses 0.01 N potassium biiodate as a receiving solution, and back-titrates with standard alkali. In this laboratory, the advantages of boric acid and potassium biiodate are combined. Because potassium biiodate is a primary standard as well as a strong stable acid, the use of a base either for titration or standardization is eliminated.

The receiving liquid is 2% boric acid, to which has been added sufficient bromocresol green–methyl red mixed indicator (3) to give a faint pink color when 5 ml. of this solution are diluted to 17 ml. with distilled water. Five milliliters of this solution are pipetted into a test tube, and the distillation is carried out as described above. Titration is carried out with 0.01 N potassium biiodate solution (4) to an end point determined by comparison with the boric acid–indicator solution (5 ml. diluted to 17 ml.).

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Optical-Crystallographic Identification of Sulfanilamide

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MANY of the chemical tests for sulfanilamide have not been specific. As an extension of similar studies in this laboratory (3, 6, 8, 9), an optical study of several derivatives of sulfanilamide was undertaken, in order to facilitate the identification of this compound.

PREPARATION AND ANALYSIS

The Schiff bases were prepared by the reaction of equimolecular amounts of sulfanilamide and aldehyde in ethyl alcohol, the mixture being warmed for about 5 minutes to ensure complete reaction (2). The product was then removed by filtration and crystallized usually from alcohol. The crystals were washed with either acetone or alcohol, depending on their solubility. Several compounds were prepared which did not form crystals of sufficient size to be of use in the determination of their optical-crystallographic properties. Except for a description of the crystal appearance of the Schiff bases from benzaldehyde and cinnamic aldehyde (15), no optical data are found in the literature.

Several of the sulfanilamide-cinchona addition compounds were prepared, following the methods described in the literature (10). Anils with sugars also were prepared by the method described in the literature (2).

The melting points of the purified compounds were determined on a "bloc-Maquenne" apparatus. No stem correction was made. Nitrogen was determined by the Gunning method (1). Concentrated hydrogen peroxide solution was used to hasten the decomposition of some of the compounds according to the method proposed in this laboratory (7).

The optical-crystallographic properties of the compounds were obtained by the use of a petrographic microscope. The refractive indexes were determined by the immersion method; the interference figures were used as a means of determining the optical orientation of the crystals. The most usual orientations are noted, in order to facilitate the use of the optical properties in the detection of sulfanilamide. The temperature at which the indexes were determined was 25° ± 1° C.

EXPERIMENTAL RESULTS

The data obtained are reported in Table I. Guided by them a method of identification based on the optical-crystallographic properties of p-chlorobenzylidene sulfanilamide has been devised.

To a small amount of the unknown on a microscope slide, a drop of water and a drop of a saturated solution of p-chlorobenzalde-hyde are added. The slide is warmed gently over a small flame. After crystals have formed, the excess water is removed by a microfilter, and the crystals are dried carefully over a small microflame. The crystals are mounted in liquids having indexes of refraction of 1.655 and 1.703. The former index corresponds to the index beta. The crystals will have a higher index of refraction than 1.703 in one position of extinction.

An alternative procedure is suggested, in order to obtain crystals that are large enough for optical-crystallographic study, when the concentration of the sulfanilamide is low. One of the cinchona alkaloid addition compounds is used in this test. Five milliliters of an alcohol or water solution of the substance, which is thought to be sulfanilamide, are placed in a small beaker, and to this are added a few milliliters of a dilute solution of quinine bisulfate. The solution is heated slowly until there is only a small volume, and then it is cooled for 15 minutes below room temperature. A small portion of the crystals is transferred to a glass slide. The crystals are washed with alcohol and then with acetone; the excess liquid is removed in each instance. The crystals are air-dried and warmed slightly to make certain that they are completely dry. Two slides of the crystals are prepared, one set of crystals mounted in an immersion liquid of refractive index 1.657 and the other set mounted in one of refractive index 1.668. The crystals become invisible in each immersion liquid at the correct position of extinction. Large crystals are obtained which give characteristic acute bisectrix interference figures. The other optical properties, which are listed for this compound in Table I, also may be determined. If additional confirmation is desired, other derivatives given in the table may be prepared and tested in a similar manner.

POLYMORPHISM OF SULFANILAMIDE

Attempts were made to isolate different crystalline phases of sulfanilamide. Three phases were found and are described.

A. Sulfanilamide Monohydrate. Sulfanilamide monohydrate was obtained by the method described by Kienle and Sayward (5) by letting a cold (20° C.) saturated solution of sulfanilamide crystallize in a refrigerator at 4° C. Transformation to anhydrous sulfanilamide is rapid at 25° C., especially if the humidity is not high.

> System, orthorhombic
> Sign, positive
> Common orientation, *Bxa*
> Elongation, plus or minus

Table I. Analytical and Crystallographic Data of Sulfanilamide Derivatives

Compound	Melting Point Block, °C.	Nitrogen Calcd., %	Nitrogen Found, %	Optical Sign	Elongation	Refractive Indexes at 25 C. Alpha	Beta	Gamma	Axial Dispersion	Crystal System
Benzylidene sulfanilamide	188	10.76	10.73, 10.70	+	±	1.494	1.676	>1.703	r > v	Monoclinic
o-Chlorobenzylidene sulfanilamide	180	9.52	9.68, 9.60	+	−	1.514	>1.703ᵃ	>1.703	r > v	Monoclinic
p-Chlorobenzylidene sulfanilamide	186	9.52	9.52, 9.46	+	±	1.486	1.655	>1.703	r > v	Monoclinic
Cinnamylidene sulfanilamide	216	9.79	9.68, 9.64	+	−	1.528	>1.703ᵃ	>1.703	None	Monoclinic
3,4-Dimethoxybenzylidene sulfanilamide	193	8.75	8.85, 8.71	+	+	1.521	1.605	>1.703	v > r	Monoclinic
2,4-Dimethoxybenzylidene sulfanilamide	197	8.75	8.72, 8.80	+	−	1.655	1.674	>1.703	v > r	Monoclinic
Furfurylidene sulfanilamide	196	11.20	11.12, 11.07	+	+	1.493	1.651	>1.703	r > v	Monoclinic
o-Hydroxybenzylidene sulfanilamide	211	10.14	10.07, 10.02	+	−	1.482	1.680	>1.703	None	Monoclinic
p-Hydroxybenzylidene sulfanilamide	204	10.14	10.20, 10.25	+	−	1.512	1.666	>1.703	None	Monoclinic
p-Methoxybenzylidene sulfanilamide	200	9.66	9.69, 9.80	+	+	1.498	1.645	>1.703	r > v	Monoclinic
m-Methylbenzylidene sulfanilamide	201	10.22	10.05, 10.11	+	−	1.492	1.661	>1.703	None	Monoclinic
o-Nitrobenzylidene sulfanilamide	183	13.77	13.77, 13.65	−	−	1.476	1.690	>1.703	None	Orthorhombic
m-Nitrobenzylidene sulfanilamide	170	13.77	13.73, 13.68	−	+	1.574	1.676	>1.703	None	Orthorhombic
p-Nitrobenzylidene sulfanilamide	175	13.77	13.79, 13.75	−	−	1.524	>1.703ᵃ	>1.703	None	Orthorhombic
Cinchonidine sulfanilamide H_2SO_4	183	8.80	8.75, 8.67	+	+	1.507	1.594	>1.671ᵇ	None	Monoclinic
Quinine sulfanilamide H_2SO_4	209	8.41	8.40, 8.35	−	+	1.596	1.657	1.668	r > v	Monoclinic
Quinine sulfanilamide 1½ H_2SO_4	186	8.71	8.84, 8.86	+	+	1.574	1.618	>1.703	None	Monoclinic
Glucoseanil sulfanilamide	211	8.38	8.28, 8.20	+	−	1.569	1.574	>1.676ᵇ	r > v	Monoclinic
Mannoseanil sulfanilamide	202	8.38	8.22, 8.28	−	+	1.581	1.615	1.636	r > v	Monoclinic

ᵃ β is only a small amount above 1.703.
ᵇ Crystals dissolve in oil above recorded refractive index.

No dispersion
No pleochroism
Alpha, 1.505
Beta, 1.639
Gamma, >1.85

B. Anhydrous Monoclinic Phase. This stable phase, as Watanabe (12) found, predominates in commercial preparations. Most desirable crystals for microscopic studies were obtained by hastening crystallization from hot acetone solution. These crystals appear to be orthorhombic between crossed Nicols, but are definitely monoclinic. The same phase, but different habit, was obtained from methanol. Crystals from the latter solution do not appear orthorhombic. Goniometric measurements and refractive indexes proved, as pointed out by Watanabe, that the crystals from acetone and methanol were the same phase.

System, monoclinic
Sign, positive
Common orientation, Bxa
Elongation, negative
Dispersion axial, slight, v > r
No pleochroism
Alpha, 1.555
Beta, 1.672
Gamma, > 1.85

Keenan (4) reports for this phase the following:

System, ?
Alpha, 1.570
Beta (ni), 1.677
Gamma, > 1.733

C. Anhydrous Monoclinic Phase. This stable phase is obtained upon crystallization from hot n-propyl or n-butyl alcohol, from chloroform, or from water on long standing. No transformation of phase C was evident after one year's standing.

System, monoclinic
Sign, positive
No dispersion
No pleochroism
Common orientation, centered Bxa
Elongation, positive (Bxa)
Alpha, 1.547
Beta, 1.633
Gamma, >1.85

The data for this phase correspond to those found in this laboratory by White (13). Van Zyp (11) reported different habits of sulfanilamide which he considered to be the same phase. Watanabe (12) reported x-ray and goniometric studies of three phases. Williams and Maresh (14) reported no quantitative data or optical-crystallographic properties in isolating five phases of sulfanilamide.

By using ten different organic solvents and water, two anhydrous phases of sulfanilamide and the monohydrate were isolated. A complete correlation between the results obtained in this laboratory and the results reported by Watanabe, Van Zyp, and Williams and Maresh was not possible.

SUMMARY

Fourteen Schiff bases, three cinchona alkaloid addition products, and two anils with sugars of the sulfanilamide have been prepared and analyzed, and their optical-crystallographic properties have been reported. Sulfanilamide has been recrystallized from different solvents and analyzed, and the optical-crystallographic properties have been reported for three distinct phases. A method of identification of sulfanilamide making use of the optical-crystallographic data of the Schiff base with p-chlorobenzaldehyde and the quinine bisulfate addition product has been suggested.

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(14) Williams, E. F., and Maresh, C., Abstracts of Papers, 104th Meeting, Am. Chem. Soc., Buffalo, N. Y., Sept. 7 to 11, 1942, p. 2L.
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RECEIVED August 15, 1949.

Correction

In the article on "Stable High-Frequency Oscillator-Type Titrimeter" [Anderson, Kermit, Bettis, E. S., and Revinson, David, ANAL. CHEM., 22, 743 (1950)], the professional connection of the authors should have been given as Fairchild Engine and Airplane Corporation, NEPA Division, Oak Ridge, Tenn.

Test for Sediment in Fuel Oil by Extraction

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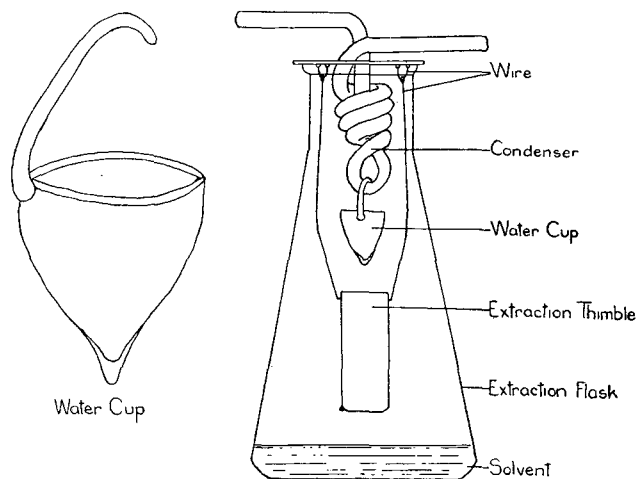
Figure 1. Extraction Apparatus

A FOOTNOTE to method D 473-48 of the American Society for Testing Materials (method Z11.58-1948 of the American Standards Association) reads:

When testing oils having high water content, difficulty due to clogging of the thimble with moisture may be overcome by interrupting the extraction when this occurs and drying the thimble in an oven before proceeding further with the extraction.

A method of overcoming the difficulty caused by water clogging the thimble has been devised which allows the extraction to be completed without interruption for drying the thimble in an oven. It is based on the fact that water and benzene (the extraction solvent) distill azeotropically but separate into two phases on condensation.

A small addition is made to the apparatus in the form of a cup which is hung on the bottom loop of the condenser (Figure 1). Any water which is distilled out of the thimble condenses with the benzene on the condenser and forms a second liquid phase which eventually collects in the cup, displacing the benzene with which it is normally filled. Glass cups which have been made at the Dominion Laboratory are conical in shape, approximately 20 mm. in diameter and 25 mm. deep, and hold 3 ml. A glass hook fused on the rim at one side is so shaped that when hung on the condenser the cup hangs with its rim reasonably level.

When the water cup is used some other means of suspending the extraction thimble than that shown in the standard method must be employed. A satisfactory suspension consists of two stiff platinum or Nichrome wires hung from wire eyelets soldered to the top plate of the condenser. The lower ends of the wires are bent up slightly and are passed through the holes in the thimble.

In use, any water contained in the oil collects in the water cup. If the cup becomes full of water, it is a simple matter to empty it after cooling the apparatus slightly.

ACKNOWLEDGMENT

The author wishes to thank the director of the Dominion Laboratory for granting permission to publish this note.

Protective Colloids in the Volumetric Determination of Chloride Ion

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THE use of protective colloids in titrations involving the precipitation of silver halides has been found advantageous by Schneider (4) in silver iodide titrations and by Lottermoser and Lorenz (2) in the Mohr method for chlorides, but has not been tested as thoroughly as is desirable. Kolthoff and Stenger (1) state that a protective colloid aids in the detection of the end point with adsorption indicators. Pierce and Haenisch (3) state that dextrin is often used in chloride titrations to prevent coagulation.

Standard solutions of silver nitrate and potassium chloride were prepared by direct weighing of the purified salts and the concentrations were checked gravimetrically; the agreement was within 1 part in 1000. As protective colloids, gum arabic, gelatin, dextrin, and agar agar were tried. A 1% solution of each was prepared and 5 ml. in a total volume of 100 ml. gave good results.

In the Mohr method all four colloids retarded coagulation of the silver chloride and made the end point much easier to detect than in their absence. Gum arabic and gelatin gave slightly more consistent results than the other two. Gelatin gave some trouble from frothing, leaving gum arabic as first choice.

When the two standardized solutions were compared by the Mohr method with gum arabic as protective colloid, 24.96 ml. of 0.1000 N potassium chloride solution required 25.19 ± 0.02 ml. of 0.1000 N silver nitrate solution in three titrations. Thus, the re-

sults by this method were found too high by about 9 parts in 1000. The dichlorofluorescein end point is much improved by a protective colloid. In comparative titrations with the four colloids the volume of silver nitrate solution required was 1 to 2 parts in 1000 less with dextrin and agar agar than with gelatin and gum arabic. Shortly before the end point in the presence of a protective colloid the color changes from a green fluorescence to a milky tan. The end point was taken as the first change from tan to pink. A very small excess of silver nitrate beyond this point changes the color to bright red.

When gum arabic was used in titrations with the standardized solutions, excellent agreement with the calculated end point was obtained. For example, several 24.96-ml. portions of 0.1000 N potassium chloride solution to which were added 45 ml. of water, 5 ml. of 1% gum arabic solution, and 0.8 ml. of 0.1% dichlorofluorescein solution required 24.97 ± 0.01 ml. of 0.1000 N silver nitrate solution. Variation of the volume of 0.1000 N potassium chloride from 10 ml. to 45 ml. with the same total volume made no difference in the precision and accuracy, nor did inclusion of 1.2 grams of calcium nitrate. It is best to keep the pH above 4.

In comparisons of the standardized solutions by the Volhard method, the silver nitrate required varied from good agreement with the dichlorofluorescein method to 2 to 4 parts in 1000 too

high. The addition of gum arabic in the back-titration with thiocyanate made the end point sharper and more distinct.

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Photometric Method for Estimation of Minute Amounts of Mercury

Use of G.E. Germicidal Ultraviolet Intensity Meter

C. W. ZUEHLKE AND A. E. BALLARD
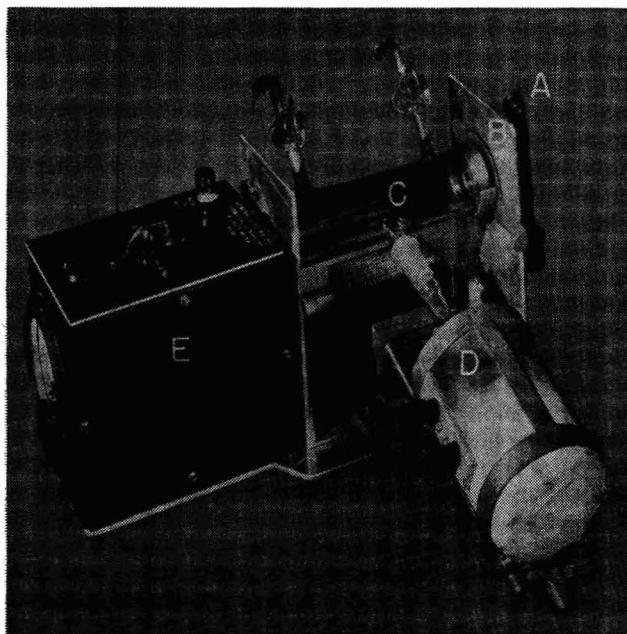
Eastman Kodak Company, Rochester, N. Y.

Figure 1. Apparatus with Lamp Housing Removed

Figure 2

Figure 3

IN A previous article (*1*) a procedure was given for the determination of 0.02 to 0.6 microgram of mercury in up to 500 ml. of solution. The method consists in collecting the mercury, volatilizing it into a quartz-ended cell, and measuring the amount of light of 2537 A. absorbed by the mercury vapor, using a specially designed ultraviolet photometer.

Recently, the General Electric germicidal ultraviolet intensity meter has been offered as a completely self-contained unit, having dimensions of 6 × 5 × 4 inches (15 × 12.5 × 10 cm.).

A study of the reproducibility and sensitivity of this instrument indicates that the substitution of this meter for the special photometer originally used makes possible the assembly of a compact and comparatively inexpensive apparatus. This should extend the use of the procedure considerably.

Figure 1 is a photograph of the apparatus with the lamp housing removed. *A* is the 4-watt G.E. germicidal lamp, *B* is the shutter, *C* is the quartz-ended sample cell, *D* is the movable furnace, and *E* is the meter. A 350-ohm rheostat for varying the intensity of the germicidal lamp and the rheostat for controlling the furnace temperature are not shown.

OPERATION OF METER

The germicidal lamp is turned on and allowed to operate at full line voltage for 10 minutes with the shutter closed. The meter circuit is balanced at zero in artificial light (in an inside
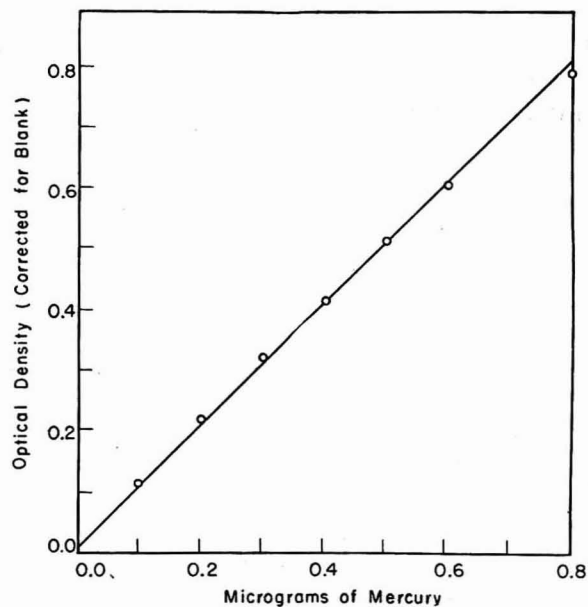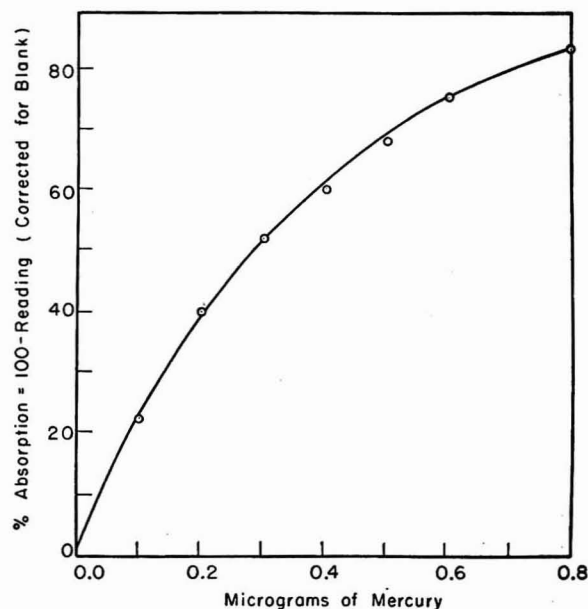
room), which is a standardization of the meter circuit. The meter is set for the range from 0 to 100 mw. per square foot, the shutter is opened, and the light intensity is adjusted by means of the lamp rheostat, to bring the needle on the meter to 1.0— i.e., 100% of scale. The shutter is closed and opened to ensure that the 0 to 100% scale deflection is obtained.

The cadmium sulfide pad containing mercury is placed in the pad-holding tube, heated by means of the movable furnace, and the procedure recommended in the original paper is followed. The data may best be recorded in terms of per cent absorption, which is 100% minus the instrument reading.

The curves given in Figures 2 and 3 were obtained by taking

known amounts of mercury in 250 ml. of water through the complete procedure.

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(1) Ballard and Thornton, IND. ENG. CHEM., ANAL. ED., **13**, 893 (1941).

CRYSTALLOGRAPHIC DATA

32. RDX (Cyclotrimethylenetrinitramine)

Contributed by WALTER C. McCRONE, Armour Research Foundation, Illinois Institute of Technology, Chicago 16, Ill.
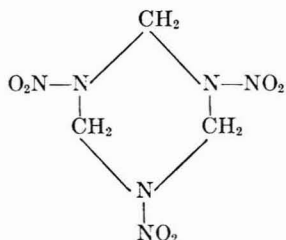
Structural Formula for RDX

R DX is the symbol for the high explosive cyclotrimethylenetrinitramine, which was developed for use during World War II. It can be crystallized from a variety of solvents including benzene, nitromethane, acetone, acetic acid, and nitric acid. It possesses one very unstable polymorphic form (II), which can be isolated only in small quantities for a few seconds during fusion studies on a microscope slide. Because of its physical instability, there is no possibility of obtaining RDX II even in laboratory recrystallizations.

RDX (I)

CRYSTAL MORPHOLOGY

Crystal System. Orthorhombic.

Form and Habit. RDX crystallizes in a wide variety of habits from needles (nitric acid) and plates (acetic acid) to massive (nitromethane, acetone). Usually flattened on 001 showing the forms: {110}, {120}, {101}, {011}, and {111}.

Axial Ratio. $a:b:c = 0.881:1:0.813$.

Interfacial Angles (Polar). $110 \wedge 1\overline{1}0 = 82° 50'$; $120 \wedge \overline{1}20 = 59°$; $101 \wedge \overline{1}01 = 85° 30'$; $011 \wedge 0\overline{1}1 = 78° 20'$.

X-RAY DIFFRACTION DATA

Cell Dimensions. $a = 11.61$ A.; $b = 13.18$ A.; $c = 10.72$ A.

Formula Weights per Cell. 8.

Formula Weight. 222.13.

Density. 1.82 (pycnometer); 1.81 (x-ray).

Principal Lines

d	I/I_1	d	I/I_1
6.69	0.62	3.13	Very weak
5.71	0.24	3.03	1.00
5.37	0.13	2.93	0.26
5.01	0.68	2.87	0.16
4.35	0.40	2.76	0.54
4.16	0.13	2.69	0.20
4.02	0.29	2.63	Very weak
3.91	0.07	2.55	0.36
3.77	0.13	2.50	Very weak
3.51	0.42	2.43	0.20
3.40	Very weak	2.36	0.17
3.30	0.50	2.28	0.07

d	I/I_1	d	I/I_1
2.25	Very weak	2.01	0.07
2.20	Very weak	1.97	0.09
2.12	0.04	1.92	Very weak
2.08	0.04	1.86	0.07

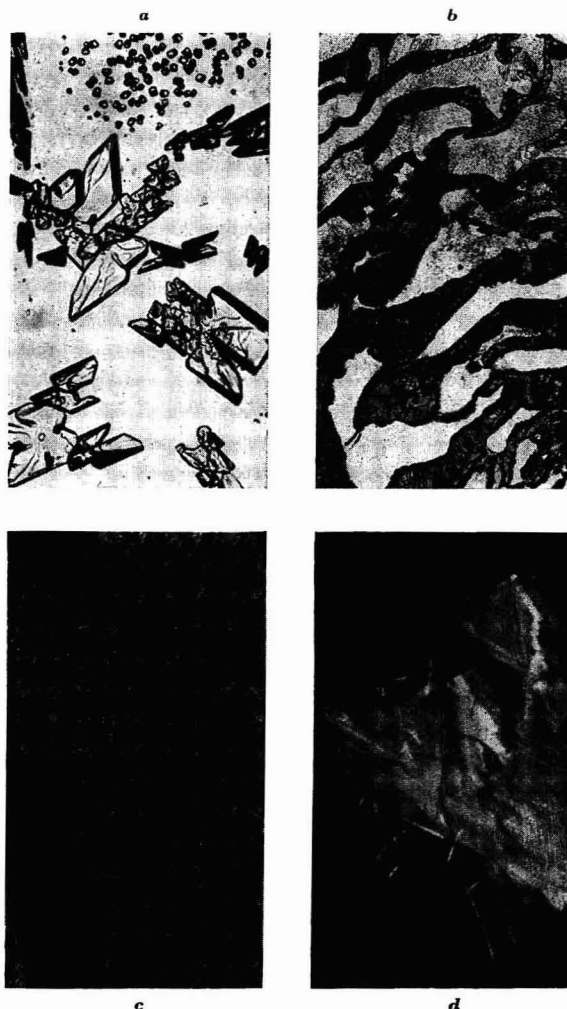**Figure 1. Photomicrographs of RDX**

a. Sublimate
b. Crystals from fusion, × 8
c. Crystals from fusion, × 160, crossed Nicols
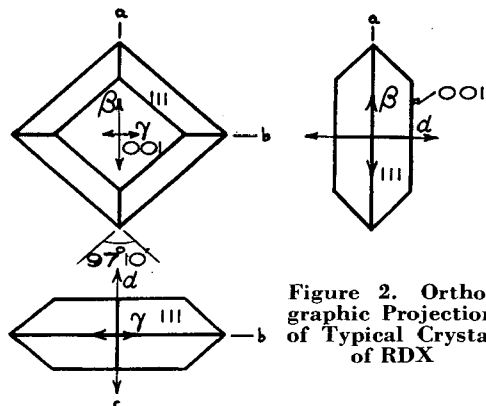d. Crystals from thymol. Needles of II, plates of I

Figure 2. Ortho-graphic Projection of Typical Crystal of RDX

OPTICAL PROPERTIES

Dispersion of RDX (20° C.) (4)

Wave Length of Light, A.	Refractive Indexes			Optic Axial Angle	
	Alpha	Beta	Gamma	2E	2V
6680	1.5725	1.5906	1.5957	95° 15'	55° 21'
5893	1.5775	1.5966	1.6015	91° 36'	53° 22'
5350	1.5827	1.6031	1.6079	87° 33'	51° 8'
5020	1.5874	1.6084	1.6130	83° 53'	49° 7'
4860	1.5895	1.6113	1.6157	82° 1'	48° 4'
4710	1.5923	1.6145	1.6187	79° 42'	46° 47'
4470	1.5970	1.6205	1.6245	75° 34'	44° 26'

Dispersion. $r > b$.
Optic Axial Plane. 100.
Sign of Double Refraction. Negative.
Acute Bisectrix. c.
Molecular Refraction (R) (5893 A.; 25° C). $\sqrt[3]{\alpha\beta\gamma} = 1.592$.
R (calcd.) = 43.7. R (obsd.) = 41.4.
FUSION DATA. RDX sublimes readily before melting with decomposition at 205° C.; platelets lying on 001 are formed.

The melt solidifies spontaneously and rapidly with large gas bubbles showing a terracelike structure. Many of the larger areas of uniform orientation show an off-center acute bisectrix interference figure with $2E = 113°$, $2H = 67°$, $v > r$ (+); characteristic of RDX (II). Usually, however, RDX (I) appears showing centered acute bisectrix or off-center optic axis figures with $2E = 92°, 2V = 53°, r > v$ (-).

RDX (II)

An unstable polymorph of RDX can be obtained by recrystallization on a microscope slide from high boiling solvents such as thymol, nitrobenzene, aroclor, and TNT. This modification has not been characterized because of the difficulty of obtaining and preserving well formed crystals. It should never be obtained on a laboratory scale; hence it should not interfere with analytical schemes based on the crystallography of RDX (I). Some of the optical properties are given above under Fusion Data.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of Irene Corvin in determining and measuring the powder diffraction data, and of John Krc in the single crystal x-ray work. Most of the work reported above was carried out at Cornell University under contract (B-123, OEMsr-193) with the Office of Scientific Research and Development (2).

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(4) Terpstra, P., Z. Krist., 64, 150 (1926).

CONTRIBUTIONS of crystallographic data for this section should be sent to Walter C. McCrone, Analytical Section, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Ill.

Titration of Functional Groups with Lithium Aluminum Hydride

SIR: Since the publication of the article, "Electrometric Titration of Alcohols Using Lithium Aluminum Hydride" [Lintner, C. J., Schleif, R. H., and Higuchi, T., ANAL. CHEM., 22, 534 (1950)], further studies in this laboratory have shown that molecular oxygen reacts rather rapidly with lithium aluminum hydride in solution. This is indicated in Table I, which shows the decrease in the effective hydride concentration in solution when dry oxygen is bubbled through the solution. This effect was not previously noticed in our analytical studies, as compensatory deterioration of the reagent probably took place in the blank determination. Furthermore, the hydrogen gas which is usually produced during the reaction period probably acted to a certain extent as a gas blanket.

Our analytical procedure has, therefore, been modified to reduce the effect of this oxidative side reaction. All analyses, including the blank, are now run under nitrogen. The hydride solutions are also stored under nitrogen.

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Table I. Effect of Oxygen on Hydride Concentration

	Bubbled with Dry Nitrogen, N	Open to Air, N	Bubbled with Dry Oxygen, N
Immediate titration[a]	0.538	0.499	0.420
Titration after 5 minutes[b]	0.539	0.427	0.082

[a] Lithium aluminum hydride-solution pipetted in and titrated immediately with magnetic stirring.
[b] Solution titrated after standing for 5 minutes under conditions indicated and with magnetic stirring.

Constant-Rate Feed Device

SIR: In connection with the note on a constant-rate feed device [ANAL. CHEM., 22, 626 (1950)], I would like to call attention to an article on the same subject [Can. Chem. Process Inds., 31, 153–4, 157 (1947)]. Basically the meters are the same. The one we have described contains two refinements which could readily have been incorporated into that of Lundsted and associates. Building the manometer into the flowmeter itself as we have done is only a minor improvement. However, we believe that use of the Mariotte principle by extending the air-inlet tube to the bottom of the liquid reservoir results in a major improvement in control.

The first reference to Zentner (IND. ENG. CHEM., ANAL. ED., 16) should read page 471 instead of 47.

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SIR: The paper by Fabris and Peacock undoubtedly describes, with additional refinements, the system outlined in our paper. We regret very much that the duplication of effort has occurred. It seems probable that we overlooked the paper because our literature survey was confined to *Chemical Abstracts* rather than the original papers, except for those references which seemed to bear directly on the mechanism of our feed system.

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Book Reviews

Quantitative Ultramicroanalysis. *P. L. Kirk.* vii + 310 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1950. Price, $5.

Anyone confronted with the task of performing analyses by micro- or submicromethods should welcome this book as a valuable aid. Written for the practical man, it presents in a detailed manner not only the techniques of the author, but those developed by Linderstrøm-Lang, Holter, Conway, Craig, Lowry, Scholander, Anfinsen, and Claff as applied to biochemical problems.

The author has made a careful effort to introduce the fundamental methods as simply and directly as possible. Important to the beginner is mention of a source of supply of equipment.

A thorough search of the literature has been made, as represented by a total of 336 references appropriately listed chapterwise. It would be desirable in future editions, however, to spend a few additional pages on an alphabetical author index for general reference.

"Quantitative Ultramicroanalysis" is recommended not only to the biochemical microanalyst who will find here useful techniques collected in one book, but also to the biologist and cytologist whose interests lie in the analysis of plant or animal tissue sections. The worker in the chemical examination of small samples of radioisotopes will find the methods described of great usefulness.

WILLIAM G. BATT

Modern Instrumental Analysis. *D. F. Boltz,* editor. Vol. I. viii + 191 pages. Edwards Brothers, Ann Arbor, Mich., 1949. Price, $3.

The editor notes the need for a suitable textbook, doubts that it will be produced by one man, and offers instead a series of papers by selected experts. This series of papers (called chapters) discusses quantitative spectrochemical analysis and its applications, mass spectrometry, optical instruments, electron diffraction, and x-ray diffraction—in that order. Each of these chapters, slightly condensed, would serve well as material to submit in response to junior or senior year assignments; and a grade of A might be expected. Each chapter, greatly expanded, might reasonably be expected to become a chapter of a suitable text on instrumental analysis.

Of the present collection, the chapter on optical instruments seems the most inconveniently compressed. Mass spectrometry is more adequately treated, although the customer's course given with the purchase of an instrument is considerably more in the classroom tradition. The chapters on spectrochemical analysis lean heavily to the metal industries, particularly to the analysis of aluminum. Applications and possible applications seem more stressed than principles and techniques in the remaining two chapters.

HARRY MATHESON
CHARLES PROFFER SAYLOR
BOURDON F. SCRIBNER

Physical Methods in Chemical Analysis. *Walter G. Berl,* editor. Volume I. xiii + 664 pages. Academic Press, Inc., 125 East 23rd St., New York 10, N. Y., 1950. Price, $12.

The modern trend in chemical analysis makes this book a very timely contribution. Volume I deals for the most part with methods based on the interaction of radiant energy and matter, leaving electrical, magnetic, and other techniques for Volume II, which is to follow. Careful planning on the part of the editor is evident in the general outline followed by the various authors of the twelve chapters. Each author, a carefully chosen authority in his field, surveys the theoretical basis of his topic, describes and discusses the types of apparatus, selection and preparation of samples, and test procedures, indicates the fields of application where the techniques have been successfully applied and where future usefulness is likely, discusses the inherent accuracy, the limitations, the experimental errors, and the evaluation of data, and cites pertinent literature references. It has obviously been the aim of the authors to present their material in such a way that the nonexpert in a given field (but well grounded in the fundamentals of both physics and chemistry) may read with understanding and acquire some degree of familiarity with the principles and practice of the various physical methods.

PAUL K. WINTER

Society for Applied Spectroscopy

THE fifth annual meeting of the Society for Applied Spectroscopy was held in New York, May 26 and 27. The program included a Symposium on Spectroscopic Sources, as well as groups of papers on emission spectroscopy, new spectroscopic methods of analysis, and infrared spectroscopy. Abstracts of the papers presented are given below.

SYMPOSIUM ON SPECTROSCOPIC SOURCES

Thermionic Emission from Carbon and the Carbon Arc. HENRY F. IVEY, Westinghouse Electric Corp., Bloomfield, N. J.

An experimental investigation of the thermionic electron emission from extruded carbon filaments gives the work function as 4.60 e.v. and $A = 46$ amperes per sq. cm. deg.[2] The mechanisms available for electron emission at the cathode of an arc were discussed. The current density has been reported to be about 500 amperes per sq. cm. At 3600° K. this can be accounted for by thermionic emission alone. Recent experiments by Cobine and others, however, indicate that the actual densities with other materials are greater than literature values by more than an order of magnitude and that this is particularly true in the early stages of arc ignition. If this situation is found to exist also for the carbon arc, it will be necessary to assume that some other type of emission is also active.

The New NSL Spec-Power. HOWARD M. BEDELL, National Spectrographic Laboratories, Cleveland, Ohio.

The NSL Spec-Power consists of three separate excitation units—a.c. spark, a.c. arc, and d.c. arc—integrated through a common control panel. The mechanical design and electrical characteristics were described. Operating data were presented for a number of different materials.

Characteristics of Spark Sources. J. H. ENNS, University of Michigan, Ann Arbor, Mich.

Certain electrical characteristics of the high voltage spark as well as some physical and electrical parameters of the analytical gap have been investigated with the aid of direct record time-of-wait curves. The time-of-wait curves were obtained by amplifying the impulses from photomultiplier tubes. These amplifying impulses were channeled into a ratio recorder, the final curves being obtained on an oscilloscope recorder. Oscillations at the analytical gap are characterized by a linear decay, because the gap resistance predominates in the spark circuit. The discharge, as measured, decayed in approximately 25 microseconds. During the first 2 to 3 microseconds atmospheric nitrogen lines predominate; the sample was volatilized under high energy excitation during the interval 5 to 8 microseconds; the arc lines appear near the end of the discharge cycle, 15 to 20 microseconds.

Time Variation of Infrared Emission from Burning Gases. JOHN T. AGNEW, Franklin Institute, Philadelphia, Pa.

The possibilities of obtaining information concerning the kinetics of a gaseous explosion from the time variation of the spectral emission from the reaction, in the spectral range 1 to 10 microns, have been investigated. A Golay pneumatic detector was used in conjunction with a low-dispersion infrared monochromator. The radiation from the explosion was chopped at a frequency of approximately 60 cp., thus giving time slices of the radiation integrated over approximately 17-millisecond intervals. By means of repeated explosions, with the monochromator set for various wave lengths, the time variation of emission over the spectral range 1 to 10 microns was determined. Variations in the properties of the characteristic emission from carbon dioxide and water vapor were noted. Other items noted were the variation of the time required to reach peak intensity as a function of wave length, and an indication of a means for calculating temperature as a function of time.

A complete description was made of an instrument used to measure simultaneously infrared radiation at various wave lengths. Because of space limitations in this instrument, use was made of internally polished silver tubes to conduct radiation of the desired wave length to individual monitoring Golay detectors. Efficiencies of 50 to 90% (depending on curvature) were quoted for these tubes.

The Hilger Raman Source Unit. RICHARD F. JARRELL, Jarrell-Ash Co., Boston, Mass.

A description was given of the new source unit for use with the Hilger Raman spectrograph. Its construction and the improvements resulting therefrom were presented.

The new Hilger Raman source unit features a design of mercury arc lamp and reflector which makes much more efficient use of the 4358 mercury line in producing Raman spectra. Four mercury lamps are spaced around a central sample tube, the whole unit being encased in a specially prepared whitened surface whose reflecting power greatly enhances excitation. Data were given for the separation of o-, m- and p-xylene and the identification of cyclohexane and carbon tetrachloride.

Some Practical Considerations in the Use of the A.C. Spark for Metallurgical Analysis. JACOB H. JURMAIN, Baird Associates, Cambridge, Mass.

This was a discussion of the practical problems which face the spectrographer in applying the high voltage a.c. spark for both low and high alloy analysis. The advantages of using a direct-reading instrument in the investigation of sources were considered. It was shown that when limitations of the photographic emulsion are obviated, and proper dilution corrections are made, the universality of the spark source is made apparent.

Source Unit Accuracies as Determined by Direct-Reading Methods. M. F. HASLER, C. E. HARVEY, AND B. R. BOYD, Applied Research Laboratories, Detroit, Mich.

With a tenfold improvement in the radiation-measuring accuracy obtained with a direct-reading instrument as compared to a spectrograph, a new and much more rigorous analysis of source unit performance can be made than was formerly possible.

It is now easy to demonstrate the importance of alloy effects and metallurgical effects, particularly in high alloy systems. In this case because different source conditions produce very different results as to the variation in composition of one element affecting the analysis of another, the selection of proper source condition is important. Precision figures collected on a variety of materials, including low and high alloy steels, tool steels, and alloys in the nonferrous group, were presented, giving results obtained with the A.R.L. high precision source unit and the multisource unit.

A Flexible Controlled Spark Generator. JOSEPH GEFFNER, Joseph Geffner Co., Weirton, W. Va.

A novel spark generator circuit has been developed which facilitates the control and measurement of such factors as spark repetition rate and discharge capacitor voltage. The circuit contains a d.c. power supply variable from 0 to 20,000 volts. A variable-speed motor-driven switch connects a discharge capacitor alternately to the power supply and to the analytical gap. The oscillation frequency and peak current of the discharge are varied conventionally by changing the inductance in the discharge circuit. Varying the power supply voltage provides an independent adjustment of peak current. Varying the switch speed permits control of the average intensity without changing the characteristics of the discharge.

Use of the Spectrochemical Series. D. L. TIMMA, Mound Laboratory, Monsanto Chemical Co., Miamisburg, Ohio.

Study of a group of elements by means of Slavin's total energy method has shown that the presence of trace amounts of extraneous elements in a sample influenced the line intensities of other elements present. The character of this effect varies with amount of extraneous element present but not in a simple linear fashion. Correlation of the data for different extraneous elements shows that the elements can be arranged in a series such that any member enhances the lines of elements above it and depresses the intensity of lines of elements below it in the series. The relative positions of the elements in this series can be predicted from their boiling points and excitation potentials.

Once established, the spectrochemical series can be used to predict the influence of extraneous elements upon line intensities or intensity ratios. Such an application can markedly reduce the error introduced by the presence of an extraneous element in a sample which is not present in the calibration standards.

The Interdependence of Spectral Radiation from the Direct Current Carbon Arc. ROBERT W. MURPHY, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., and Socony-Vacuum Laboratories.

The interaction of the anode constituents of the direct current arc was studied for the system of magnesium oxide in a cored graphite electrode. Using short-period exposures as a measure of intensities, the conditions of the arc at any instant of time can be represented as a point on an $I(Mg)$ vs. $I(C)$ curve. The curve is an inverse relation of higher order and shows a marked dependence on current. Variations of anode size and form, dilution of magnesium oxide with graphite, and limited water cooling appear only to shift the representative point along the curve. The exposure per unit weight of magnesium oxide produced by a "total energy" burning is related to the predominant region of the curve and, in turn, to the initial anode conditions.

EMISSION SPECTROSCOPY

Application of Geiger-Müller Tubes for Spectrochemical Analysis. O. G. KOPPIUS, Philips Laboratories, Irvington-on-Hudson, N. Y.

A detector of lead in air was described. It utilizes a spark source for the excitation of the lead spectrum, a small quartz spectrometer for the dispersion, and a quartz Geiger-Müller counter for the detector of the radiation. The lower limit of detection is of the order of 20 micrograms of lead per cubic foot of air. The instrument is portable and ideally suited to locate areas of high lead concentration in air.

Determination of Sodium and Potassium in Refractory Materials Using the Flame Photometer. FRANK M. BIFFEN, Johns-Manville Research Center, Manville, N. J.

A method has been devised by which refractory materials are sintered with calcium carbonate as in the J. Lawrence Smith method, and sodium and potassium are determined on the water extract using the flame photometer. Consideration is given to

the calcium present in the extract. Results obtained by this method appear to be at least as accurate as, and probably more accurate, than those obtained using the J. Lawrence Smith method, and the time necessary to complete the analysis is cut in half.

Factors Affecting Precision in Spectrochemical Analysis with Buffers. PAUL E. LIGHTY, Lime Crest Research Laboratory, Newton, N. J.

The manner in which precision and accuracy are affected by buffer material and concentration, sample fineness and matrix, electrode geometry, gap length, current constancy, internal standard, line pairs, and pretreatments of sample, was studied, and a method was evolved which provides standard deviations of 10% or better for the elements and materials investigated.

The method adopted resembles in some respects those described by Harvey (Harvey, C. E., "Method of Semiquantitative Spectrographic Analysis," Glendale, Calif., Applied Research Laboratories, 1947), and by Weaver and Brattain [Weaver, J. R., and Brattain, R. R., ANAL. CHEM., 21, 1038–41 (1949)], in that lithium carbonate is used as a flux, but the errors are reduced to the dimensions of a quantitative system by the use of nickel as an internal standard, and adherence to other conditions is found to be functionally important.

NEW SPECTROSCOPIC METHODS OF ANALYSIS

Determination of Sulfur in Petroleum Fractions by X-Ray Absorption. S. W. LEVINE AND A. H. OKAMOTO, Atlantic Refining Co., Philadelphia, Pa.

A Geiger-Müller spectrometer has been used for absorption measurements to determine the sulfur content of petroleum fractions. The sulfur content is calculated from the difference in absorption between the sample and a pure hydrocarbon standard of approximately the same density. The method minimizes uncertainties due to variations in the carbon-hydrogen ratio of the sample and to fluctuations in the intensity of the x-ray beam, so that an accuracy of 0.02% sulfur can be attained for samples containing less than 2% sulfur.

X-Ray Fluorescent Analysis. LO-CHING CHANG, Columbia University, New York, N. Y.

The speaker discussed the theoretical background, the equipment outlay, advantages, limitations, possible errors, and applications of the x-ray fluorescent method of analysis. The method was related to the quantitative determination of elements in metallic and nonmetallic substances.

Neutron Spectroscopy in Chemical Analysis. T. I. TAYLOR, Columbia University, New York, N. Y.

A review of the properties of neutrons and their interactions with matter shows a number of possible applications to chemical analysis. As the velocity or the wave length of neutrons is changed, interesting variations are found in the magnitude and the nature of these interactions. Resonance absorption occurs for many elements at particular neutron velocities and these may

be used for qualitative and quantitative determinations. Neutron spectrometers useful in such studies were described. Both neutron transmittance measurements and radioactivation by neutrons already have been applied successfully to a number of analytical problems.

Radio Frequency Mass Spectrometer. WILLARD H. BENNETT, National Bureau of Standards, Washington, D. C.

A mass spectrometer has been developed which uses velocity selection rather than magnetic deflection. A low voltage radio frequency alternating potential is applied to each of three grids of a fourteen-grid tube. The operating principles were described and some of the results obtained with the instrument were presented.

INFRARED SPECTROSCOPY

Report of Activities and Progress of the Infrared Punch-Card Committee. CARROLL CREITZ, National Bureau of Standards, Washington, D. C.

Arrangements with the National Research Council for handling the committee's finances are proceeding satisfactorily. A card identical with that adopted last year is now available for hand-plotting spectra. The Wright-Patterson Air Force Base has, by means of a fund transferred to the National Bureau of Standards, initiated the production of punch cards bearing infrared spectra. Data for the bibliographic cards are being checked against existing bibliographies. Solicitation of spectra for inclusion in the file was made. Spectra of compounds of reasonably high purity and on which physical properties have been determined are especially desired. Directions for preparation of spectra for printing were given.

Infrared Spectrometer with Cathode Ray Presentation. H. POWELL, Anglo-Iranian Oil Co., Sunbury-on-Thames, England.

An infrared spectrometer with visual presentation on a long-persistence cathode ray tube and suitable for use in an industrial laboratory was described. The performances of the instrument with a Bell Telephone Laboratories thermistor bolometer and high speed Hilger-Schwarz vacuum thermopile, respectively, as radiation detectors were illustrated by reference to traces of hydrocarbon spectra. The effects of band width of the display unit and of scanning speed on the over-all resolution of the spectrometer were also illustrated. The resolving power at the present rate of scanning, which covers approximately 3.0 mu anywhere in the region 2 to 15 mu in 12 seconds, is considered sufficient for most work on hydrocarbon molecules.

A Direct-Recording Infrared Spectrophotometer Utilizing Memory Standardization. W. S. GALLAWAY, National Technical Laboratories, South Pasadena, Calif.

The application of the memory standardization technique for the recording of infrared spectra directly in per cent transmittance was discussed. The problems involved and the advantages to be gained by this approach were considered and some performance curves of the Beckman instrument were presented.

Symposium on Thin Films

F. A. HAMM, *General Aniline & Film Corporation, Easton, Pa.*

THIS Symposium on Thin Films, the third of an annual series of symposia sponsored by the Armour Research Foundation of Illinois Institute of Technology, was held at the Sheraton Hotel, Chicago, Ill., on June 8, 9, and 10. The prior Symposia on Light and Electron Microscopy and on Resolution and Fine Particles formed an appropriate background, so that the subject of thin films was a natural sequel in what promises to be an interesting series of related meetings. The familiar sight of many of those who attended the earlier Armour symposia plus the appearance of new faces representing many walks of science lends weight to the idea that thin films are of considerable general interest. Some 200 people representing many branches of chemistry, physics, and engineering shared their knowledge in a cooperative and pleasingly informal way. Last year's symposium at which no formal papers were read had been considered as an experiment. The same atmosphere in which informality and spontane-

ous audience participation prevailed was thoroughly enjoyed again this year. Success in the experiment has been realized; consequently the Armour Research Foundation would do well to consider the continuation of this novel technique for conducting a meeting.

The cochairmen, W. C. McCrone and C. F. Tufts, organized the program so that the various technical aspects of the general subject of thin films were properly evaluated. These aspects were discussed at four sessions appropriately labeled formation, geometry, structure, and problems and applications. The chairmen for these sessions were R. D. Heidenreich, Bell Telephone Laboratories; Henry Levinstein, Syracuse University; L. O. Brockway, University of Michigan; and Allan T. Gwathmey, University of Virginia, respectively. A panel of "experts" had also been chosen to aid the chairmen. The choosing of so-called experts must usually be done advisedly. This symposium

was no exception. It developed that many of the real experts were members of the audience. Fortunately they graciously, and with an air of good humor, cooperated in the dissemination of their pertinent knowledge.

W. E. Mahin, director of research of the Armour Research Foundation, opened the symposium with a few welcoming remarks.

Immediately after the first session on formation had been opened, it became apparent that the definition of terms and the assignment of parameters were no easy matter. After some deliberation and argumentation, it was agreed that each individual was rightfully entitled to define what is meant by a thin film in terms of parameters that most appropriately suited the problem. Methods of detection and formation and specifications on geometry were outlined. Again these considerations might have been discussed at great lengths because they are obviously almost unlimited in number. As a matter of general agreement it was concluded that thin films are interfaces between two other phases. These interfaces are coherent, have relative dimensions, and affect the surface properties, not the bulk properties.

The evaporation of metals and dielectrics in general is of tremendous interest both commercially and academically. Structure and environmental factors affecting structure were discussed for several materials. Germanium when evaporated onto silica at 25° C. was shown by electron diffraction to be glassy. When the target was at 400° C., the germanium deposit was crystalline. Furthermore, the deposit consists of large and small spheres, with the large spheres growing at the expense of the smaller ones, when evaporation is continued. Thus growth must occur equally in all directions. The higher vapor pressure of the smaller spheres at the elevated temperature presumably accounts for their decrease in size. Furthermore, the heat of condensation and the degree of orientation for evaporated films of metals such as aluminum are greater if the condensing substrate is highly crystalline, as in the case of mica as compared with glass.

The evaporation of metals such as silver and aluminum and dielectrics such as magnesium fluoride and zinc sulfide to form films of controlled thickness in the preparation of mirrors, monochromatic filters, dichroic filters, beam splitters, etc., was discussed from the standpoints of theory and practice. One enigma has still not been solved: how to prepare front-surfaced aluminum mirrors without pinholes. Furthermore, the oxidation of evaporated metal films cannot be prevented by surface coating. The well known relations between refractive index and thickness of film and reflectivity or transmissivity were illustrated with samples of filters, beam splitters, and mirrors.

The formation of highly polished surfaces of metals by electrolytic polishing (anodic reaction) was also described. The surface of aluminum can thus be more highly polished than in any other way.

Effects of grain size and oxide formation on the reflectivity and electrical resistivity of evaporated metal films are of interest, too. The presence of residual gases has only a second-order effect on the grain size and oxide formation. Thick films of many metals such as silver, gold, copper, and chromium have a higher electrical resistivity than thin films or the bulk metals because of their porosity.

It was somewhat surprising to learn that gold "blacks" are not black because of their sponginess or particle size distribution. Small amounts of tungsten, up to 5%, cause the "black" appearance in a manner not fully understood.

Thin films of organic materials were strikingly illustrated by the "dark" and "bright" series of interference colors produced by a wedge film of barium stearate on glass. Monolayers of this long-chain compound are about 25 A. thick. Complementary interference colors may be readily produced by varying the refractive index of the supporting medium to values above and below that of the oriented organic film. These step wedges of

color find extended use in estimating with good accuracy the thickness of any surface film that exhibits an interference color. The refractive index of the film should be known if the thickness is to be accurately determined. Because these wedge films of oriented barium stearate are readily prepared, they should find considerable use in many laboratories.

The use of thin films of organic molecules has applications in ore flotation processes. This involves the consideration of wettability and nonwettability as related to the contact angle, which in turn is related to concentration, chain length, size of terminal polar group, etc., of compounds such as the fatty acids. One interesting question that arose was: Why are the nonpolar ends of these long-chain molecules oleophobic at all? Xanthates strongly adsorb on zinc sulfide in the presence of copper ions because they react with these ions to form a very thin film of surface microcrystals. This crystalline surface film prevents the zinc sulfide ore from being wet by water; the technique has found industrial use.

The subject of measuring the thickness of a variety of thin films was treated in a general way. The technique employed is naturally predetermined by the nature of the film. Microbalances, surface tension balances, absorption of monochromatic electrons and x-rays, interferometers, etc., were all discussed. Modified interferometric methods are enjoying success, especially in the field of evaporated films.

Two new electron microscopes were described at a special Friday evening session. A. C. van Dorsten of the Philips Research Laboratories, Eindhoven, the Netherlands, who is at present touring this country, described the development and application of the new Philips EM-100 electron microscope. This electromagnetic instrument employs five lenses; two are intermediate lenses between the objective and projector lenses. Consequently the instrument is readily adapted to a transmission diffraction camera. A variable accelerating voltage (40, 60, 80, and 100 kv.), a variable-object diaphragm for narrowing the field for diffraction, easy conversion to diffraction, easy change of specimen, and an extremely low order of objective lens astigmatism are some of the features of the new instrument. The instrument will be available in this country.

R. G. Picard, Radio Corporation of America, described the new permanent magnet electron microscope (EMT) which had been announced several months ago. The use of permanent magnet lenses results in a simpler, less expensive instrument, which is capable of resolving 100 to 150 A. This instrument, operable at 1500 ×, 3000 ×, or 6000 ×, should find widespread use, especially in shouldering some of the burdens resting on many of the larger, more universal instruments that are now overworked, especially from the standpoint of routine service analysis. The instrument was on display throughout the three-day meeting.

The success of this meeting should materially aid in making this Armour symposium an annual affair. The subject of next year's meeting is awaited with interest.

The Analyst's Calendar

Electron Microscope Society of America. Hotel Statler, Detroit, Mich., September 14 to 16. Eighth annual meeting
Instrument Conference and Exhibit. Instrument Society of America, Buffalo, N. Y., September 18 to 22
Fourth Symposium on Analytical Chemistry. Louisiana State University, Baton Rouge, La., January 29 to February 1, 1951

An Electromagnetic Sealed-System Agitator. Charles F. Raley and William A. Mosher, University of Delaware, Newark, Del.

IN order to study the effect of oxygen under pressure upon solutions of drying oils, it became necessary to devise an apparatus which would embody an efficient agitator, would be completely sealed, and would have no metal parts in contact with the reagents. Because it is difficult to take accurate pressure readings during the course of a reaction when using an externally driven agitator, owing to the problem of preventing gas leakage at the point of entry, the principle of the solenoid-operated plunger was employed.

This concept is, of course, not new; many reports of solenoid-operated agitators have appeared in the literature (1–5). However, the agitator presented here has simplicity and efficiency, and the advantages of all-glass construction. The plunger has been in operation for over 1500 hours with good results.

The agitator is ideally suited for a surface reaction, where it is desirable to keep a fresh surface of solution exposed to the action of the gas. The complete reaction vessel is shown in Figure 1.
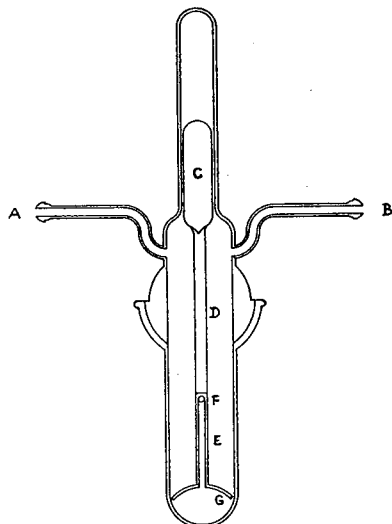

Figure 1

Arm A is connected by means of a 12/5 spherical joint to the gas reservoir. A spherical joint is used because it can be tightly clamped to resist leakage. Arm B is connected in the same manner to a U-type manometer. The two halves of the reaction vessel are joined by a 65/40 spherical joint. The reaction vessel, together with the gas reservoir, is immersed in a constant-temperature bath up to the bottom of the two arms.

The upper part of the plunger consists of a glass bulb, C, 18 mm. in outside diameter × 7 cm., filled with iron powder which has the function of acting as a pole piece, but reduces heating effects due to eddy currents. To this bulb is attached the stem, a length of 7-mm. outside diameter borosilicate glass rod, D, 10.5 cm. long, to which is sealed a 5.5-cm. length of 7-mm. outside diameter borosilicate glass tubing, E. A hole, F, is blown in the side of the tubing near the junction with the rod. The other end of the tubing is attached to a bell-shaped piece of glass, G, which is about 2 mm. smaller in diameter than the inside diameter of the reaction vessel. The neck of the reaction vessel is a piece of borosilicate glass tubing 20 mm. in inside diameter and 12 cm. long. Around it is placed a solenoid coil connected to a source of intermittent voltage.

The timing switch connected to the solenoid was constructed from relays which were available in this laboratory. A satisfactory commercial unit, however, is the Flexopulse, made by the Eagle Signal Corporation, Moline, Ill. The solenoid coil consists of approximately 200 feet of No. 20 B.&S. gage enameled solid copper wire wound on a 1-inch brass spool, 2 inches long. Although the solenoid coil was rated at 24 volts direct current in its original application, good results are obtained with 17 volts alternating current from an autotransformer. The coil has been used with an "on" time of 1 second, and an "off" time of 4 seconds.

The dimensions of the apparatus may be varied to suit the need, so long as adequate clearance for the plunger is maintained. The neck of the reaction vessel must be long enough to provide free space above the plunger bulb after maximum upward travel.

In operation, the agitation of the liquid is twofold. When the solenoid coil is energized, the plunger rises rapidly enough to cause gas to be drawn down through the hollow stem and to disperse into the liquid as small bubbles. When the coil is de-energized, the plunger falls of its own weight, causing a column of liquid to rise in the hollow shaft and spurt through the hole in the side against the wall of the reaction vessel. In this way a fresh surface of liquid is constantly presented to the gas phase.

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Pressure Regulator for Chlorine Cylinder. Julian Dorsky, Koppers Company, Inc., Mellon Institute, Pittsburgh, Pa.

STANDARD pressure regulators such as those commonly used on oxygen and nitrogen cylinders are not available for chlorine. Regulators designed for noncorrosive gases cannot be used for chlorine because they contain rubber parts which deteriorate rapidly. Commercial regulators with silver, tantalum, and platinum parts for chlorine service are relatively expensive.

For several years the author has used a modified, inexpensive air-pressure regulator for chlorine. The accompanying sketch shows how a Harris Calorific Co. Model 48 brass line regulator was modified. The modification consists in replacing the rubber seat with one machined from Teflon rod and covering the rubber diaphragm with 0.02-inch Teflon sheet. Other commercial regulators can be converted to chlorine service similarly.

If the regulator is to be used on a cylinder containing liquid chlorine, it should be suitable for 250 pounds per square inch working pressure. Fittings must be provided to connect the regulator to the chlorine supply and to the apparatus wherein the chlorine is to be used. The regulator can be used without a pressure gage by plugging the hole provided for the gage. If a gage is desired, it must be constructed of corrosion-resistant material.