INDUSTRIAL AND ENGINEERING CHEMISTRY ANALYTICAL EDITION

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ANALYTICAL EDITION

PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY . WALTER J. MURPHY, EDITOR

The Mass Spectrometer as an Analytical Tool

H. W. WASHBURN, H. F. WILEY, AND S. M. ROCK Consolidated Engineering Corporation, Pasadena, Calif.

Discussing the mass spectrometer as an analytical tool, the paper describes the method of analysis, presents results obtained with this method, and gives information regarding the commercial instrument that is now in use.

THE demands upon the petroleum and chemical industries for large quantities of aviation gasoline, synthetic rubber, and other war materials have resulted in employing many new processes on a large scale. These new processes in general are more complex than those formerly employed in industry. To develop such new processes and to put them into operation necessitates a large amount of preliminary and coordinated analytical work.

These technological advances have therefore required a parallel advance in the art of analysis both as an aid to the development of new processes and for the analytical control of the plants after they have been put into operation.

One of the new methods of analysis which are now being employed is the mass spectrometer method. It is the purpose of this paper to discuss the mass spectrometer as an analytical tool: the method of analysis with the mass spectrometer, a few results obtained with this method, and the commercial instrument now in use. charged fragments. This feature enables substances of the same molecular weight, but of different molecular structure, to be distinguished from each other (2).

The ionization chamber and associated electron source or filament are shown schematically in Figure 1 at a. The ions are pulled out of chamber a by means of the electric field existing between electrodes d, e, and f. Ions enter the analyzer tube with a high velocity and are sorted out according to their mass by the action of a magnetic field. The magnetic field causes heavy ions to follow a circular path which is of greater radius than the path followed by lighter ions. The radius of the path for an ion of given mass can be made smaller or larger by varying the electric field produced between electric field, ions of each mass can be caused to fall successively on the collector, c, where their quantity is measured by amplifying and recording equipment. The resulting record shows the relative numbers of ions of each mass which appear at c.

Mass Spectra

Figure 2 shows the automatically recorded mass spectra of *n*-butane and of a paraffin-olefin mixture, C_2 through C_4 . It takes about 10 minutes to make a single record. When operating in a routine manner a sample can be run every 20 minutes.

In order to make the records more easily understood it is necessary to explain that there are four traces, all recorded simultaneously and having different degrees of sensitivity. The top trace has unit sensitivity, the second has a sensitivity of one third, the third a sensitivity of one tenth, and the fourth or bottom trace a

Principle of Operation of Mass Spectrometer

In general, a mass spectrometer is a device for sorting molecules. Figure 1 is a diagrammatic sketch of the Dempster or 180° type of mass spectrometer. The gas mixture to be analyzed enters through the gas inlet to chamber a.

Before the molecules are sorted, they are given an electric charge, so that they can be forced to move by the combined action of electric and magnetic fields. The production of an electric charge on a molecule, or ionization, is accomplished by bombarding the molecules with a stream of electrons in an ionization chamber. In practice the energy in the bombarding electrons is usually made sufficiently high to break the molecules into



TABLE I. ANALYSIS OF DEPROPANIZER OVERHEAD

Mass	M, Mixture Peaks	n-Butane	Iso- butane	Propane	Ethane	Methane	Σ, Sum of Component Spectra	$M - \Sigma$, Resid- uals
15	167.3	1.0	1.6	30.4	23.0	110.3	166.3	+1.0
16	134.4	0.0	0.0	0.9	0.8	132.7	134.4	0.0
26 27 28 29 30 31	$ \begin{array}{r} 146.1 \\ 361.6 \\ 777.8 \\ 593.1 \\ \hline 130.0 \\ 2.4 \\ \end{array} $	$ \begin{array}{r} 1.6 \\ 10.8 \\ 9.3 \\ 12.5 \\ 0.3 \\ \end{array} $	0.9 12.1 1.2 2.6 0.0	37.6 183.0 275.3 467.8 10.0	106.4 158.0 494.4 105.6 119.7 2.5	···· ···· ····	146.5 363.9 780.2 588.5 130 2.5	$-0.4 \\ -2.3 \\ -2.4 \\ +4.6 \\ 0.0 \\ -0.1$
38	24 0	0.5	1.2	21.9		10.000	23.6	+0.4
39	98.0	4.3	8.7	84.6			97.6	+0.4
40	14.7	0.6	1.3	13.0			14.9 93.7	-0.2
42	49.9	3.9	15.6	30.2			49.7	+0.2
43	207.4	32.2	49.8	124.5			206.5	+0.9
44	145.3	1.0	1.6	142.7			145.3	0.0
45	4.6	0.0	1313	4.6	FT . Res		4.6	0.0
50 51 52	0.6 0.5 0.1	0.3 0.3 0.1	$0.3 \\ 0.3 \\ 0.1$				0.6 0.6 0.2	$0.0 \\ -0.1 \\ -0.1$
53	0.6	0.3	0.3				0.6	0.0
54	0.1	0.1	0.0	· · · · ·	 23216 	mentle ac	0.1	+0.0
56	0.5	0.3	0.2				0.5	0.0
57	2.5	0.9	1.6				2.5	0.0
58	5.0	3.8	1.2	une (cuta	1		5.0	0.0
59	0.2	0.2	0.0	10 101		us and the	0.2	0.0
		Compu	tation of	% of n-an	d isobuta	ne	Mole	%
		Fron	n peak 57	: 0.503 p	n + 0.65	$4p_i = 2.5$		(1)
		Fron	n peak 58	: 2.10 pn	+0.498	$3p_i = 5.0$		(2)
n-Buts Isobut	ane	when and	$e p_n = 0$	% n-butan isobutane	e		= 1 = 2	.8 -000
Propa	ne	(145.3	- 1.0 -	- 1,60) 0.	269	To uto al	= 38	.4 (3)
Ethan	e	(130.0	- 0.3 -	-0 - 10.	0 0.3173		= 38	.0 (4)
Metha	ine	(134.4	- 0 -	0 - 0.9 -	- 0.8) 0.	140	= 19	.4 (5)
		Underh	nea coen	icients are	obtained	from callb	rations.	

sensitivity of one thirtieth. This device enables the height of any peak to be recorded within better than 1 per cent accuracy over a range in magnitude of 250 to 1.

The abscissas, or horizontal scale values, on the mass spectra at which peaks occur, represent molecular weights corresponding to the different charged fragments obtained when *n*-butane or a C_2 to C_4 gas mixture is bombarded with an electron stream. The ordinate or vertical scale at each of these masses is a measure of abundance of the particular fragment which is formed.

For any given gas the particular fragments formed depend for the most part upon the number and type of atoms in the molecule. The relative abundance of the different fragments, or pattern of the mass spectrum, depends upon the structure of the molecule.

The mass spectrum, therefore, depends on the structure of the molecule, as well as upon the type of atoms of which the molecule is composed—for example, if this mass spectrum were for isobutane it would have peaks at the same masses but their relative heights would be different. It is this dependence of the mass spectrum upon the structure of the molecule that enables the isomers of a compound to be separately determined.

Principles of Analysis

If now the mass spectrum of an unknown mixture is obtained, employing a suitable technique, it will be a composite mass spectrum and can be considered as being a summation or superposition of the mass spectra of all the components of the mixture. The mass spectrum of the C_2 through C_4 mixture shown is such a composite spectrum. The analysis of the mixture consists of the unraveling of the mixture spectrum. Through methods developed in the Consolidated Engineering Corporation laboratory, this unraveling has been made much simpler than was originally thought possible. One other point of interest here is that all peaks recorded are not generally needed for an analysis. The peaks which are not used for calculating the mixture are used as a check on the accuracy of the analysis. They are employed to indicate calculation errors, instrumental errors, or failure to take account of a gas in a mixture. This final check on an analysis has been found to be very valuable.

In order to complete the analysis of a mixture from its composite spectrum, it is necessary to know the mass spectra of all its components. These spectra are obtained by running pure gases through the instrument and are called calibrations. The record of the *n*butane in Figure 2 is an example.

An explanation of the general methods of analysis would involve more discussion than space permits. However, the extremely simple examples shown in Table I will serve to clarify some of the previous remarks.

In the first column are listed the masses or molecular weights at which peaks occur on the mass spectrum of the unknown mixture. In the second column are recorded the peak heights read from the automatic record of the mixture.

The analysis of the mixture may be obtained in the following manner: The only components contributing to peaks at mass 57 and 58 are n- and isobutane. The percentages of n- and isobutane are computed from simultaneous Equations 1 and 2 shown at the bottom of the table. In these equations the underlined numbers are taken from calibration records obtained by running pure nand isobutane. From the determination of the percentages of n- and isobutane and from their



biointido bas sie di TABI	LE II. WET	GAS moon with life (2)
computations unless the and a sufficient amount	Mass Spectrometer Mole %	Fractionating Column Mole %
N2 Methane Ethane Propane Isobutane n-Butane Isopentane	1.184.14.94.71.11.70.7	87.44 4.60 4.30 0.72 1.47 0.55
n-Pentane C₄ + C₄ naphthenes C₄ naphthenes C₄ naphthenes	0.5 0.2 0.6 0.3 0.1	
		Time Required for Analysis by Complete Direct Method (Tables II and III)
Mass spectrometer (instrumen Mixture Prorated calibration	it time)	25 4
Mixture Prorated calibration Computing	nemn s (Ime)	20 4 80
Total man-hours		2.25

TABLE III. WET GAS

(Two analyses of this mixture on fractionating column A and two on B are compared with mass spectrometer analysis.)

	Fracti Colu	onating mn A	Fractic Colu	mn B	Mass Spectrometer
		Mole p	er cent	the state	Mole %
H2 N1		1000	with the	state 2	0.2 0.4 0.2
CH4 C2He	$91.500 \\ 4.395$	91.600 4.210	91.517 4.372	91.557 4.320	89.9 4.1
C2H2 i-C4H10	1.942 0.612 0.619	1.942 0.583) 0.699	1,968	1.969	1.0
n-C4H10	1.231	1.282	1,200	1.202	and of
n-CoH12	0.227	0.222	0.491	0.488	0.1
Ce Ci+	$\begin{array}{c} 0.232\\ 0.149\end{array}$	0.230 0.162	0.236 0.161	0.230 0.168	23:
CaHeO		122 *** 10 11	s inkd	Huse, olen	and 10 1.4 list

calibration spectra, the contributions of n- and isobutane to each of the masses listed can be readily computed. These values are shown in the third and fourth columns.

If now the mass 44 contributions of n- and isobutane are subtracted from the mixture 44 peak, the remaining peak is due entirely to propane. The per cent propane in the mixture is computed from this remainder peak and from the sensitivity of the 44 peak to propane. This simple calculation is shown in Equation 3 where the underlined value, 0.269, is the sensitivity in per cent per division obtained from the propane calibration.

Similarly, the amount of ethane can be computed by subtracting the 30 peak contributions of the heavier components from the mixture 30 peak. This determination is shown in Equation 4.

Equation 4. The same procedure is used in calculating the amount of methane as indicated in Equation 5.

If the apparatus were perfect, if there were no errors in the computation, and if all constituents in the mixture were taken into account, the sum of these component spectra for any given mass would be equal to the mixture peak. The comparison of the sums of the component spectra for each mass with the mixture peak of the corresponding mass therefore offers an excellent check on the reliability of the analysis.

The sums of the component spectra are shown in column 8. In order more clearly to show the agreement of this summation column with the mixture column, the difference between these two columns is shown in column 9. Because of the method of computation, the residuals will be zero on the masses used for computing the mixture—viz., 16, 30, 44, 57, 58. The residuals on the peaks not used for determining the analysis of the mixture are a measure of the accuracy of the analysis. In this case all residuals are less than 1 per cent of the respective mixture peaks. This shows that the analysis is of good accuracy and that all substances present in detectable amounts have been accounted for. The ability of this method to detect unexpected components is illustrated in Tables II and III. The unexpected naphthenes in one case and acetone in the other were detected by the relatively large residuals obtained when the analysis was first made, assuming that these constituents were not in the mixture.

The method of computation illustrated in Table I was described to show how the mass spectra of the components of a mixture superimpose to give the spectrum of the mixture and how the unused peaks may be used to check accuracy of the analysis. The particular method used for determining the separate components is applicable to only the simplest of analyses. A large amount of work has been directed to the development of short-cut methods for analyzing more complicated mixtures. The computing manual which explains these methods is over 100 pages in length.

Times Required for Analyses

The length of time required to make analyses with the mass spectrometer is very short, as is shown in the examples which follow.

Times are shown for the complete direct method of analysis. These times in most cases are somewhat longer than would normally be encountered in production analyses, as will be seen from the explanation below. In three examples (Tables IV, V, VI) times are also shown for the comparison method of analysis, which is faster and may be used for control purposes.

In the complete direct method calibrations of critical components of a mixture are run on the same day on which the mixture is run, and computations are carried through at a large number of masses in order to obtain a check on the accuracy of the analysis as well as to discover unexpected constituents. In general, calibrations will consume about 2 or 3 hours per day of mass spectrometer time when the direct method is used. In the examples which follow, the value given for man-hours includes a prorated time for the calibrations.

If it is not desired to check for unexpected compounds and general accuracy of analyses, it is unnecessary to carry through computations for a large number of masses. Considerable time can therefore be saved in computing and tak-

TABLE IV. SYNTHETIC C_1 TO C_4 PARAFFIN-OLEFIN MIXTURE (Composition computed from the manometer synthesis is compared with

	mass spectrome	ter anarysis.)	
	Manometer Synthesis	Mass Spectrometer —Mole per cent	Difference
Methane Ethylene Ethane Propene Isobutane Isobutene Butene-1 Butene-2 n-Butane	$ \begin{array}{c} 11.3\\ 1.5\\ 22.1\\ 11.9\\ 31.1\\ 5.0\\ 4.4\\ 5.0\\ 0.7\\ 7.0\\ \end{array} $	$ \begin{array}{c} 10.9\\ 1.7\\ 21.4\\ 11.8\\ 31.0\\ 5.0\\ 4.7\\ 6.2\\ 0\\ 7.3 \end{array} $	$ \begin{array}{r} -0.4 \\ +0.2 \\ -0.7 \\ -0.1 \\ -0.0 \\ +0.3 \\ +1.2 \\ -0.7 \\ +0.3 \\ \end{array} $
Al grant matelling		Time Requ Complete direct method <i>Min</i> .	ired for Analysia Comparison (control) method <i>Min</i> .
Mass spectrometer (in Mixture Prorated calibration Taking data from reco Mixture Prorated calibration Computing	strument time) 1 rd (technician's ti 1	me) 20 12 20 12 12 130	20 4 15 1 80
Total man-hours For n-, isobutane, an hour	nd total butenes of	3:25 nly, 0.75	(i) (jourplet

17 -	1 1		ЪΤ	-	\mathbf{n}
v n	1. 1	n .	IN.	n .	м
		· · ·		. .	~

	Тан	BLE V.	TYPICAL FE	ED STO	cks	
	Catal	ytic Polym	crization	A	eid Alkyla	ation —
	Manom- cter	Mass spectrom- cter Mole per c	Difference	Manom- eter	Mass spectrom eter Mole per	Difference
Propene Propane Isobutane Isobutene Butene-1 Butene-2 n-Butane Isopentane	$ \begin{array}{r} 1.0\\ 2.1\\ 9.8\\ 13.7\\ 15.0\\ 14.0\\ 42.4\\ 0.5 \end{array} $	$1.1 \\ 2.0 \\ 9.2 \\ 12.7 \\ 16.5 \\ 14.1 \\ 42.4 \\ 0.5 \\ $	$ \begin{array}{c} +0.1 \\ -0.1 \\ -0.6 \\ -1.0 \\ +1.5 \\ +0.1 \\ 0 \\ 0 \end{array} $	1.02.014.8010.05.0 $64.21.0$	$ \begin{array}{r} 1.2 \\ 2.0 \\ 14.9 \\ 0 \\ 10.6 \\ 4.6 \\ 63.8 \\ 0.9 \\ \end{array} $	+0.2 +0.1 +0.6 -0.4 -0.1
n-Pentane Pentenes	0.5	0.6	$+0.1 \\ -0.1$	0.5	0.5 1.5	0 0
				Time Comp dire metl Mi	Required olete C oct ood n.	for Analysis Comparison (control) method <i>Min.</i>
Mass spectro Mixture Prorated c. Taking data f	meter (in alibration	strument t	ime) ian's time)	25 10	Tin	25 3.5
Mixture Prorated c: Computing	alibration			25 10 140	to days	15 1.5 75
Total m	an-hours			3.5		2

ing data from the records in the partial direct method, since only the masses used directly in the solution need be considered. In some cases both the computing time and record reading time will be cut approximately in half.

The values given for total man-hours in the complete direct method should therefore be considered as upper limits. These times would normally be encountered only when using the mass spectrometer for experimental rather than production analyses.

If it is desired to use the spectrometer for control purposes, the time for analysis can be reduced below that attainable by either direct method, since in general there will be a large number of samples of similar composition. This permits the use of the comparison method of analysis, which eliminates a large portion of both calibration and computation and is therefore faster than the direct method.

The comparison method is essentially a comparison between an unknown sample and a standard sample. If the mass spectrometer is to be used for control purposes-for example, to indicate a change in the composition of a streamvery rapid results can be obtained with the comparison method. Such control can be accomplished merely by

making periodic runs on the stream and comparing the mass spectra thus obtained with the mass spectrum of a standard mixture which is run once each day. Any change in the difference between the spectrum of the stream and the spectrum of the standard mixture will indicate a change in the composition of the stream. In addition, the change in composition can be computed from this difference spectrum; or a complete analysis can be made from this difference spectrum and a knowledge of the composition of the standard mixture.

The comparison method of analysis just described may be used to advantage whenever a large number of samples with similar composition are to be run in a single day. There are three main advantages in using this method: (1) Complete calibrations need be made only about once a month, thus

reducing to practically zero the prorated calibration time. (2) All data necessary for complete analysis are obtained, but it is unnecessary to carry out computations unless the composition of the sample has changed a sufficient amount to be of interest. This reduces to zero the computing time for some samples. (3) When it is desired to obtain a complete analysis, the computing time is materially less than re-quired by the direct method. The times given for the comparison method in Tables IV, V, and VI demonstrate the rapidity with which complete analyses can be obtained by this method.

With either the direct or comparison methods a large number of samples can be run in a day. For example, with a C₄ feed stream as illustrated in Table V, fourteen samples can be run by the direct method and seventeen samples by the comparison method in an 8-hour day. The corresponding numbers for the C_4 cut free of C_5 shown in Table VI are 16 and 24 samples per 8-hour day.

In some cases when only the abundance of one or two components of a mixture is required, the analysis can be made rapidly, whether or not there are a large number of samples of similar composition. For example, in a C1 through C4 paraffin-olefin mixture, if only the mole per cents of n- and isobutane and total butenes are desired, the total time is about 40 minutes. In the determination of butadiene in a C_1 to C_4 mixture or in a C_4 cut, the time is only 30 minutes.

Analyses Made with the Mass Spectrometer

Some important mixtures which have been analyzed with the mass spectrometer to date are:

- Dry gas
- 2. Wet gas
- 3. n- and isobutane mixtures
- C_1 through C₄ paraffin and olefin C_3 through C₅ paraffin and olefin 4.
- 5.
- 6. C4 paraffins, olefins
- 7. C4 paraffins, olefins, and diolefin
- C_6 paraffins, clefins, diolefins, and cyclic C_6 through C_6 paraffins, cyclics, and aromatics 8 Q

10. Determination of benzene, toluene, and xylenes in gasoline

11. Determination of small amounts of diethylbenzene in ethylbenzene

Examples of depropanizer overhead and n- and isobutane mixtures have been previously published (1).

TABLE VI. SYNTHETIC C. PARAFFIN-OLEFIN-DIOLEFIN MIXTURES

	Manom- eter	Mixture 1– Mass spectrom- cter fole per cen	Differ- ence	Manom- eter	Mixture 2- Mass spectrom- etcr Vole per cen	Differ- ence	Manom- eter	Mixture 3- Mass spectrom- eter Mole per cer	Differ- ence
Propene Butadiene Isobutane Isobutene Butcnc-1 Butene-2 <i>n</i> -Butanc	0.9 66.6 0 0.9 7.1 6.9 17.6	0.4 67.2 0.6 1.0 8.1 5.5 17.2	-0.5+0.6+0.1+1.0-1.4-0.4	0 92.6 0 1.9 5.5 0	0 92.5 0 0.2 2.0 5.3 0	$0 \\ -0.1 \\ 0 \\ +0.2 \\ +0.1 \\ -0.2 \\ 0$	$0\\3.8\\0\\30.4\\31.4\\34.4\\0$	$0\\3.8\\0\\28.9\\29.2\\38.1\\0$	$0 \\ 0 \\ -1.5 \\ -2.2 \\ +3.7 \\ \cdots$
	n oor oor hurre- namit		in for col	ty of the		Time Com dir met M	Required plete ect hod in.	for Analysi Comparison (control) method <i>Min</i> .	
Miss Pro Takin	spectrome cture rated calil	bration	cobnicier	ie time)		2	0 7	15 5	
Mi: Pro Comp	rated calil outing	bration	Conniciai	(a tille)		2 9	0 7 5	15 5 50	
T	'otal man-	hours				2.	5	1.5	
Butac	itene only	, min.				3	5	100.1.1970	

	Mix	TURE		
		M.	ass Spectrom	eter
	Synthetic	5-6-42	5-7-42	5-8-42
	And a second sec	Mole p	er cent	
Isopentane	11.3	10.2	10.4	10.5
Pentene-1	28.8	31.4	25.7	31.6
lsoprene	19.0	19.7	20.3	20.2
n-Pentane	11.9	10.5	11.0	10.4
2-Methylbutene-2	19.3	19.0	20.6	18.7
Cyclopentane	9.7	9.2	12.1	8.6
		Tin by	ne Required for	or Analysis ect Method
			Min.	
Mass spectrometer (in	astrument time)			
Mixture	State of the second state		25	
Prorated calibratio	n		28	
Taking data from reco	ord (technician's t	time)		
Mixture	TRUMP DELEMENT		25	
Prorated calibratio	n		28	
Computing			195	
Total man-hours			5	

WET GAS MIXTURE. Table II shows the comparison between the results obtained on a wet gas mixture by a fractionating column and the mass spectrometer. The main point of interest in this analysis is that the mass spectrometer was able to detect small quantities of naphthenes.

Table III shows the comparison between two fractionating columns and the mass spectrometer. Perhaps the most interesting point in this example is the fact that the mass spectrometer was able to determine the presence of a small amount of acetone. The presence of acetone was probably caused by a contaminated sample bottle. If the mass spectrometer analysis is corrected for the presence of acetone, the maximum discrepancy between these corrected results and the fractionating column results is only 0.4 mole per cent.

These two examples illustrate the power of the mass spectrometer method to detect unexpected substances in a sample, even when these substances have the same molecular weight as other components in the mixture—the molecular weight of acetone is the same as that of n- and isobutanes.

 C_1 TO C_4 PARAFFIN-OLEFIN MIXTURE. Table IV shows the results of the analysis of a synthetic mixture containing C_1 to C_4 paraffins and olefins. In the column labeled "Manometer" is shown the composition of the mixture in mole per cent as synthesized with the aid of a mercury manometer. The next column shows the results of the analysis obtained with the mass spectrometer, while the last column shows the discrepancy between the manometer and mass spectrometer determinations.

The example in Table IV was selected to illustrate what is probably the authors' average accuracy on this type of mixture. In general, the total butenes and separate paraffins are determined to within the same accuracy. However, the separation of the butenes, and particularly the separation of butene-1 and butene-2, is less accurate because of the similarity of their mass spectra. Average errors in determining the separate butenes are about three times the average errors in determining the separate paraffins.

If small amounts of C_5 (say 1 per cent) are present in a mixture such as shown, the times are increased by about 15 minutes. The probable error in separating the butenes is increased about 0.5 per cent.

If larger amounts of C_5 paraffins and olefins are present, the accuracy of the determination of the total butenes is not affected. The determination of the accuracy with which the butenes can be separated in the presence of large amounts of C_5 is at present awaiting additional data.

 C_3 TO C_5 PARAFFIN-OLEFIN MIXTURE. Table V shows the results obtained on two synthetic mixtures with compositions similar, respectively, to polymerization plant and alkylation plant feed streams. These mixtures contain a small amount

of C_5 paraffins and olefins. The results show that good accuracy can be obtained on the separate determination of the C_4 's, when as much as 3 per cent of the C_5 's is present. The effect on accuracy and analysis time of the presence of larger amounts of pentenes is at present awaiting additional data, as in the previous example.

C₄ PARAFFIN-OLEFIN-DIOLEFIN MINTURE. Table VI gives analyses of three synthetic C₄ mixtures containing butadiene in addition to paraffins and olefins. In each case the composition as obtained in the manometer synthesis is compared with the mass spectrometer analysis. The presence of small or large amounts of butadiene in a mixture of this type can be detected with an accuracy of about ± 0.3 per cent. When the partial concentration of butadiene is about 50 per cent, the average accuracy of its determination is about ± 0.7 per cent. The accuracy of determining the other components of these mixtures is only slightly affected by the presence of butadiene.

The third analysis shows a relatively large error in the separation of butene-1 and butene-2. In spite of the fact that large amounts of butenes are present, this error is larger than that normally encountered. It is included here, so that the poor as well as the typically good results will be illustrated.

C₅ PARAFFIN-OLEFIN-DIOLEFIN AND CYCLIC MIXTURE. Table VII compares three mass spectrometer analyses obtained on three consecutive days on a synthetic C₅ mixture containing paraffins, olefins, isoprene, and cyclopentane, with the composition reported from the synthesis. This mixture did not contain all the C₅ olefins or diolefins, simply because the pure components were not available. However, the mixture could still be analyzed if all components normally encountered in such a mixture were present, although the accuracy in separating the individual olefins would probably not be so good as is shown in this table. "Synthetic" rather than "Manometer" is used in the tables whenever the sample was prepared by a laboratory other than the Consolidated Engineering Corporation.

			ALC: NOT THE	The second second second		and the state
TABLE V	III. C ₆	ARAF	FIN SY	NTHETICS		
(Two Cs mixtures were successive days. Cor	analyzed by nposition fro	the mom syn Mi Spect	ass spec thesis is ass trom-	trometer me given for co	thod o mpariso Ma Speet	n two on.) ass rom-
	Synthetic	6-25	6-26	Synthetic	6-25	6-26
	Mole	per cen	t	Mole	per cen	1
2,2-Dimethylbutane Cyclopentane 2,3-Dimethylbutane 2-Methylpentane 3-Methylpentane n-Hexane	3.82 0 12.03 6.16 77.99	3.5 0 12.5 6.8 77.2	3.5 0 0.3 12.3 7.3 76.6	26.40 0 36.24 20.26 17.10	26.1 0.5 35.7 20.8 16.9	25.9 0 0.2 36.4 20.6 16.9
			by	Complete Di	rect M	ethod
				Min	1.	
Mass spectrometer (inst: Mixture Prorated calibration	rument time)		21 15	52	
Mixture Prorated calibration Computing	(teenmeran	a time)		2: 1: 120	2	
Total man-hours		alab ¹	ST'BR	3.20	5 minge	of in

C₆ PARAFFIN MIXTURE. Table VIII shows two analyses of synthetic mixtures containing C₆ paraffins. In each case, the analysis was made on two different days to see how well the mass spectrometer results would reproduce on this type of mixture.

 C_6 - C_6 PARAFFIN-CYCLIC AND AROMATICS. Table IX shows the analysis of a mixture containing C_5 and C_6 paraffins, cyclics, and aromatics. Since this mixture was not a syn-

LYCHOLD STATEMENT OF CALLS	A LINE LONG LAND	A PECKALLES	121248-0-00110	01.852 (SOH)	Lot-24
TABLE IX. MIX	TURE OF C5 A	ND C6 PAR.	AFFINS,	Cyclics	, AND
	ARON	AATICS			
Hydrocarbon	Fractionation (100-Plate) Column	Ultraviolet Absorption Mole p	Mass Spectrom eter	Diffe	rence
Pentanes 2,2-Dimethylbutane Cyclopentane 2,3-Dimethylbutane 2-Methylpentane 3-Methylpentane n-Hexane Methylcyclopentane Benzene	3.8 14.0 1.6 9.4 33.0 13.9 12.8 8.7 2.9	··· ··· ··· 2.0	3.715.02.07.732.214.613.59.32.1	$\begin{array}{r} -0.1 \\ +1.0 \\ +0.4 \\ -1.7 \\ -0.8 \\ +0.7 \\ +0.6 \\ -0.8 \end{array}$	+0.1
		Ti by	me Requi Complete	red for A Direct M	nalysis Iethod
Mass spectrometer (ir Mixture Prorated calibratio Taking data from reco Mixture Prorated calibratio Computing	nstrument time) n ord (technician's n	time)	10	25 23 25 23 30	tuode Ela si padro di un
Total man hours			1 4	25	

thetic, the table shows the comparison between the results obtained with a mass spectrometer and by a combination of refractive index readings and temperature readings taken on a large number of small fractions obtained from a 100-plate fractionating column. The two analyses are in fairly good agreement. Results of the determination of benzene by ultraviolet absorption are also shown.

The time required by the mass spectrometer in this case is extremely short as compared with the fractionating time which in this case was 10 days, 24 hours a day. Even in the case where the unknown mixture contains C_7 's in addition to C_5 and C_6 , a preliminary relatively rapid fractionation can be made to cut out the C_7 's, and the total time for preliminary fractionation and the mass spectrometer analysis is still materially shorter than the time required by fractionation alone.

GASOLINE AND AROMATICS. Table X shows the analysis for the benzene, toluene, and xylene in a synthetic gasoline. If ethylbenzene had also been present in this mixture, its amount could have been separately determined. The major portion of the analysis time given was consumed in preparation of the sample preliminary to its introduction into the mass spectrometer. This preparation is done on an auxiliary apparatus and so does not consume any spectrometer time. The time for the actual spectrometer run and prorated calibration is only 28 minutes. Combined computing and instrument time is thus only 45 minutes. Sample preparation time for this type of mixture can be materially reduced as the bottling method is improved.

DETERMINATION OF DIETHYLBENZENE IN ETHYLBENZENE. Table XI shows the results of eight tests on the determination of small quantities of diethylbenzene in ethylbenzene. This example is representative of a number of analyses which can be made with the mass spectrometer to check the purity of a particular compound. In this case the minimum amount of impurity that could be detected without making special adjustments is about 0.02 per cent. If a small amount (down to 0.02 per cent) of isopropylbenzene were also present in these mixtures, its quantity could be determined.

Mass Spectrometer for Commercial Use

In order to make the mass spectrometer useful for routine analysis it was necessary to develop an instrument which was reliable, reasonably simple to operate, and at the same time capable of obtaining accurate mass spectra of gas and liquid mixtures. The accuracy of the Consolidated Engineering Corporation mass spectrometer is demonstrated by the results of the analyses given above.

The commercial apparatus has been designed conservatively, so that it will require a minimum of service. In order to test the reliability of operation, the mass spectrometer in this laboratory was operated in a routine manner over a period of 4 months, during which time from 15 to 20 runs a day were made. This number of runs was obtained in an 8-hour day. However, in order to simulate 24-hour-a-day operation, all voltages were left on at all times during the 4 months with the exception of Sundays. During this period, in addition to many experimental runs, over 200 analyses were carried out on synthetic mixtures made in the laboratory and on mixtures sent in by oil companies which were interested in the possibilities of this new method of analysis.

Figure 3 shows a commercial model of the Consolidated Engineering Corporation mass spectrometer. In the center background is the electromagnet which produces the uniform magnetic field in which the mass spectrometer proper is placed. Immediately to the left of this magnet is the sample inlet system and evacuation apparatus. In the right foreground are the oper-

TABLE	X. SYN'	THETIC G.	ASOLIN	E AND AR	OMATICS	
(Composition of trometer analys	otained from sis for two numbe	n the synth mixtures er of other	contai bydroc	compared wining aroma arbons.)	ith the man tics and	ss spec- a large
	Synthetic	Mass Spectrom- eter	Dif- fer- ence	Synthetic	Mass Spectrom- eter	Dif- fer- ence
	1110	ne per cent		110	te per cent	
Nonaromatics ^a Benzene Toluene Xylene	49.1 12.7 37.9	49.1 12.5 38.4	$ \begin{array}{c} 0 \\ -0.2 \\ +0.5 \\ \cdots \end{array} $	52.9 5.7 21.0 20.3	55.0 5.7 21.8 17.5	+2.1 0 +0.8 -2.8
no molecular		porces on		Time Req by Partis	uired for A Direct I Min.	nalysia Method
Mass spectromet Mixture Prorated calib	er (instrum ration	ent time)	(Second		25 3	
Taking data from Mixture Prorated calib	record (tec ration	chnician's ti	me)		10 1	
Computing Sample preparet	ion				10	
Tetal	BUCTOBLE			tive house		a theo
1 otal man-f	lours			2 hou	rs 50 minu	tes
^a Nonaromatic cyclopentane, c and "isopetene".	cs: n-hexan yclohexanc,	e, 2-methyl n-heptan	pentano e, met	e, 2,3-dimeth hylcyclohexi	ylbutane, r ane, "isoo	nethyl- ctane'',

TABLE XI. SMALL AMOUNTS OF DIETHYLBENZENE IN NEARLY PURE ETHYLBENZENE

(Determination of diethylbenzene in ethylbenzene in eight different concentrations. Impurity added in synthesis is compared to mass spectrometer analysis.)

Mixture	Synthetic	Mass Spectrometer Mole per cent	Difference
1 2 3 4 5 6	$\begin{array}{c} 0.036\\ 0.071\\ 0.235\\ 0.479\\ 0.789\\ 2.41\end{array}$	0.033 0.066 0.22 0.44 0.76 2.2	$ \begin{array}{r} -0.003 \\ -0.005 \\ -0.02 \\ -0.04 \\ -0.03 \\ -0.2 \end{array} $
8	4.02 7.97	3.6 8.0	-0.4
		Time Req by Partie	uired for Analysis- al Direct Method Min.
Mass spectrome Mixture Prorated calib	ter (instrument time pration	deterministion of s acquiritéd in the	25 3 constant
Mixture Prorated calib Computing Sample preparat	pration	A vetado-veta	10 1 10 120
Total man-	hours de coiteste	2 hou	irs 50 minutes



FIGURE 3. COMMERICAL MODEL OF THE CONSOLIDATED MASS SPECTROMETER

ator's table and the cabinet which houses the automatic recording apparatus and power packs. These power packs supply closely regulated voltages to the spectrometer and electric power to the magnet.

The routine operation of the apparatus for analyzing gas and liquid mixtures is relatively simple. The main operations are (1), the manipulating of the proper stopcocks to introduce the sample into the apparatus, and (2), the throwing of the proper switches to initiate the automatic recording of the data.

The data are recorded on photographic paper by a recording oscillograph.

In order to increase the reliability of the instrument and further to simplify its operation, several automatic protective devices have been installed to avoid damage to the instrument in an emergency. To a large extent, these protective features prevent the loss of operating time and allow relatively unskilled operators to take data.

The handling of sampling and sample containers in a refinery may be greatly simplified by using the mass spectrometer method, since the sample required is so minute. Only 0.1 cc. of gas at atmospheric pressure need be introduced into the inlet sample bottle. This extremely small size may be of decided advantage in some laboratory experiments.

In the refinery the size of sample should be picked which is best adapted to easy sampling and handling. Cylinders of about 100-cc. capacity should be very satisfactory.

Summary

The mass spectrometer method has several distinctive features:

1. A large number of samples, in some cases as many as 20, can be analyzed in an 8-hour day with one mass spectrometer 2. Mixtures containing up to 15 or more components can be analyzed.

3. Results can be computed in such a manner as to indicate whether the analysis is sufficiently accurate, and whether any unexpected components are present.

4. Results are practically independent of the skill and judgment of operators and computers.

5. Only a small sample is required for analysis, 0.1 cc. usually being sufficient.

Conclusion

As indicated by the examples given, advances in techniques of analysis using the mass spectrometer have been extremely rapid. As in the case of any new development, the field is constantly expanding. New problems extending the use of the instrument are continually being proposed and solved. Evidence is accumulating which indicates that analyses which are prohibitively time-consuming by other methods will be relatively readily analyzed by means of the mass spectrometer. The examples given in this paper should therefore not be considered as representing the limits of the method.

Acknowledgment

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Analytical Chemistry of the Rare Earths

Average Atomic Weight of the Rare Earths in a Mixture

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The oxalate to oxide, oxalate to permanganate, method for determination of the average atomic weight of the rare earth in a mixture has been studied, using pure materials and mixtures of known composition. An important source of error lies in the standardization of the permanganate solution. To minimize the error this operation should employ as a standard that rare earth which is the principal component of the mixture.

A KNOWLEDGE of the average atomic weight of the rare earths in a mixture allows the composition to be calculated if only two earths are present or provides sufficient data for such a calculation if the percentages of all but two of the components may be determined in other ways.

Analytical methods suitable for routine determinations of the atomic weights of the rare earths are few. The oxide to sulfate method of Schützenberger (7) is of historical interest only, since the many possible errors in the conversion to anhydrous sulfate render its use unreliable. The choice is apparently among the method of Feit and Przibylla (3) in which a weighed amount of oxide is dissolved in excess dilute sulfuric acid and the excess titrated with standard base; the oxalate to oxide, oxalate to permanganate, method of Gibbs (5); and the chloride to silver method, first used for a rare earth by Baxter and Chapin (1). Of these the first-named is unreliable for mixtures of the earths of weaker basicity, while the last is too time-consuming for routine application. The oxalate method is probably intermediate with regard to both the time required for the determination and the accuracy obtained.

The method involves the following steps: precipitation, washing, and oven-drying of the oxalate; determination of the oxalate to oxide ratio by the ignition of weighed portions of the partially dehydrated oxalate, followed by dissolution of weighed portions of the same sample of oxalate in sulfuric acid and titration of the oxalate content with standard permanganate solution. The average atomic weight is calculated from the formula, A/B = (2 R. E. + $3O)/3C_2O_3$, where A is the weight of rare earth oxide, $R. E._2O_3$ which corresponds to B, the weight of C_2O_3 found in the titrated samples.

Experimental

A preliminary investigation of the accuracy of the method was made, using certain spectrographically pure rare earths of the cerium group. The data are shown in Table I. The calculation:

$$\frac{2\text{La} + 3\text{O}}{3\text{C}_2\text{O}_3} = \frac{\frac{\text{Gram of oxide obtained}}{\text{Gram of oxal. ignited}} \times \text{gram of oxalate titrated}}{N \text{ of KMnO}_4 \times \text{m. eq. of } \text{C}_2\text{O}_3 \times \text{ml. of KMnO}_4 \text{ used}}$$

2La + 48	$\frac{0.1863}{0.3208} \times 0.1218$
216.06	$0.02526 \times 72.02 \times 51.40$
	2×1000
	$L_{2} = 130 4 \pi$

While the precision of the experimental results is satisfactory for the desired purpose, the accuracy is not. In all cases the atomic weights are slightly high.

As a result of searching the method for errors leading to high values it appeared likely that the oxalate titer of the permanganate against National Bureau of Standards sodium oxalate (dried overnight at 140° C.) was not the same as that obtained against the oxalate content of rare earth oxalate dried at 110° C. for a similar period of time. A possible explanation of this, in turn, might be that some nitratooxalate (6) contaminates the oxalate of the rare earths when the latter is precipitated in the usual way (4).

A comparison was therefore made between the normality of potassium permanganate solutions as determined by standardization against Bureau of Standards sodium oxalate on the one hand and against the pure rare earth oxalate itself on the other. Table II lists the results obtained in this series of determinations. It is evident that the oxalate titer of the permanganate solution as determined against the oxalate of the rare earth concerned is greater than that determined against sodium oxalate except in the case of gadolinium. The trend is consistent and is toward closer agreement of the two normalities with decrease in basicity of the rare earth (increase in atomic number) and the change in this difference may be significant.

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	TABLE I.	ATOMIC	WEIGHTS OF	Some CI	ERIUM GROU	JP EART	HS
Rare Earth Oxide	Weight of Oxalate ^a Titrated <i>Gram</i>	Volume of KMnO4 Used Ml,	N KMnO4 ^{98.} Na2C2O4	Weight of Oxalate Ignited Gram	Weight of Oxide Obtained Gram	Calcd. Atomic Weight	Inter- national Atomic Weight. 1941
La ₂ O ₃	0.1218 0.1090	$51.40 \\ 45.80$	$ \begin{array}{c} 0.02526 \\ 0.02526 \end{array} $	$ \begin{array}{r} 0.3208 \\ 0.3953 \end{array} $	0.1863 0.2294	139.45 140.03	
Nd2O3	0.1022 0.0860	40.50 34.12	0.02515 0.02515	0.2214 0.2338	Av. 0.1247 0.1321	139.74 145.54 145.88	138.92
Sm2O3	0.1132 0.0896	$\begin{array}{r} 43.15\\34.10\end{array}$	0.02467 0.02467	0.2099 0.3056	Av. 0.1153 0.1673	145.71 151.25 150.93	144.27

^a It follows from the data in Table I that the weight of water remaining in the oxalate after partial dehydration at 110° C. could be calculated readily. Such materials are no longer hydrated with 9 or 10 molecules of water although they may have been precipitated as ennea- or decahydrates. Further investigation of this point is planned.

In view of these results it was decided that the permanganate solution in all cases should be standardized against a pure sample of the oxalate of that rare earth which appears to be most abundant in the mixture concerned.

Recommended Procedure

The experimental procedure is the same for the standardization of the permanganate solution against the oxalate of a rare earth of known atomic weight as it is for the use of the permanganate thus standardized in the determination of the

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TA	BLE II. C	OMPARISO	N OF STA	NDARDIZ	ATION ME	THODS		samariu
Rare Earth Oxide	Weight of Oxalate Titrated Gram	Volume of KMnO4 Used Ml.	Weight of Oxalate Ignited C Gram	Weight of Oxide Ibtained Gram	N KMnO4 vs. R. E. Oxalate	N KM ^{TR.} Na ₂ C ₂	nOa Oa	solution together the mix
La ₂ O ₃	$\begin{array}{c} 0.1195 \\ 0.0782 \\ 0.0982 \\ 0.1303 \end{array}$	51.20 33.55 41.00 54.50	0.2005 0.2017 0.4747 0.6367	0.1178 0.1183 0.2761 0.3703	$\begin{array}{c} 0.02525\\ 0.02517\\ 0.02505\\ 0.02561\end{array}$	$\begin{array}{c} 0.024 \\ 0.024 \\ 0.025 \\ 0.025 \\ 0.025 \end{array}$	94 94 45 45	ized aga the mix
Nd2O3	$\begin{array}{c} 0.1421 \\ 0.1275 \\ 0.1301 \\ 0.1562 \end{array}$	55.35 49.60 51.70 62.00	0.1410 0.1912 0.5301 0.4457	$0.0775 \\ 0.1049 \\ 0.3034 \\ 0.2551$	$\begin{array}{c} 0.02516 \\ 0.02514 \\ 0.02568 \\ 0.02571 \end{array}$	$\begin{array}{c} 0.024 \\ 0.024 \\ 0.025 \\ 0.025 \end{array}$	94 94 45 45	the calo must b
Sin2Oa	$\begin{array}{c} 0.1595 \\ 0.1251 \\ 0.2386 \\ 0.1043 \end{array}$	60.70 47.65 89.40 39.20	$\begin{array}{c} 0.2544 \\ 0.2530 \\ 0.4198 \\ 0.6214 \end{array}$	0.1410 0.1405 0.2347 0.3468	$\begin{array}{c} 0.02505\\ 0.02508\\ 0.02566\\ 0.02554 \end{array}$	$\begin{array}{c} 0.024 \\ 0.024 \\ 0.025 \\ 0.025 \end{array}$	94 94 45 45	greater employe The
Gd2O3	0.1528 0.1182 0.1784 0.1487	50.95 44.10 64.60 53.85	$\begin{array}{c} 0.5778 \\ 0.8658 \\ 0.5724 \\ 0.4277 \end{array}$	$\begin{array}{c} 0.3238 \\ 0.4851 \\ 0.3205 \\ 0.2394 \end{array}$	$\begin{array}{c} 0.02488\\ 0.02485\\ 0.02559\\ 0.02557\end{array}$	$\begin{array}{c} 0.024 \\ 0.024 \\ 0.025 \\ 0.025 \\ 0.025 \end{array}$	94 94 67 67	possibly taining
	TABLE III	STAND	ARDIZATIO	N AGAIN	IST LANTH	ANUM	OXALAT	Applique
	Weight	Volume	Weight	Weip	ht Ox	ide	M Ec	nolda
Sample	Oxalate Titrated Gram	KMnO4 Used Ml.	Oxalate Ignited Gram	Oxic Obtai Gra	le to Or ned Titr m Gr	valate ated	of C ₂ O ₁	N of KMnO4
III	$\begin{array}{c} 0.1792 \\ 0.1564 \end{array}$	47.80 41.70	0.2005 0.2017	0.11 0.11	78 0.1 83 0.0	053 917	$\begin{array}{c} 0.03601 \\ 0.03601 \end{array}$	0.04056

average atomic weight of an unknown mixture. The calculations involving data from the former operation are shown below

About 1 gram of the pure rare earth oxide standard (or of the unknown oxide mixture) is dissolved in 50 ml. of water containing 7 ml. of 15 N nitric acid. After complete dissolution has oc-curred, the solution is diluted to 100 ml. and heated to boiling and the rare earth oxalate is precipitated by the slow addition of a hot solution of 10 grams of oxalic acid dihydrate in 50 ml. of water.

Since the presence of even small amounts of oxalic acid in the precipitate will seriously affect the final result, it is important that the oxalate be thoroughly washed. This operation should consist of two washings by decantation with 100-ml. portions of hot water followed by a washing on a filter, removal to a beaker, and another series of decantations. After a final washing on a filter the wet oxalate is removed to a beaker, the supernatant liquid decanted, and the precipitate dried at 110° C. for 8 to 12 hours

From the partially dehydrated oxalate are removed two samand ignited in an electrically heated muffle furnace to constant weight at 900° C. In this ignition it is advisable to put the oxalate into a cold furnace and to allow the temperature to rise slowly, since the dry powder is very easily blown from the crucible by the escaping gases if rapid heating next to the walls is allowed to occur.

Two other oxalate samples, each of about 0.15 gram, are removed, accurately weighed, and dissolved in 20 ml. of warm 10 N sulfuric acid. These solutions are diluted with 100 ml. of water, sulfuric acid. These solutions are diluted with 100 hill of water, heated to 90°, and titrated with standard potassium permanganate solution. The normality of this oxidant is conveniently either 0.04 or 0.025 N (ca. 1.26 or 0.79 gram of potassium permanganetic sector)nate per liter of solution), depending upon the amount of pure material available for standardization as well as upon the weight of sample available for the desired study.

The data in Table III illustrate the standardization of such a permanganate solution against lanthanum oxalate.

 $\frac{2\text{La} + 3\text{O}}{3\text{C}_2\text{O}_3} = \frac{0.1053}{x N \text{ KMnO}_4 \times 47.80 \times 0.03601}$ $2 \times 138.92 + 3 \times 16$ 3×72.02 x = 0.04056

Results and Discussion

In order to examine the usefulness of the method, a binary mixture of known composition was prepared and studied. Accurately weighed amounts of pure lanthanum oxide and amarium oxide were taken and dissolved in nitric acid, the olutions were combined, and the oxalates were precipitated ogether. The average atomic weight of the rare earth in he mixture was then determined according to the recomnended procedure. The permanganate used was standardzed against lanthanum oxalate, the principal constituent of he mixture, as well as against Bureau of Standards sodium xalate, and both of the resulting normalities were used in he calculation. The results are shown in Table IV. It nust be concluded that the accuracy obtained is much reater if standardization against the rare earth oxalate is mployed.

The oxalates of cerium, praseodymium, terbium, and ossibly of neodymium yield on ignition various oxides conaining some or all of the rare earth in a higher oxidation

state. Their exact behavior in mixtures is not yet certainly defined nor the influence of cerium certainly understood. It is therefore advisable to remove cerium before the atomic weight is determined; this may be accomplished quantitatively by the use of the iodate method (4). Praseodymium and terbium cannot be thus removed, so that their behavior on ignition must be accepted, for the present, as resulting in an unavoidable error. These elements are rare, however, and for usual mixtures the error will be small.

For mixtures rich in these elements the ignition product may be assumed to be $Pr_6O_{11}(2)$ and $Tb_4O_7(8)$. The behavior of neodymium under the prescribed ignition conditions is still incompletely known, but it is certain that it is not oxidized to a valence higher than 3 when cerium alone is present. The influence of cerium and praseodymium together has not vet been fully investigated, but the behavior of these elements in the ignition of various mixtures is being studied and will form the subject of a later paper in this series.

TABLE IV.	ANALYSIS	OF A MIX	TURE OF	KNOW	N COMP	OSITION
Standard	N KMnO4	Atomic Weight of Mixture	La Calcd. %	Sm Calcd. %	Actual La %	Actual Sm %
$Na_2C_2O_4$ La ₂ (C ₂ O ₄) ₃	$\begin{array}{c} 0.02560 \\ 0.02580 \end{array}$	143.48ª 142.20 ^b	$\begin{array}{c} 60.4 \\ 71.5 \end{array}$	$39.6 \\ 28.5$	$\begin{array}{c} 69.2\\ 69.2 \end{array}$	30.8 30.8
^a Average of ^b Average of	143.78 and 142.48 and	143.17. 141.91.				

Acknowledgment

It is a pleasure to acknowledge the aid given by B. S. Hopkins of the University of Illinois to this and other investigations soon to be reported. He has generously loaned several rare earths of high purity; without these the authors would have been unable to proceed.

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Potential Service Performance of Lubricating Oils

Laboratory Evaluation

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The corrosion and stability apparatus and method of test are introduced as means for the preliminary evaluation of the quality of lubricants. The distinctive feature of the test is the use of a felt wiping action on the bearing surface to simulate the action of the journal in the engine. Application of the test to twenty oils upon which

I^T IS universally agreed that the ultimate criterion of the quality of a lubricant is efficient performance in the engine for which it is designed. This fact will remain permanent, since the development of bench methods, which seek optimum control of variables and elimination of extraneous factors, inevitably leads to departures from the actual engine. It is scarcely possible that accurate reproduction of an engine in its entire scope will ever be realized in a noncombustion type of laboratory apparatus.

The existence of many laboratory apparatus and methods of test, several of comparatively recent origin, testifies to the need for means of evaluating oils which can cope economically

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extensive engine data have been reported establishes it as capable of predicting the oxidation stability and potential corrosivity of lubricants with accuracy sufficient to warrant the use of the test as a useful and reliable tool, in both research and control, to eliminate much of the more costly and time-consuming engine testing.

and practically with the great bulk of testing required either in the development of improved lubricants or in the control of oils in production. Such service is far too formidable for even small-scale test engines. When laboratory tests are available in such numbers, the presentation of a new apparatus perhaps requires justification. It is generally true that each test was developed specifically to evaluate a particular feature which the originators deemed important and worthy of emphasis. The tests, existent prior to the development of the present apparatus, represented a wealth of knowledge and experience from which could be selected the outstanding feature of individual cases, for incorporation into the new corrosion and stability apparatus. For example, severe conditions of aging lead to the simultaneous occurrence



FIGURE 1. DETAIL AND FLOW DIAGRAM OF CORROSION AND STABILITY APPARATUS



FIGURE 2. CORROSION AND STABILITY APPARATUS Metal support for reaction chamber removed and rotor raised

of oil oxidation and corrosion, a feature of several tests; a large oil charge facilitates the determination of products of deterioration and evaluation of oxidation stability, an objective of the Underwood test (11); freedom from materials other than glass and aluminum eliminates stray catalytic effects and lessens the cleaning problem; the use of a vigorous stirring action in the oil acknowledges a merit common to the Indiana stirring oxidation (5) and the MacCoull corrosion (6) tests; venting the reaction chamber with air is a feature also common to many tests; finally, the use of a felt wiping action on the bearing surface, which resembles more closely the earlier technique of Clower (3) than that of the thrust bearing corrosion machine (10), incorporates a feature re-cently suggested as essential in the accurate evaluation of corrosivity of oils toward copper-lead bearings. In addition, the new apparatus and method of test have been designed to constitute a durable, inexpensive apparatus capable of evaluating in 5 hours the essential characteristics of a lubricant, and hence are amenable to either research or control application.

Corrosion and Stability Apparatus

A major premise upon which the present apparatus and test are based is that it is possible, empirically and artificially, to age an oil in the laboratory in a manner comparable with the aging which it experiences under conditions of service. Rigid control of the important variables, temperature, catalysis, time, and concentration of reactants, is important to obtain satisfactory reproducibility. Compatible with the above premise, simplicity in design has been sought rather than reproduction of any mechanical features of an engine. It is recognized, however, that factors, operative and influential in an engine, must of necessity remain extrinsic to a laboratory test—for example, fuel, fuel combustion products, dirt, etc. The correlation between laboratory test and engine is thereby limited, and the necessity of retaining the engine as a final criterion over all laboratory tests becomes apparent. The degree of correlation which has been obtained between engine performance and the corrosion and stability test is sufficient to establish the latter as a useful tool for the preliminary evaluation of lubricants.

APPARATUS. The corrosion and stability apparatus is illustrated in complete assembly by diagram in Figure 1 and by photograph in Figure 2. In Figure 3 the glass parts of the apparatus are pictured dismantled and in Figure 4 the metal and felt units are similarly illustrated.

For convenience in description, the apparatus can be divided into four assemblies.

Reaction Vessel (Figures 1 and 3). The reaction vessel is fashioned out of two Pyrex beakers of 1- and 2-liter capacity, which are joined at their rims by a ring seal. The space between the beakers, which is equipped with a reflux condenser, serves as a vapor bath and provides a convenient and precise method for supply of heat and control of temperature.

The heat medium may be any material which has a constant boiling point coincident with the desired temperature of test.

INDUSTRIAL AND ENGINEERING CHEMISTRY



FIGURE 3. GLASS EQUIPMENT OF CORROSION AND STABILITY APPARATUS

B. Cover
C. Reflux condenser
D. Combined thermocouple well and air inlet
E. F. G. Manometrie flowmeters

For standard testing, aniline (b. p. 363° F.), conventionally purified by drying and redistillation, is most frequently used. However, wide ranges of temperature have been covered in applipurified by drying and redistillation, is most frequently used. However, wide ranges of temperature have been covered in appli-cation of the apparatus by use of the following materials: water (212° F.), chlorobenzene (270° F.), bromobenzene (313° F.), pseudocumene (337° F.), aniline (363° F.), and naphthalene (424° F.). In the bottom of the inner beaker there is a square recess, slightly larger than 2.8 \times 2.8 cm. (1.125 \times 1.125 inches) and about 0.6 cm. (0.25 inch) in depth. The reaction chamber is covered by an essentially flat glass lid, and a seal is effected by a flat ground-glass contact between the lip of the reaction cham-ber and the cover. Through the center of the cover passes the shaft of the aluminum rotor. Also from the center of the cover extends a lead to a water aspirator which serves to prevent fumes of deteriorating oil from being dispersed into the laboratory. Displaced to one side of the central opening through the cover there is a female ground-glass joint which accommodates a com-bined thermocouple well and an air inlet to the reaction chamber. Through this opening, samples of oil can be taken, if desired, with only momentary interruption of operation. The over-all volume of the reaction chamber is approximately 850 to 900 ml. *Wiping and Stirring Assembly* (Figures 1 and 4). Into the square recess in the bottom of the reaction chamber fits the aluminum bearing insert holder, called the "anchor" (Figure 4, C), which consists of an aluminum disk, from the bottom of which extends a square protrusion and into the top of which is sunk a square precess.

C), which consists of an aluminum disk, from the bottom of which extends a square protrusion and into the top of which is sunk a square recess. The square protrusion from the bottom of the anchor fits into the recess in the bottom of the reaction chamber and is cushioned by a square felt pad cut to dimensions and about 0.3 cm. (0.125 inch) in thickness (Figure 4, B). This fea-ture prevents rotation of the anchor during operation and holds the bearing insert stationary during a run. The recess in the top of the anchor accommodates the square bearing inserts, $2.8 \times$ 2.8 cm. (1.120 \times 1.120 inches), and of thickness 0.25 cm. (0.1 inch), sufficient for the surface of the bearing to extend about 0.75 cm. (0.03 inch) above the surface of the anchor (Figure 4, D). 0.75 cm. (0.03 inch) above the surface of the anchor (Figure 4, D).

Laterally through the cylindrical section of the anchor are bored four radial holes which are placed along two perpendicular diameters. These conduits converge in a larger hole bored co-axially through the anchor. A hole bored perpendicularly through the bearing insert is of the same size and coincides with the one extending coaxially through the anchor. This system of ducts through anchor and bearing insert provides a means which,

in conjunction with the design of the felt in conjunction with the design of the felt wiping pad, ensures an even and continual flow of lubricant over the bearing surface. The bearing inserts, of course, can be of any available metal or alloy; copper, alumi-num, lead, copper-lead, cadmium-nickel, and lead-flashed copper-lead have been employed. The wiping and stirring actions are pro-vided by an aluminum-felt unit which is called the "rotor" (Figure 4, A). The aluminum portion of the rotor consists of a shaft which is chucked into a conven-tional, bench-type drill press. At the lower

a shaft which is chucked into a conven-tional, bench-type drill press. At the lower extremity of the shaft is an aluminum disk, extending up into the bottom of which is a cylindrical recess placed coaxially with the disk and shaft. Extending down from the "ceiling" of the recess are aluminum spikes which embed themselves in the felt wiping pad (Figure 4, E) and prevent its slipping during rotation. The felt wiping pad is fashioned out of a cylindrical pad of felt of diameter such that a snug fit is ensured with the recess in the rotor and of sufficient thickness (0.9–1.25 cm., 0.375– 0.5 inch) to extend about 0.3 cm. (0.125 inch) below the surface of the rotor. In general, the nature of the felt used is not critical, a limiting factor being that it shall critical, a limiting factor being that it shall not disintegrate during the course of a run. Normally, SAE F3 gray backcheck felt (95 to 100 per cent wool) is used; SAE F1 white backcheck (100 per cent wool) has been found satisfactory.

white backeneck (100 per cent woor) has been found satisfactory. On the face of the pad, which wipes the bearing insert during operation, is cut a pat-tern which is represented in the diagram of Figure 1, and shown by photograph in Figure 4, E. Briefly, this pattern, which is cut most conveniently with a razor blade, consists of two perpendicular, triangularly prismatic troughs which extend along diam-eters of the surface. In addition to the two troughs, four pie-shaped pieces are cut from the four sectors formed by the cross of the troughs. The complete pattern is cut to the same depth, about 2.3 mm. (³/₃₂ inch). During operation of the apparatus, the face of the pad rests upon the bearing insert and wipes a circular area 2.8 cm. (1.125 inch) in diameter. No weight other than that of the rotor-spindle assembly is applied; in the apparatus now in use this amounts roughly to 2.7 kg. (6 pounds). As the machine operates, the oil on the surface of the bearing is swept outward through the troughs in the felt by centrifugal force, more oil is then pumped up through the radial and coaxial holes of the anchor and bearing, and thus continual contact is assured between oil and bearing.

and coaxial holes of the anchor and bearing, and thus continual contact is assured between oil and bearing. An extremely vigorous stirring action is imparted to the oil by means of four aluminum fins located on the periphery of the disk of the rotor (Figure 4, A). The fins are placed at equal distances and are pitched at an angle of about 45° in such a manner that the oil is lifted as the rotor travels in the clockwise direction. *Gas Train* (Figure 1). Although any gas phase can be swept through the apparatus, dried air is most generally used. The air is passed first through 20° Baumé, aqueous sodium hydroxide, then through concentrated sulfuric acid, and finally through a cartridge of glass wool or cottor to remove any entrained parti-

cartridge of glass wool or cotton to remove any entrained parti-cles. The flow of air is metered by means of a manometric-type flowmeter. From the flowmeter the air passes directly through the top of the reaction vessel by means of the combined thermo-couple well and air inlet. The air simply passes through the yapor space and is not bubbled through the oil; efficient contact between air and oil is assured by the vigorous agitation of the oil supplied by the rapid stirring. The air passes from the reaction chamber through the top of the reactor, along the shaft of the rotor. The rate of air flow generally used, 600 ml. per minute, allows a complete change of atmosphere approximately once each minute.

Mounting Accessories (Figure 2). For simplicity and convenience the corrosion and stability apparatus employs a conven-tional, bench-type drill press. Power is furnished by means of a $1/_{a}$ -hp. motor. Speed of revolution of the rotor is determined by the characteristics of the motor and reduction pulleys provided as standard features of the equipment. For standard testing, a speed of 1310 r. p. m. is used. However, variation has been investigated at 660 and 2410 r. p. m. Constancy of rotation is readily maintained within satisfactory limits (± 1 per cent at 1310 r. p. m.) and is checked periodically by means of a tachometer.

Reaction vessel and vapor bath

LABLE I.	STANDARD	CONDITIO	NS FOR CO	RROSION	AND STAB	ILITY
TES	TS ON LUE	RICANTS O	F SAE-10	AND 30	GRADES	

SAE grade of lubricant	10	30
Designation of test	C and S-10	C and S-30
Temperature (both oil and bearing), ° F.	363	363
Duration of test, hours	3	5
Oil charge, grams	225	225
Rotor speed, r. p. m.	1310	1310
Rate of air venting, ml. per minute	600	600
Bearing insert	The second second	a far in a
Туро	Cu-Pb	Cu-Pb
Total area, sq. cm.	7.89	7.89
Area wiped, sq. cm.	6.17	6.17
Ratios		
Total area of bearing per gram of oil,		
sq. cm.	0.0351	0.0351
Wiped area of bearing per gram of oil,		
sq. cm.	0.0274	0.0274

Heat is supplied to the vapor bath by means of a Chromolax ring heater of 750-watt capacity. The power supply to the heater is controlled by a Varitran. Variation of heat output facilitates more rapid heating up and the wide range of heat available in-creases the range of temperature at which operation may be con-ducted. The apparatus has been run at temperatures ranging from room temperature to 218° C. (424° F.). A simple steel framework, which can be of any convenient de-sign, supports the reaction vessel and holds it from slipping under the effect of the high speed rotation. It has been found expedient to insulate the reaction vessel by wrapping it with asbestos paper

the effect of the high speed rotation. It has been found expedient to insulate the reaction vessel by wrapping it with asbestos paper. More efficient utilization of heat is thus realized, as well as the elimination of erratic and localized overheating or subcooling. The top of the reaction chamber is held firmly in place by a gentle pressure exerted through a rubber cushion and a Transite ring which is bolted to the steel framework by means of four bolts with wing nuts.

THE WIPING ACTION. Whereas in other features the corrosion and stability apparatus does not depart markedly in

principle from earlier techniques, the nature of its felt wiping action on the bearing surface is distinctive. In agreement with Clower (3), who reported that a leather wiping action improved the reproducibility of corrosion measurements of this type, the felt wiping action has been found to contribute satisfactory precision. A felt wiping action is, of course, completely artificial in terms of service. The conditions existing at the bearing-journal site of an engine have been reproduced in the thrust bearing corrosion machine (10) which permits the study of corrosion of a loaded bearing under conditions essential to hydrodynamic lubrication. Loading the bearing in the glass equipment of the corrosion and stability test is impossible and hence the new apparatus does not realize this fundamental aim of the thrust bearing

corrosion machine. The wiping action of the corrosion and stability apparatus is designed to remove the products of corrosion in analogy to the action of the journal in an engine. It has been repeatedly observed that it does not interfere with the deposition on the bearing of lacquer films by oils which are noncorrosive in an engine, presumably because of the protection afforded the bearing by the deposition of the products of oil oxidation.

Operation of the Corrosion and Stability Apparatus

CONDITIONS OF TEST. In Table I are listed the conditions of test which have been usefully employed in the evaluation of the potential service performance of SAE-10 and 30grade motor oils. These conditions were selected as those which permitted satisfactory correlation between the laboratory test and the 36-hour Chevrolet engine test (1). Subsequently, these tests have been found capable of predicting with reasonable accuracy the behavior of lubricants in the Standard Caterpillar and General Motors Diesel engine tests (2, 4).

A standard corrosion and stability test is conducted under the conditions listed in Table I in accordance with the following simple procedure:

1. The bearing surface (Figure 4, D) is polished successively on several emery papers, the final polishing being given with 4/0paper. It is then washed with a light naphtha and acctone, dried, and weighed to 0.1 mg.

After insertion into the recess of the reaction chamber of the felt cushioning pad and the aluminum anchor (Figure 4, B and C), the heat-transfer medium is brought to boiling.3. When the vapors of the heat medium are observed in the



- $\frac{A}{B}$

	(On the bas	is of the four SAE correlati	ion oils of 30-viscosity grad	le)	
Property	a structure doubt	SAE Correlation Oil B-1	SAE Correlation Oil B-2	SAE Correlation Oil B-3	SAE Correlation Oil B-4
Bearing weight loss, mg. per sq. cm.	C and S-30 Engine test Rating, C and S-30 Rating, engine	$\begin{array}{r} 0.81 \ \pm \ 0.15 \ (19\%) \\ 16 \ \pm \ 6 \\ 2 \\ 3 \end{array}$	$\begin{array}{r} 6.4 \ = \ 0.2 \ (3.1\%) \\ 54 \ = \ 40 \\ 4 \\ 4 \end{array}$	1.44 = 0.04 (2.8%) 14 = 6 3 2	$\begin{array}{r} 0.54 \ \pm \ 0.07 \ (13\%) \\ 10 \ \pm \ 9 \\ 1 \\ 1 \\ 1 \end{array}$
Increase in neutral- ization No., mg. of KOH per gram	C and S-30 Engine test Rating, C and S-30 Rating, engine	$\begin{array}{r} 0.8 \ \pm \ 0.15 \ (19\%) \\ 2.3 \\ 1 \\ 2 \end{array}$	$\begin{array}{r} 4.8 \ \pm \ 0.4 \ (8.3\%) \\ 5.3 \\ 4 \\ 4 \end{array}$	$\begin{array}{c} 1.20 \neq 0.04 \ (3.3\%) \\ 1.6 \\ 2 \\ 1 \end{array}$	$\begin{array}{c} 2.6 \ \pm \ 0.1 \ (3.7\%) \\ 4.6 \\ 3 \\ 3 \end{array}$
Increase in viscosity at 100° F., S. U. scconds	C and S-30 Engine test Rating, C and S-30 Rating, engine	$\begin{array}{r} 68 \ = \ 12 \ (18\%) \\ 490 \\ 2 \\ 3 \end{array}$	160 = 14 (8.8%) 373 3 2	$\begin{array}{c} 24 \ \pm \ 2 \ (8.4\%) \\ 91 \\ 1 \\ 1 \end{array}$	$287 = 19 (6.6\%) \\ 1040 \\ 4 \\ 4 \\ 4$
Naphtha-insolubles, % by weight	C and S-30 Engine test Rating, C and S-30 Rating, engine	0.00-0.01 1.72 3	0.01-0.02 0.78 2	0.00-0.01 0.45 1	1.17 = 0.01 (0.9%) 2.81 4 4
Chloroform-solubles, % by weight	C and S-30 Engine test Rating, C and S-30 Rating, engine	< 0.01 1.38 3	<0.01 0.48 2	0.00-0.01 0.12 1	$1.16 = \begin{array}{c} 0.01 \\ 2.57 \\ 4 \\ 4 \end{array}$
Increase in Conradson carbon residue, % by weight	C and S-30 Engine test Rating, C and S-30 Rating, engine	0.17 2.16 1 2	$\begin{array}{r} 0.92 \pm 0.8 \\ 2.25 \\ 3 \\ 3 \end{array}$	$\begin{array}{c} 0.34 \ \pm \ 0.04 \ (12\%) \\ 1.29 \\ 2 \\ 1 \end{array}$	$1.02 \pm 0.03 (2.9\%) \\ 2.56 \\ 4 \\ 4$

TABLE II. CORRELATION OF C AND S-30 WITH THE 36-HOUR CHEVROLET ENGINE TEST



CORRELATION DATA BETWEEN C AND S-30 AND FIGURE 5. 36-HOUR CHEVROLET ENGINE TEST

reflux condenser, 225 grams of the test oil are introduced into the reaction chamber.

4. The oil is judged to be sufficiently heated for introduction of the bearing when vapors are again observed in the reflux con-denser. The weighed bearing is then fitted into position. In the case of opaque oils, a Nessler tube is conveniently employed as a spyglass, facilitating visual observation when the closed end is held down against the anchor.

5. After the bearing has been put into place, the apparatus is completely assembled. The rotor in which a fresh felt wiping pad completely assembled. The rotor in which a fresh felt wiping pad has been placed is rested on the bearing (Figure 4, A and E), and the cover (Figure 3, B), rubber cushioning ring, and Transite clamping ring are assembled and clamped into position with the four wing nuts (Figure 2). The shaft of the rotor is chucked into the drill-press spindle and the rotor is gently lowered until it rests on the bearing. At this point the motor is started to test the apparatus; if everything is in order, operation will proceed smoothly. Occasionally the wiping pad will become displaced from its recess in the rotor; this can be detected when the stirring mechanism is started and can be immediately rectified. The combined thermocouple well and air inlet is set into place, and, to avoid freezing, its ground-glass joint is lubricated with the oil under test. The stirrer should not be set into motion with the rotor raised, since the fins may not clear the thermocouple well and breakage will result.

6. A few minutes, about 10 to 15, are allowed after assembling the apparatus for the oil to come back to temperature after cooling during exposure to atmosphere during the introduction of the bearing. Again this can be judged by appearance of reflux in the condenser. Temperature readings are taken on a Leeds & Northrup indicating potentiometer, the thermocouple having been set in place. To obtain representative temperature meas-urements, stirring should be in operation, since the thermocouple well may not be sufficiently immersed in the oil otherwise. When reflux is again well up in the condenser, the air flow is started and adjusted to the desired rate by means of the calibrated manometric flowmeter, the stirring started, and zero time recorded. The equilibrium temperature is usually attained in from 3 to 5 minutes. Finally, the suction is supplied to the exit from the reaction chamber (by water aspirator) to prevent dispersing into the laboratory the fumes of deteriorating oil.

7. Normally very little attention is required by the corrosion and stability apparatus during the course of the run. Routine checks are made periodically of the temperature, air flow, and water flow through the condenser and any necessary adjustments made.

8. At the termination of a run, the supply of near to the bath bath is discontinued, the air flow is stopped, and the suction which has drawn off vapors from the reaction vessel is cut off. However, flow of cooling water through the condenser is allowed to continue until the heat medium has cooled well below boiling.

(On the basis of the four SAE correlation oils of 10-viscosity grade)						
Property	ider of procision is a	SAE Correlation Oil B-11	SAE Correlation Oil B-12	SAE Correlation Oil B-13	SAE Correlation Oil B-14	
Bearing weight loss, mg. per sq. cm.	C and S-10 Engine test Rating, C and S-10 Rating, engine	$\begin{array}{rrr} 0.79 \ \pm \ 0.02 \ (2.5\%) \\ 12 \ \pm \ 3 \\ 2 \\ 3 \end{array}$	$\begin{array}{rrrr} 1.7 & \pm & 0.2 & (12\%) \\ & 50 & \pm & 28 \\ & 4 \\ & 4 \end{array}$	$\begin{array}{c} 0.8 & = 0.2 \\ 8 & = 3 \\ 2 \\ 2 \end{array}$	$\begin{array}{c} 0.24 \pm 0.05 \ (21\%) \\ 2 \pm 1 \\ 1 \\ 1 \end{array}$	
Increase in neutral- ization No., mg. of KOH per gram	C and S-10 Engine test Rating, C and S-10 Rating, engine	$0.9 \neq 0.1 (11\%)$ 1.8 1 1	$\begin{array}{r} 2.8 \ \pm \ 0.2 \ (7.1\%) \\ 6.4 \\ 4 \\ 4 \end{array}$	$\begin{array}{c} 1.25 \ \pm \ 0.05 \ (4.0\%) \\ 1.95 \\ 2 \\ 2 \end{array}$	$\begin{array}{r} 1.7 \pm 0.3 \ (18\%) \\ 4.5 \\ 3 \\ 3 \end{array}$	
Increase in viscosity at 100° F., S. U. seconds	C and S-10 Engine test Rating, C and S-10 Rating, engine	$\begin{array}{c} 24 \ \pm 3 \ (12\%) \\ 316.3 \\ 1 \\ 4 \end{array}$	$38 \pm 5 (13\%) \\198.1 \\4 \\3$	$\begin{array}{r} 28 \ = \ 2 \ (7.1\%) \\ 47.1 \\ 3 \\ 1 \end{array}$	$\begin{array}{r} 23 \ \pm \ 6 \ (20\%) \\ 162.3 \\ 1 \\ 2 \end{array}$	
Naphtha-insolubles, % by weight	C and S-10 Engine test Rating, C and S-10 Rating, engine	$\begin{array}{r} 0.04 \ \pm \ (< 0.005) \\ 2.42 \\ 1 \\ 4 \end{array}$	$\begin{array}{r} 0.32 = 0.02 \ (6.3\%) \\ 1.16 \\ 3 \ (2)^{a} \\ 2 \ (2)^{a} \end{array}$	$\begin{array}{c} 0.26 \ \pm \ 0.06 \ (23\%) \\ 0.80 \\ 2 \ (1)^{a} \\ 1 \ (1)^{a} \end{array}$	$\begin{array}{c} 0.62 \ \pm \ 0.02 \ (3.2\%) \\ 1.95 \\ 4 \ (3)^{a} \\ 3 \ (3)^{a} \end{array}$	
Chloroform-solubles, % by weight	C and S-10 Engine test Rating, C and S-10 Rating, engine	$\begin{array}{r} 0.015 \ \ \pm \ 0.005 \\ 1.68 \\ 1 \\ 3 \end{array}$	$\begin{array}{c} 0.27 \ \pm \ 0.01 \ (3.7\%) \\ 0.49 \\ 3 \ (2)^{a} \\ 2 \ (2)^{a} \end{array}$	$\begin{array}{c} 0.22 \ \pm \ 0.02 \ (9.1\%) \\ 0.18 \\ 2 \ (1)^{\alpha} \\ 1 \ (1)^{\alpha} \end{array}$	$\begin{array}{r} 0.58 \pm 0.04 \ (6.9\%) \\ 1.89 \\ 4 \ (3)^{a} \\ 4 \ (3)^{a} \end{array}$	
Increase in Conradson carbon residue, % by weight	C and S-10 Engine test Rating, C and S-10 Rating, engine	$\begin{array}{rrr} 0.12 & \neq 0.02 & (17\%) \\ 2.20 & 1 \\ 4 \end{array}$	$\begin{array}{r} 0.375 \ \pm \ 0.005 \ (1.3\%) \\ 1.89 \\ 3 \\ 3 \end{array}$	$\begin{array}{r} 0.12 \ \pm \ 0.04 \ (33\%) \\ 0.95 \\ 1 \\ 1 \end{array}$	$\begin{array}{r} 0.4 \ \pm \ 0.1 \ (25\%) \\ 1.67 \\ 4 \\ 2 \end{array}$	
^a Figures in parenthese	es represent relative ratin	gs if oil B-11 is eliminated fr	om consideration.			

TABLE III. CORRELATION OF C AND S-10 WITH THE 36-HOUR CHEVROLET ENGINE TEST

The apparatus is disassembled immediately, and the oil is siphoned from the reaction vessel. These manipulations are made immediately at the completion of a run, since it is considered important to keep at a minimum the "overexposure" of the bearing to the hot deteriorated oil. 9. After removal from the apparatus, the bearing insert is washed in solvents as it was prior to its initial weighing. Adhering particles of sludge are removed by gentle weighing. Adher-

9. After removal from the apparatus, the bearing insert is washed in solvents as it was prior to its initial weighing. Adhering particles of sludge are removed by gentle swabbing with cotton, but no abrasion severe enough to cause erosion of metal is employed. When clean, the surface of the bearing is examined visually for evidence of erosion or uneven wiping. Erosion is indicated by deep concentric scratches in the surface, whereas uneven wiping results in polished areas unevenly distributed on the 'high' areas of the surface. When dry, the bearing is reweighed to evaluate the extent of corrosion which has occurred during the run.
 10. The aged oil is subjected to analysis for properties which

10. The aged oil is subjected to analysis for properties which are regarded conventionally as measures of extent of deterioration—e. g., neutralization number, saponification number—increase in viscosity, and naphtha-insolubles.

CLEANING THE APPARATUS. The apparatus is thoroughly cleaned after each run. While still warm, the reaction vessel is first swabbed out with dry cotton. Kerosene is then introduced and the walls of the vessel are briskly rubbed with cotton. Successive washes then follow with naphtha and acetone until the solvents remain uncolored. The cover, rotor, and anchor are likewise washed with kerosene, naphtha, and acetone. Both felt cushioning pad and felt wiping pad are discarded after each run.

Occasionally it is necessary to employ more drastic cleaning procedures. The metal parts can be abraded with steel wool, care being taken to rinse off all metal particles after such treatment. Steel wool is never used on the reaction vessel; rather a prolonged exposure to bichromatesulfuric acid cleaning solution is employed. This can be effectively accomplished by filling the vessel with the acid and bringing the vapor bath to reflux.

Experimental Results

In their development the standard corrosion and stability tests were correlated with the 36-hour Chevrolet engine test, since considerable data (7) are available from the recent correlation program carried out among several laboratories on this engine test under the supervision of the subcommittees



FIGURE 6. CORRELATION DATA BETWEEN C AND S-10 AND 36-HOUR CHEVROLET ENGINE TEST

TABLE IV. CORROSIVITY-ZONE SCHEDULE FOR JUDGING POTEN-TIAL CORROSIVITY OF LUBRICANTS FROM RESULTS OF CORROSION AND STABILITY TESTS

		Weight Loss o ing Insert in	f Cu-Pb Bear- C and S Test
Zone	Description	SAE-10 oils	SAE-30 oils
	term Temperatur	Mg. per	sq. cm.
I	Noncorrosiye	< 0.5	< 0.75
II	Borderline to mildly corrosive	0.5-1.0	0.75-1.5
III	Mildly corrosive to corrosive	1.0-1.5	1.5-2.0
IV	Excessively corrosive	>1.5	>2.0
TOD -	No. States and	180-11-11-11-11-11-11-11-11-11-11-11-11-11	

of Sub-Division B of the Lubricants Division of the Society of Automotive Engineers.

CORRELATION OF C AND S-30 WITH THE 36-HOUR CHEV-ROLET ENGINE TEST. In Table II and Figure 5 are presented the correlation data for corrosion and stability on 30-grade oils and the 36-hour Chevrolet engine test.

The precision of C and S-30 is strikingly good for this type of test, as concerns both potential corrosivity and oil deterioration. verage error for these data expressed as average deviation from the mean is ± 8.2 per cent.

Some reversals will be observed. Oils B-1 and B-3 are re-versed by the laboratory test from their relative ratings in the versed by the laboratory test from their relative ratings in the engine in respect to corrosivity, increase in neutralization number, and increase in carbon residue, and B-1 and B-2 are reversed as concerns increase in viscosity. The reversal of B-1 and B-3 in corrosivity is not considered serious, since one third of the participating engine laboratories either rated these oils in the same order as did the C and S-30 or rated them as equal. Further, the averages for all engine laboratories on the corrosivity of these two oils separated them by only 14 per cent of the lower figure (16 mg. per sq. cm. for B-1, 14 mg. per sq. cm. for B-3) which is well within the precision of the engine test. The reversal of B-1 and B-2, in respect to increase in viscosity, occurs again with two oils on which the

with two oils on which the least differentiation was

made by the engine. The C and S-30 found most difficult the reproduction of engine performance as regards formation of sludge and insoluble bodies in these oils. It is logical that the interfering factors attributable to the fuel, fuel combustion products, dust, and dirt, in-fluential in the engine but absent in the laboratory test, will concentrate their effect in regard to this particular manifestation of deterioration. Nevertheless, it is evident that C and S-30 distinguishes B-4 as the worst oil in regard to naphtha-insolubles, chloroform-solubles, and increase in carbon residue.

Neither the corrosion and stability nor the engine test rates the corrosivity of the oils in the same order as in development of neutralization number. Thus, further evidence is pro-vided of the inadequacy of neutralization number as a criterion of the development of corrosivity.

CORRELATION C OF AND S-10 WITH THE 36-HOUR CHEVROLET EN-GINE TEST. In Table III and Figure 6 are presented the correlation data for corrosion and stability on 10-grade oils and the 36-hour Chevrolet engine test.

relatively high order of precision is maintained in C and S-10; average error for these data is = 13.4 per cent. Ample margin is provided to differentiate readily between oils of reason-

ably different quality. The C and S-10 rated oils B-11 and B-13 of equal corrosivity within the precision of the test, whereas the engine test rated B-11 more corrosive than B-13. However, as can be judged from the precision figures for the engine tests (included in Table III) the ranges in corrosivity covered by both oils are sufficient to permit a reversal.

Correlation between laboratory and engine tests on viscosity crease is poor; however, development of naphtha-insolubles, increase is poor; however, development of naphtha-insolubles, chloroform-solubles, and increase in carbon residue agree satis-factorily with the one exception of oil B-11. As in the case of the 30-grade oils, here again there is no correla-

tion between development of neutralization number and corrosivity.

Tables II and III indicate that extent of corrosivity and oil deterioration in the corrosion and stability tests falls short of that in the engine test. Standard conditions have been selected deliberately to maintain deterioration in the laboratory test less severe than that in the engine, since the converse might be expected to imperil the validity of the test. Furthermore, it can be judged impossible to find a single set of conditions which would deteriorate all oils to the same extent as does the engine, since the ratio between deterioration in the corrosion and stability apparatus and the engine is not constant for different oils. For example, increase in severity of conditions in the laboratory test sufficient to increase the neutralization number change for oil B-1 to its value in the engine (from 0.8 to 2.3) would be expected to cause the deterioration of oils B-2 and B-3 to exceed that

				1	Statistics in state	
	TABLE	V. CAND	S-30 DATA	AND ENGINE	DATA	
IOn Grou	n I oils (SAE-4	() grade) of S.	A. E. Cranker	ase Oil Stabilit	v Research Con	nmitteel
	Oil	Oil	01	Oil	Oil	Oil
	4	5	6	7 10	8	9
		С	and S-30 Dat	8		
Cu-Pb weight loss,		deteriorre	to mini an in			(0.00.000)
mg. per sq. cm. Belative rank	0.50 ± 0.08	0.68 ± 0.16	2.0 ± 0.3	0.34 ± 0.10	0.93 ± 0.10	$-(0.08 \pm 0.02)^{\circ}$
∆ Neutralization No.,		0	0	and illoant sh	disigna bas	dislopery ni seemo
mg. of KOH per	00+09	170.0-	98 + 07	2 5 - 0 2	10+02	$-(0.2 \pm 0.0)$
Relative rank	2	1.75 ± 0.05	2.8 -0.7	5 5	1.5 - 0.2	1
Δ Saponification No.,						
gram	7 ± 2	3.3 ± 0.4	6.8 ± 0.9	5.3 = 1.7	3.5 ± 1.0	$-(0.75 \pm 0.05)$
Relative rank	5	2	5	4	2	but bort borter
Viscosity increase at	20 + 3	63 + 4	40.5 ± 0.5	80 = 10	92 ± 6	21 ± 0.0
Relative rank	20 - 0	4	3	4	6	1
Naphtha-insoluble,	0.01.0.09	1 49 - 0 01	0 02 0 01	16+09	1.70 ± 0.07	10.04
Relative rank	1	1.42 4 0.04	2	1.0 - 0.2	5	2
Over-all relative		Jacid W 315	Halan Liber	an in the second second	BE STATE WILL	time and free basis
rank	Z	3	9	4	in the second	if (E-215 orth 10kg
	Report of S.	A. E. Crankca	se Oil Stabilit	y Research Co	mmittee (8)	
Over-all relative rat-						
ings on basis of		2	A stands	e	1	1 1
Relative service rat-	4	0		0 00 0	a distant	artes field we have
ings	2	411 IN	6	3	5	tents in 18 totals
Oil No.			Service De	escription		
23		is own ber	A LOUIS LOUIS CON	duranta ator		
4 A very 5 Judged	good oil but ne	ot quite so good	d as the best	d ring sticking	tendencies	
6 Because	of insufficient	service data, it	is impossible	to rate this am	ong other oils.	Shown in labora-
7 Cluden	to be stable at	low temperatu	re, but sticks	rings quickly a	t high tempera	ture.
8 A very	poor oil which	had caused ev	ery sort of tre	buble generally	considered to	arise from lack of
stabil	lity; a bad slu	dge maker and	ring sticker;	unquestionab	ly this oil has t	he poorest service
9 Free fre	om ring sticking	g and troubles	arising from 1	ack of stability		In their devel
4 Gain			Suerra letter			
b Loss.				ald all a share	(Signalian)	detablector overtre
c This ranking on	niricelly establ	ished as follow	e' corrosivit	v and nanhtha	insoluble rank	ings weighted each

as unity; A neutralization No., A saponification No., and viscosity increase rankings weighted each as one third.

September 15, 1943

	TABLE VI	CANDS	DATA AND ENGINI	DATA			
[On group III oi	la (SAE-20 grad	e) of the S. A	. E. Crankcase Oil S	itability Re	search Commit	teel	
	Oil 1	3	Oil 14-		Oil	15	
		0	10 D to				
- included with the arts	a weather and	C ai	IG S DELE				
Cu-Ph weight loss mg	C and S-10	C and S-30	C and S-10 C	and S-30	C and S-10	C and S-30	
Relative rank	0.32 ± 0.00 1	$0.64 \\ 2$	0.28 ± 0.05 1	0.39 1	2.36 ± 0.02 3	4.3 3	
of KOH per gram Relative rank	2.0 ± 0.2 2	3.0 2	0.25 ± 0.05 1	$0.5 \\ 1$	5.0 ± 0.6	11.4 3	
of KOH per gram Relative rank	3.4 ± 0.0 2	$\frac{5.6}{2}$	$-(0.6 \pm 0.2)^a$	3.7 1	19 ± 3 3	28 3	
100° F., % Relative rank	46 ± 2	87 2	2.4 ± 0.0	4.6	53 ± 6	280 3	
Naphtha-insoluble, % Relative rank	1.3 ± 0.1	1.7	0.02-0.04	0.02	0.01	0.06	
Over-all relative rank 6	2	2	ablim 1	1	3	3	
Repo	ort of S. A. E. C	rankcase Oil	Stability Research C	committee ((9)		
Over-all relative ratings	south hards		in sides which has		and the second		
on basis of test engines Relative service ratings	3(close to 1	No. 15)	1 (much the b	est)	2(close to No. 13)		
Oil No.			Service Description				
13 An oil ge	nerally rated of	low stability	; in sludge forming	and ring st	icking, its beha	vior is not	
14 An oil wi long-tin and en	hich has shown me mild conditio	very good or ns stability h	idation stability cha as been satisfactory i	nacteristics n both gasol	under both s ine and Dicsel o	evere and equipment	
15 An oil of under	medium stabilit severe operating	y; has work conditions.	ed out successfully in	a wide fiel	d of application	, but fails	
^a Loss. ^b This ranking empirica unity; Δ neutralization N	lly established a lo., Δ saponificat	s follows: c ion No., and	orresivity and napht viscosity increase rar	ha-insolubl hkings weig	e rankings weig hted each as one	hted each as third.	

attained in the engine. Of course, an interfering factor in this concern is the practice of adding make-up oil during the engine test, a feature which is influential in determining the

TABLE VII. CAND	S-30 DATA AL	ND ENGINE D	ATA
[On group IV oils (SAE-60 grade)	of S. A. E. Cra Committee]	inkcase Oil Stat	oility Researc
	Oil 16	Oil 17	Oil 18
C	and S-30 Data		
Cu-Pb weight loss, mg. per sq. cm. Relative rank ∆ Neutralization No., mg. of KOH per gram Relative rank ∆ Saponification No., mg. of KOH per gram Relative rank Viscosity increase at 100° F., % Relative rank Naphtha-insolubles, % Relative rank Over-all relative rank ^a	0.72 ± 0.17 1.8 ± 0.6 11.4 ± 0.3 45 ± 7 $0.03-0.04$ 1	$\begin{array}{c} 0.35 \pm 0.11 \\ 2 \\ 0.30 \pm 0.05 \\ 5.6 \pm 1.1 \\ 9.5 \pm 0.5 \\ 0.02 - 0.03 \\ 1 \\ 2 \end{array}$	$\begin{array}{c} 0.13 \pm 0.03 \\ 1 \\ 0.1 \pm 0.0 \\ 1 \\ 0.6 \pm 0.1 \\ 01 \\ 0.04 \\ 1 \\ 1 \end{array}$
Report of S. A. E. Crankcas	e Oil Stability	Research Com	mittee (9)
Over-all relative rating on basis of test engines Relative service ratings	3 2 ·	2 3	1
Oil No.	Service Des	cription	
16 An oil of medium	stability chars	acteristics: rea	sonably satis-

10	An on of medium stability characteristics; reasonably satis-
5.955 A.V	factory under a fairly wide range of operating conditions
	but not entirely suitable for all types of operation
17	An oil of low stability characteristics; capable of reasonably
	satisfactory performance under relatively easy service con-
	ditions; distinctly unsatisfactory in high performance
	engines in moderately severe service
18	An oil of high stability; superior from standpoint of lacquer,

sludge, and ring sticking; possess high stability rating over widest possible service range

 a This ranking empirically established as follows: corrosivity and naphtha-insoluble rankings weighted each as unity; Δ neutralization No., Δ saponification No., and viscosity increase rankings weighted each as one third.

extent of oil deterioration as measured by the properties of the final oil sample. A more satisfactory expedient would be to measure deterioration as a function of time. This is conveniently achieved in corrosion and stability tests by sampling the oil charge at intervals during a run. The importance of time as a variable influential among the factors affecting oil deterioration and bearing corrosion is discussed in a companion communication (12).

DEFINITION OF PER-MISSIBLE LIMITS OF COR-ROSIVITY. From the data of Tables II and III a scale for rating the potential corrosivity of lubricants of these two viscosity grades has been drawn up. It is, of course, recognized that no sharp line of demarkation between noncorrosive and corrosive oils

can be made. Judgment is based, rather, on "zones" of corrosivity in accordance with the schedule outlined in Table IV.

EVALUATION IN CORROSION AND STABILITY APPARATUS OF LUBRICANTS CIRCULATED BY S. A. E. CRANKCASE OIL STABILITY COMMITTEE $(\mathcal{S}, \mathcal{G})$. With the conditions of test selected upon the basis of the results obtained on the B oils as described above, various correlation oils selected by the S.A.E. Crankcase Oil Stability Research Committee have been studied in the corrosion and stability apparatus, since they provided further opportunity to ascertain the accuracy with which the laboratory test predicts engine service. Oils of SAE-40 grade (Nos. 4 through 9) and of SAE-60 grade (Nos. 16 through 18) were subjected to conditions of test selected for SAE-30 grade oils (C and S-30); oils of SAE-20 grade (Nos. 13 through 15) were tested under the conditions of both C and S-10 and C and S-30. It was elected to examine these oils under both the milder and more severe conditions, since no set of conditions has been established for 20-viscosity grade oils, because of the lack of engine data of the desired scope as provided in the B oils of the S. A. E. committee.

In Table V are presented the results, both from the engine and C and S-30 studies on the SAE-40 grade oils. In each case the relative ratings as established by the corrosion and stability test agree either equally well or more closely with the service ratings than do the over-all ratings based upon the performance of the oils in the test engines. Oils 5, 7, and 8, which are described as sludging oils in service, tended to develop excessive amounts of naphtha-insolubles in the laboratory test. In regard to corrosivity, if the scale developed for SAE-30 grade oils be employed, distribution of the six oils among the various zones of corrosiveness is as follows:

Zone I Zone II	Oils 4, 5, 7, 9 Oil 8	Noncorrosive Borderline to mildly
Zone III	Oil 6	corrosive Mildly corrosive to
		corrosive

INDUSTRIAL A	ND EN	GINE	ERING	CHE	MI	STI	RY
	1.5	-		Two	of	the	fo

	TABLE	s VIII. Ev	ALUATION	IN CORRO	SION AND STAL	BILITY TEST OF I	FRAVY-DUTY AL	L-PURPOSE LUB	RICANTS	Aller Aller Aller Aller Aller Aller Aller Aller Aller	
aity index (Dean and	V IIO		Oil B		Oil C	Oil D	OilE	OilF	Oil G	0il H¢	oil I ¢
vis) riscosity grade ive	100 30 Inhibitor deter	gent Inhi	50 30 bitor deter	gent	190 30 Inhibitor	80 30 Inhibitor de-	90 30 Nane	90 30 Inhibitor de-	90 30 Inhibitor de-	100 10 Inhibitor de-	87 10 Inhibitor de-
atory test b weight loss, mg. per sq. cm.	C and S-3(1.25 ± 0.0	30	C and S-3(0.75		C and S-30 0.48	C and S-30	C and S-30 1.6 ± 0.2	C and S-30 2.0 ≠ 0.1	C and S-30 I.I ± 0.1	C and S-10 0.44	C and S-10 1.3 ± 0.1
H per gram	1,0 = 0,0	and the second	0.7		0.1	0.7	1.7 ± 0.2	$0.55 \Rightarrow 0.05$	0.45 ± 0.05	0.4	0.8 ± 0.2
If per gram sity increase at 100° F. %	4.5 7.1		4.0 20 0.00			-10 0 01	$\begin{array}{c} 9.3 \pm 0.3 \\ 27 \pm 1 \\ 0.12 \pm 0.04 \end{array}$	4.0 ± 0.5 6.5 ± 1.2 0.10 ± 0.00	3 ± 2 8.1 ± 0.5 0.06 ± 0.02	2.8 4.0 0.03	5 ± 1 27 0.07
sivity rating	Zone II, bord to mildly corr	erline Zon osive mil	e II, border idly corrosive	line to	Zone I, non- corrosive	Zone III, mildly cor- rosive to cor-	Zone III, mildly cor- rosive to cor-	Zone IV, excessively corrosive	Zone II, borderline to mildly cor-	Zone I, noncorrosive	Zone III, mildly cor- rosive to cor-
te testa	in a la la la	2	17 18 18	2	2	TOSIVE	3	0	3	93	3
ring neutrotion No me of	18 .	のの日日の		28		924	5-50	42-106	12		28
H per grant	ADD anita			.95		· · · · · ·	0.2	0.4	0.3	· · · · · ·	0.6
Baponincation No., mg. of H per gram				.4	No. of Street, or Stre			6.7	5.1		4.8
sity increase at 100° F., %		No lo stan	4	11			5	11	14		57
tha-insoluble, %			0	20			0.14	0.42	0.49		0.77
sivity rating	Satisfac Cor tory siv	ro- Sati	sfac- Accel y but	ptable mildly osive	Satisfactory	Corrosive	Tendency to be corrosive	Corrosive	Satisfactory	Satisfactory	Above bor- derline in corrosivity
Ongine test designations: 1 3	Caterpillar Diese General Motors Caterpillar 3-A I	al 240-hour tes Diesel 500-hou Diesel 120-hou	tt (2) ur test (4) r test (2)				b Properties of lubr H and I contained	icant sampled at 3 also a pour-point o	384th hour of 500- depressant.	hour test.	Densel Marine Ma

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Nap (instruction)

Two of the four oils which fall in the noncorrosive zone I (oils 5 and 7) nevertheless display considerable tendencies to develop acids as judged by neutralization number. Their failure to become corrosive may be attributed to deposition of protective films on the bearing surface; this is compatible with their development of high naphtha-insolubles.

Table VI lists the data on the SAE-20 grade oils. The laboratory test rated the three oils in the same order under both the milder and more severe conditions. It is felt, since in the S. A. E. committee's report (9) it is emphasized that these oils are moderate-duty lubricants and not designed for heavy-duty service, that the milder conditions of test are more appropriate. This is substantiated by the fact that under the more severe conditions, oil 15 is oxidized more severely in the laboratory test than in the engine. The practice, however, of testing SAE-20 grade lubricants under the conditions of C and S-10 is by no means generally employed. For heavy-duty, all-purpose oils, it is preferred to apply the more severe conditions of test, since there is thus provided a factor of safety compatible with the service the lubricant may be called upon to render.

Consideration of the order of rating by the corrosion and stability tests reveals that oil 14 is definitely superior to oils 13 and 15, which is consistent with both the test engine and service ratings. In regard to these latter two oils, it may be judged that No. 13 would be unsatisfactory from sludging trouble and No. 15 affords insufficient protection against corrosion of copper-lead bearings. The relatively great deterioration of oil 15 exhibited by high neutralization number, saponification number, and viscosity increase is due probably in part at least to catalysis by metal removed from the copper-lead bearing. Severe oil oxidation is frequently observed accompanying high weight loss with this type of bearing. In the absence of this factor of catalysis, the differentiation obtained in the corrosion and stability tests between oils 13 and 15 with respect to stability would probably not be so marked. Corrosivity ratings, in accordance with the zone schedules of Table IV for the 20-grade oils, are:

Zone I Oils 14, 13 Noncorrosive Zone IV Oil 15 Excessively corrosive

It may be judged that oil 13 fails to become corrosive through the protection afforded to the bearing surface by the deposition of products of oil oxidation (naphtha-insolubles).

In Table VII are presented the results obtained upon the oils of SAE-60 viscosity grade. It will be seen that the corrosion and stability test and the test engines rate these three oils in the same order, whereas both show a reversal with respect to the service ratings of oils 16 and 17. This reversal may be due to the selection of insufficiently severe conditions for the laboratory test properly to evaluate lubricants of this high viscosity grade. It appears likely, however, that greater difference in quality exists between oil 18 and either of oils 16 and 17 than exists between oils 16 and 17 themselves, and this is clearly disclosed by the corrosion and stability test. All three SAE-60 grade oils rate as noncorrosive (zone I on the schedule for 30-grade oils). Nevertheless, there is sufficient variation among the corrosivities of the three lubricants for definite individual differentiation well outside the precision of the laboratory test.

HEAVY-DUTY ALL-PURPOSE LUBRICANTS. An application in which the corrosion and stability apparatus has been usefully employed is the preliminary examination of lubricants prior to protracted approval tests in heavy-duty type engines. From the experience gained thus far, it has been judged that the corrosion and stability characteristics of oils can be predicted with reasonable accuracy on the basis of the zone schedules drawn up in Table IV and analysis of aged oils.

Table VIII presents data on several heavy-duty, allpurpose lubricants of both SAE-10 and 30 grades which have been evaluated in the corrosion and stability test and an engine test. Excellent agreement will be observed between the corrosivity predicted from the corrosion and stability test and that observed in the engine. In some cases oxidation is more severe in the laboratory test than in the engine, as judged by the properties of the final oil sample. That this is probably caused by the practice of adding make-up oil during the engine test is indicated by the properties of the sample of oil B removed from the engine at the 384th hour of the 500hour test. At this point, the properties of the used oil indicate greater deterioration than was obtained in the laboratory test. It is possible, in general, to obtain a useful and reasonably accurate idea of the stability characteristics of an oil from the analysis of the oil aged in the corrosion and stability tests. These used oil properties are furthermore helpful in accounting for the corrosiveness of an oil and in disclosing inherent weaknesses of lubricants, such as susceptibility to catalysis by metals, etc.

METAL CATALYSIS. In the standard corrosion and stability tests, as defined by the conditions of Table I, the only real source of catalysis by metals of the deterioration of the oil is the copper-lead bearing insert, since aluminum is generally recognized to be relatively inactive. This constitutes definitely a departure from conditions of an engine in which exposure to metals, principally iron, is outstanding. However, the conditions selected as standard were chosen empirically in order to obtain favorable comparison between corrosion and stability tests and engine performance. On the oils discussed in this paper, this was achieved without inclusion of extraneous metal catalysts. However, ample provision has been made in the design of the apparatus for the inclusion of catalysts, and the importance of this factor is fully recognized by the authors. It is visualized that extension in the scope of the apparatus, as well as improvement in accuracy and hence usefulness of the test, may be effected through the addition of catalysts.

The utility of the corrosion and stability tests has been established through the experience gained in the examination of such lubricants as are described in Table VIII. Despite the failure to correlate exactly with the engine behavior of the oils upon which extensive engine data are available, the extent of correspondence has been sufficient to inspire confidence in the laboratory test. By submitting lubricants, the engine performances of which have not been evaluated, to a corrosion and stability test appropriate to viscosity grade, it is possible to determine whether the more expensive and time-consuming engine test can profitably be run.

Summary and Conclusions

This communication describes the corrosion and stability apparatus and presents results obtained with it in its application as a tool useful in predicting the potential service performance of lubricants. Correlation of the results of the test with behavior of oils in various types of engines is considered to be generally satisfactory, since no laboratory test of this type can take into account all the factors operative in the engine. The corrosion and stability apparatus is simple, inexpensive, and durable; the conditions of test are such that convenient application is possible for either research or control purposes. In design, the apparatus is broadly flexible and, therefore, as variations are made in engines and their conditions of operation, it should be possible to modify the test to compensate for them.

The corrosion and stability apparatus has been extensively employed in these laboratories in the study of the factors affecting bearing corrosion. The effects of variation of the important physical factors, such as time, temperature, catalysis, concentration of reactants, and type of bearing alloy, have been followed in the corrosion and stability apparatus. Discussion of this work is presented in a companion communication (12).

Acknowledgment

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It is also desired to express appreciation to the Society of Automotive Engineers for permission to use unpublished data on the oils used in the correlation program of the S. A. E. Crankcase Oil Stability Research Committee.

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Coprecipitation of Chromate with Barium Sulfate

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The coprecipitation of chromate with barium sulfate has been studied quantitatively under carefully controlled conditions. Acidity, rate of precipitation, ratio of chroniate to sulfate, and time of digestion were varied in turn.

The results obtained support the view that for the most part the chromate coprecipitated is probably in the form of barium chromate in mixed crystals with barium sulfate.

THE error caused by coprecipitation of dissolved substances with barium sulfate in gravimetric analysis has been widely recognized. Studies of coprecipitation of various anions have been reported recently (δ , δ), but chromate has been omitted from detailed consideration. Kolthoff (2) and Manov and Kirk (3) have considered briefly the coprecipitation of chromate with barium sulfate during volumetric analysis for sulfate by the method originally devised by Andrews (1). Their methods were, however, not precise, since conditions were not rigidly controlled and the amount of chromate coprecipitated was estimated by analyzing the filtrate rather than the precipitate. The authors' preliminary experiments showed that inconsistent results are obtained unless conditions are carefully controlled.

In neutral solution barium chromate is precipitated nearly quantitatively whether or not sulfate is present. Barium sulfate ordinarily is precipitated from acid solutions, however, in the presence of a slight excess of barium ion. Willard and Schneidewind (7) in presenting their widely accepted method of analysis for sulfate in chromium plating baths, state: "Barium chromate is so insoluble in dilute acids that it almost invariably contaminates the barium sulfate, and if

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sufficient acid is used to prevent this, incomplete precipitation occurs." This statement is an oversimplification, since barium chromate will not precipitate by itself, even in the rather dilute acid solutions from which it is customary to precipitate barium sulfate, unless the chromate concentration is high. Coprecipitation of chromate with barium sulfate from acid solution is presumably due for the most part to the formation of mixed crystals, since barium sulfate and barium chromate are isomorphous. Other causes may account for a small proportion of the coprecipitation of chromate, perhaps as sodium chromate or dichromate.

The coprecipitation of barium chromate with barium sulfate in acid solution is unusual in that the concentration of chromate ion is very low, although there is a "reservoir" of potential chromate ions in the solution, since in the presence of acid, equilibrium exists among CrO_4^{--} , $HCrO_4^{-}$, and $Cr_2O_7^{--}$ ions in aqueous solution:

 $2\mathrm{CrO_4^{--}} + 2\mathrm{H_3O^+} \rightleftharpoons 2\mathrm{HCrO_4^-} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{Cr_2O_7^{--}} + 3\mathrm{H_2O}$



OF TIME IN SECONDS OF ADDING PRECIPITANT O. Without stirring

The greater the concentration of hydrogen ion, the lower is the concentration of chromate ion. As barium dichromate is not isomorphous with barium sulfate, the extent of mixed crystal formation is largely dependent on the acid concentration. Other factors which might be expected to affect the amount coprecipitated, whether from mixed crystal formation or from other causes, are rate of addition of the precipitant, concentration of chromate, and length of time of digestion of the precipitate.

This paper reports the results of a study of the extent to which chromate is coprecipitated with barium sulfate, one condition at a time being altered while the others were held constant.

Procedure

The chromate in a given barium sulfate precipitate was determined by the method described by Meldrum, Cadbury, and Lucasse (A). The precipitate was fused with sodium carbonate and the melt allowed to cool and then disintegrated with water. The mixture was filtered and the filtrate acidified and analyzed iodometrically for chromate.




FIGURE 3. VARIATION OF COPRECIPITATION WITH CONCENTRA-TION OF SODIUM CHROMATE, SODIUM SULFATE HELD CONSTANT

O. Amount of acid constant Excess acid constant

The reagents and solutions were prepared as described in the paper previously referred to (4).

Sodium sulfate solution containing about 0.3 gram of sodium sulfate in 25 ml. was introduced from a 25-ml. pipet into a 200-ml. Erlenmeyer flask, and the desired amounts of dilute hydrochloric acid, water, and sodium chromate solution were added. The flask was fitted with a reflux condenser, in the top of which was placed a cork carrying a glass tube of 1-mm. bore. This "diffusion tube" was intended to prevent loss of vapor and consequent change of concentration. Its effectiveness was demonstrated by refluxing an acid solution for 3 hours, cooling, and titrating a measured sample with standard base. Comparison with similar samples which had not been refluxed showed no detectable change in acid concentration during boiling.

The flask with its contents was placed on a hot plate and heated to boiling, the diffusion tube was removed, and 25 ml. of barium chloride solution of such concentration as to supply a slight excess of barium ion were added from a dropping funnel through the condenser. The diffusion tube was replaced and the precipitate was digested by boiling gently on the hot plate. The mixture was then cooled and filtered, the paper burned off, and the precipitate weighed and treated as described above to determine the amount of coprecipitated chromate. VARIATION OF ACID CONCENTRATION. Twenty-five-milliliter

VARIATION OF ACID CONCENTRATION. Twenty-five-milliliter portions of equimolar solutions of sodium sulfate and sodium chromate were mixed, and the desired amount of hydrochloric acid was added from a buret, together with enough water to make the volume of acid plus water 75 ml. The total volume of the solution, after addition of 25 ml. of precipitant, was thus 150 ml. The precipitant was added dropwise through a fine capillary tube, so that its addition took from 15 to 19 minutes. With this slow rate of addition boiling, with its resultant stirring effect, was continuous. The mixture was digested for 3 hours, after which the hot plate was turned off. The flask was allowed to cool for 45 minutes, then removed from the hot plate, and cooled rapidly in ice water to 20° C. The precipitate was filtered off and treated as described above.

All factors were thus kept constant except the acid concentration, which could be varied at will. Tests showed that even in the most concentrated acid solutions used no oxidation of hydrochloric acid took place.

chloric acid took place. VARIATION OF RATE OF ADDITION OF PRECIPITANT. Equal volumes (25 ml.) of equimolar solutions of sodium sulfate and sodium chromate were again used, together with 15 ml. of 2.068 N acid and 60 ml. of water. When the solution was boiling steadily, 25 ml. of precipitant were added through the condenser as before, the time of addition being noted. When addition was slow, as in the experiments in which the acid concentration was varied, gentle boiling produced adequate stirring. When the cool precipitant was added rapidly, however, boiling stopped for a while. Two series of runs were made: one without auxiliary stirring, and one using a long stirring rod operated through the condenser, turned by a low-speed motor. The other factors, such as time of digestion, were kept constant as before.

VARIATION OF CHROMATE CONCENTRATION. The quantity of sodium sulfate was held constant as before, but the ratio of sodium chromate to sodium sulfate was varied over the range from 1 to 10 to 10 to 1 while other conditions were held constant. Since the amount of acid necessary to convert chromate into dichromate (assuming completeness of reaction) increased as the concentration of sodium chromate was increased, "constant acid concentration" was defined in two different ways: constant total acid, and constant excess acid. No determinations were made at constant pH.

The first set of determinations was carried on with a constant amount of acid regardless of the amount of chromate present: 25 ml. of 2.068 N acid were more than sufficient, according to the stoichiometric equation, to convert all the chromate into dichromate.

In the second set of experiments, 25 ml. of 2.068 N acid were added in addition to the amount calculated for the conversion of chromate into dichromate. Other conditions were the same as when the acid concentration was varied.

VARIATION OF TIME OF DIGESTION. Equal volumes (25 ml.) of equimolar solutions of sodium sulfate and sodium chromate were mixed, 15 ml. of 2.068 N acid and 60 ml. of water were added, and the precipitant was added slowly to the hot solution as before. The period of digestion was considered to begin as soon as the last drop of precipitant was added. At the end of the time of digestion, the mixture was cooled in ice water as rapidly as possible to 20° C., and the precipitate was filtered off and analyzed.

Results and Discussion

The results are plotted in Figures 1 to 4, in each of which the ordinates represent the number of milligrams of chromate, calculated as barium chromate, coprecipitated with about 0.5 gram of barium sulfate (0.502 gram in Figure 1, 0.546 gram in Figures 2, 3, and 4). Each point on Figures 1 and 4 represents the average of two or more determinations.

When the acid concentration is varied (Figure 1) the amount of chromate coprecipitated decreases regularly with increasing acid concentration. Coprecipitation drops off nearly to zero at high acid concentrations, but from the analytical point of view this is no advantage, since barium sulfate becomes appreciably soluble when the acid concentration exceeds 0.5 N. In very dilute acid, the results are inconsistent.

When rate of addition of precipitant is varied (Figure 2), the results are less regular, but the general trend is definite: the more rapidly the precipitant is added, the greater is the amount of chromate coprecipitated. Stirring reduces the amount only a little.

When the chromate-sulfate ratio is varied (Figure 3), the results are what would be expected: the greater the ratio, the more chromate is coprecipitated; and the more acid there is present (lower curve), the less chromate is coprecipitated.

From Figure 4, showing variation in time of digestion, it is clear that in order that coprecipitation may not be too great, the mixture must be digested for an hour or more. Times longer than 3 hours have little additional effect. The most



FIGURE 4. VARIATION OF COPRECIPITATION WITH TIME OF DIGESTION

TABLEI	RESILTS	WITH	VARYING	TIMES	OF	DIGESTION
INDLD I.	TECHOUTIN	PP T T T T	1 TITET TIAC	TTUTT	Or	TAUPOLION

Time	TP-4-1				
Digea-	Weight	BaCrO	BaSO4	NB2SO4	TALL, LUDON
tion	of Ppt.	Found	Found	Found	Error
Hours	Gram	Gram	Gram	Gram	Gram
0	0.5734	0.0275	0.5459	0.3323	-0.0004
0	0.5678	0.0245	0.5433	0.3307	-0.0020
1/8	0,5666	0.0237	0.5429	0.3304	-0.0023
1/8	0.5693	0.0233	0.5460	0.3324	-0.0003
1/1	0.5672	0.0222	0.5450	0.3318	-0.0009
1/3	0.5657	0.0224	0.5433	0.3307	-0.0020
1/2	0.5592	0.0185	0.5407	0.3291	-0.0036
1/2	0,5600	0.0200	0.5400	0.3287	-0.0040
3	0.5640	0.0179	0.5461	0.3324	-0.0003
3	0.5640	0.0171	0.5469	0.3328	+0.0001
10	0.5637	0.0168	0.5469	0.3328	+0.0001
10	0.5628	0.0159	0.5469	0.3328	+0.0001
24	0.5607	0.0152	0.5455	0.3321	-0.0006
24	0.5615	0.0153	0.5462	0.3325	-0.0002
antistics.	to the bol	vi wala bahb	a sont unatio	(mentpend) is	an heating

likely explanation for this is that most, if not all, of the coprecipitation remaining after 3 hours is due to mixed crystal formation. However, without additional evidence, such as x-ray examination of the crystals themselves, this interpretation cannot be considered as proved. The excess above the minimum is probably due to one or more of the other causes of coprecipitation.

The data from which Figure 4 is plotted are shown in columns 1 and 3 of Table I. (Similar tables for the other graphs are unnecessary.)

Assuming that all the chromate in the precipitate is in the form of barium chromate, the weight of barium sulfate is found by subtracting the weight of barium chromate from the weight of the precipitate. In column 3 is given the amount of chromate found from the titration, converted to the equivalent amount of barium chromate. This is subtracted from the total weight of the precipitate, column 2, to obtain the weight of barium sulfate, given in column 4. This in turn is multiplied by the gravi-metric factor, 0.6086, to convert to sodium sulfate, given in column 5. The difference between this and 0.3327, the number of grams of sodium sulfate taken each time, is called "error", listed in column 6.

Since the errors are small when the precipitate is digested for 3 hours or more, it is apparent that the assumptions made are valid. When the precipitate is not digested long enough, the errors are larger and negative in sign. This would be accounted for if the chromate, calculated as barium chromate, were actually coprecipitated in part as sodium chromate, sodium dichromate, or chromic acid.

Similar analysis of the data from which the other graphs were plotted indicated that when the precipitate is formed under the best analytical conditions, with slow addition of the precipitant and sufficiently long digestion, chromate is coprecipitated as barium chromate. Appreciable negative errors at high acid concentrations are in accord with the well-known fact that barium sulfate is somewhat soluble in strongly acid solutions.

Since the investigations of Nichols and Smith (5) and of Schneider and Rieman (6) were made under conditions different from the authors', no direct comparison is possible between the amount of chromate coprecipitated and the amounts of other anions as found by these workers. Their investigations were made in neutral solutions, for example, whereas this investigation was of necessity in acid solution, since chromate would precipitate virtually completely in the presence of excess barium ion in neutral solution. Other factors making a direct comparison impossible include differences in concentration and in rate and temperature of precipitation.

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Moderately Large Extractor-Percolator Assembly

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ANY large-scale Soxhlet-type extractors have been reported in the literature, yet a simple modification of the original continuous Soxhlet extractor has proved to be the most useful in the author's laboratory when a moderately large extraction is to be made. This modified extractor can also be used as a percolator of the automatic type, the choice of function depending only upon the method used in packing the extraction chamber.

A diagram of the apparatus is shown. The upper rim of a standard 2-gallon glass percolator is ground flat with 280-mesh Carborundum powder, so that a desiccator lid fits it snugly. If both the percolator rim and the desiccator lid are given a final grinding with 800- or 1000-mesh Carborundum powder, no lubrication of the joint will be required even with petroleum ether or diethyl ether as extracting solvent. This final grinding, how-ever, is time-consuming and, for most purposes, unnecessary. A piece of glass tubing, 15 mm. in diameter, is irregularly flanged at one end, and bent as indicated in the diagram so as to avoid back-drip directly into the boiler. This tube, or "chimney", carries the solvent vapors from the boiler to the condenser. A cotton plug is packed around this chimney where it contacts the neck of the percolator; for percolation, this plug is all that is required. A diagram of the apparatus is shown. The upper rim of a the percolator; for percolation, this plug is all that is required. If true extraction is desired, however, a 2.5-cm. (1-inch) layer of clean sea sand or other inert, finely divided material is placed on top of this cotton plug in order to retard the rate of downflow of solution. solution. Finally, on the neck of the percolator is placed a rubber stopper of the appropriate size to fit the boiler, and an efficient

condenser is attached to the upper opening of the desiccator lid by means of another rubber stopper.

For an extraction, the packing should not extend above a level which is 5 cm. (2 inches) below the top of the chimney tube. Ordinarily, channeling around this tube does not occur if the material to be extracted is 40-mesh or finer, so that the packing operation requires extract

so that the packing operation requires no great care. The rate of boiling of the solvent is so regulated that a layer of liquid about 1.25 cm. (0.5 inch) deep remains on top of the material being ex-tracted.

For a percolation procedure, the packing plug consists of cotton only, and the rate of boiling is immaterial, so long as the rate of percolation is not exceeded.

Occasionally, the drip from the condenser tends to dig a hole in the top layers of the marc even in an extraction.

This may be overcome by placing a small watch glass, convex side down, or a small piece of filter paper on the marc. After an initial warming-up of 5 to 10 minutes, the solvent that condenses in the chimney is remarkably small, because of the insulating effect of the marc packed around it.

Quantitative Determination of Benzene

In the Presence of Cyclohexane

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RECENT paper (1) by Corson and Brady reported A the development of a method for the determination of small amounts of benzene in cyclohexane by measuring the heat of reaction of benzene with a nitrating acid. The . paper brought out two useful points: the composition of the nitrating acid producing the best results, and the variation in reaction heat due to changes in the initial or starting temperature of the reaction.

By making a number of changes, both in the method and in the design of the reaction apparatus, it has been possible to develop a more rapid and practical procedure.

Apparatus and Reagents

When using the method described by Corson and Brady (1), which required removal of the stirring device and insertion of a thermometer whenever a temperature reading was necessary, some difficulty was encountered in manipulation of the apparatus. This was especially noticeable in experimental work when it was necessary to take temperature



FIGURE 1. EQUIPMENT FOR REACTION-HEAT TEST

readings a minute or two apart. In addition, an error was introduced when the room temperature changed between any two readings, because both the stirrer and the thermometer, when removed, changed to room temperature and were then replaced in the vacuum flask. Then, too, each time one or the other was removed some of the solvent was lost.

It was discovered that the stirrer paddle, which consisted of a 7-mm. glass rod with 19 mm. of one end flattened to a width of 13 mm. and turning at 3000 r. p. m., was not a very efficient stirring device for a two-

phase mixture, such as cyclohexane and nitrating acid. This poor mixing tended to lengthen the time of complete reaction between the benzene and the nitrating acid. Therefore, with a 10- to 20-minute period in which to meas-ure the temperature rise, any change in the room temperature and subsequent change in the rate of radiation of heat from the vacuum flask introduced a considerable error.

To overcome these difficulties, it was necessary to construct the apparatus shown in Figures 1 and 2, and to adjust the amount of nitrating acid used, to en-sure thorough mixing. The sure thorough mixing. results which follow point out the distinct advantages of this redesigned reaction heat apparatus.

REAGENTS. Nitrating Acid. Mix 2 volumes of 69 to 70 per cent nitric acid (density 1.41) with 1 volume of 95.5 per cent sulfuric acid (density 1.82).

Cyclohexane, density 1.82). 20° C. 0.7781, freezing point 6.0° C.

Benzene, density at 20° C. 0.8790, freezing point 5.5° C.

General Procedure

The procedure found most satisfactory for routine work and used, with slight modifications, in the experiments described in this paper, is as follows:

Weigh 50 grams of sample into a 120-ml. (4-ounce) tared bottle (small neck, plastic top) and place this and the bottle of nitrating acid in a constant-tempera-ture bath at 68° F. Pipet 50 ml. of nitrating acid in the vacuum flask and place the flask on the



FIGURE 2. ASSEMBLY OF REACTION-HEAT APPARATUS

Motor stirrer, 1600 r. p. m. Thermometer, Taylor 4No. 21,520, length 18 inches, range 45° to 100° F. Vacuum flask, 2 × 10 inch, silvered Glass bearing Glass tir shaft Level of mixture while stirring Level of acid while stirring Class propeller, 1 × 0.25 inch, approximately 40° pitch Felt-lined metal container

C.

- D.
- E.F.G.H.
- T.



FIGURE 3. REACTION HEAT DERIVED FROM KNOWN MIXTURES OF BENZENE AND CYCLOHEXANE

AT.	Difference	between	initial	temperature	and	temperature	after	3	minutes	of	stirring
				reaction	mix	ure					
			Nitrat	ing acid, same	8 88 3	No. 2. Table I	I				

TABLE I. H	REACTION-HEAT	CEST DATA	(FIGURE 3)
Weight Percentage of Benzene	Initial Temperature	ΔT	Room Temperature
	° F.	° F.	° F.
0.0 0.5 1.5	69.90 71.01 71.25	-0.60 2.20 7.80	74 77 76
2.0 2.5	70.32 70.72 70.75	10.80 13.50	76 76 76
4.0 5.0	71.22 71.10	22.20 27.60	76 76

stirring device as shown in Figure 2. After 3 minutes of standing, start the motor, and after approximately 1 minute record the "initial" temperature which will be about 70° F. Stop the motor. Pour the sample from the 4ounce bottle into the vacuum flask and start the motor. Take readings after 1, 2, 3, and 5 minutes of stirring. The difference between the temperature at 3 minutes and the initial temperature is a measure of the benzene content of the sample which is determined from Figure 3.

Discussion

EFFECT OF STIRRING PERIOD. The nitration is complete after 2 minutes of stirring, as shown in Figure 4. Any slope to the curve after the 2-minute period is a result of radiation from the vacuum flask, since the initial temperature of 70° F. is below the room temperature, which is 74° to 76° F.

EFFECT OF IMPROPER MIXING. The most important point in this discussion is the efficiency in the mixing of the reacting substances. It was found that any change in the design of the apparatus, the quantity of reacting substances, or the speed of stirring, which tended to lessen the mixing effect, greatly increased the reaction time and lessened the precision of the results. On the other hand, any change which increased the mixing effect beyond that of the apparatus described in this paper, made almost no change in the results, except to decrease slightly the time of complete reaction. In fact, results were very satisfactory when 100 ml. of nitrating acid and 50 grams of sample were used in a larger vacuum flask (6.25 cm., 2.5 inches in inside diameter) than the one described in this paper.

EFFECT OF STRENGTH OF NITRATING ACID. The effect of acid concentration was tested with acids of the composition shown in Table II. Figure 5 shows that No. 2 acid mixture is very satisfactory. It also has the advantage of being the one most easily prepared from ordinary laboratory c. P. acids and has been chosen therefore for use in the general procedure. A slight variation in the acid strength will not cause any appreciable error in the results. Figure 6 illustrates the variation in ΔT with the time of reaction for a 2 per cent benzene in cyclohexane mixture when nitrating acids of different strengths are used. A similar variation was found to hold true in 0.65, 3.0, and 4.0 per cent benzene-cyclohexane mixtures.

EFFECT OF CERTAIN IMPURITIES IN THE SAMPLE. It was found necessary to determine benzene in cyclohexane which contained a small amount of acetone and methyl alcohol. The reaction between these impurities and the nitrating acid caused a considerable rise in temperature. This difficulty was overcome by extracting the sample with water, and drying with calcium chloride. Any appreciable amount of water in the sample would no doubt cause a rise in temperature. However, a mixture of cyclohexane and benzene contains only 0.01 per cent of moisture when saturated at room temperature.



FIGURE 4. VARIATION IN ΔT WITH TIME OF REACTION FOR VARIOUS MIXTURES OF BENZENE IN CYCLOHEXANE Initial temperature, approximately 70° F. Nitrating acid, same as No. 2, Table II Stirring motor was stopped after first 10-minute period





 ΔT . Difference between initial temperature and temperature after 3 minutes of stirring reaction mixture

Results

The accuracy of the results obtained by the described method is indicated in Table III. These results were obtained on knowns made from mixtures of cyclohexane from

TABLE	II. Compo (Fig	SITION OF AND	VITRATING A 6)	CIDS
Acid No.	HNO3	HNO2	H2SO4	H2O
	%	%	%	%
1	42.94	0.16	38.35	$ \begin{array}{r} 18.55 \\ 20.61 \\ 22.13 \end{array} $
2	41.32	0.01	38.06	
3	40.58	0.01	37.28	
4	39.77	0.01	36.54	23.68



Initial Tem- perature	Benzene Present	Benzene Found	Difference
° F.	State of the state	-Weight percentage	
$\begin{array}{r} 7.82 \\ 7.75 \\ 10.63 \\ 10.87 \\ 10.48 \\ 10.40 \\ 10.82 \end{array}$	$ \begin{array}{r} 1.50\\ 2.00\\ 2.00\\ 2.00\\ 2.00\\ 2.00\\ 2.00\\ 2.00 \end{array} $	$1.50 \\ 1.47 \\ 2.00 \\ 2.04 \\ 1.97 \\ 1.95 \\ 2.02$	$0.00 \\ -0.03 \\ 0.00 \\ +0.04 \\ -0.03 \\ -0.05 \\ +0.02$
$ \begin{array}{c} 10.98\\ 10.79\\ 16.30\\ 16.35\\ 21.78\\ 22.08 \end{array} $	2.00 2.00 3.00 3.00 4.00 4.00	2.05 2.02 3.00 3.00 3.95 4.02	$ \begin{array}{r} +0.05 \\ +0.02 \\ 0.00 \\ 0.00 \\ -0.05 \\ +0.02 \end{array} $



Figure 6. Variation in ΔT with Time of Reaction for Four Strengths of Nitrating Acid

various sources, and benzene. Different batches of nitrating acid were used in the course of the experimentation. In each case the acids were made up to approximately the same strength in accordance with the method outlined under reagents.

Summary

The method described in this paper was found to be very workable and rapid, giving a high degree of precision and accuracy. A similar method has been developed to determine benzene in ethylene dichloride and in propylene dichloride, following the same general procedure and using the same strength of acid. However, it was necessary to draw a separate curve of ΔT against per cent benzene for each solvent, as the heat of the nitration reaction in the presence of different types of solvents was not the same.

Acknowledgment

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Determination of Surface Oxidation of Bituminous Coal

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A number of methods for determining the extent of surface oxidation of bituminous coals were examined qualitatively, and two, carboxyl group determination and thermal decomposition of surface complex, were examined in detail. The carboxyl group determination, though rather insensitive, can be used to determine the extent of surface oxidation, but examination of the gaseous products obtained by thermal decomposition of oxidized coals was a more sensitive procedure, particularly in the case of high-rank coals.

T HAS long been recognized that the oxidation of coal, such as may take place during storage, has a very marked effect on its properties during subsequent carbonization.

Jamieson and Skilling (9) used actual carbonization of stored coals to study these effects. Schmidt, Elder, and Davis (19)made carbonization tests on mildly oxidized Pittsburgh coal, measuring the relation between the yields and characteristics of the carbonization products, and the oxygen fixed on the coal in the oxidation process. The main effects found were the increased yield and hardness of the coke, the decreased yield of tar, and the

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increased amount of carbon dioxide in the gas as the oxidation proceeded. They did not carry the oxidation so far as to destroy completely the coking properties. Coking tests on oxidized coals have also been made by Reilly and co-workers (1, 4, 5), Michaelis (13), Kucherenko (11), Purdon (16), and Rees (17).

That weathered coals have properties similar to humic acids was suggested by Stadnikov, Suiskov, and Ushakova (20) and later by Voitova (26). Syskov (22) and Syskov and Ushakova (23) used the absorbing power of oxidized coal for barium hydroxide for evaluation of the extent of the oxidation. Similar measurements with iodine, oxalic acid, and methylene blue gave negative results. Another group of investigators, Karavaev, Rapoport, and Kholler (10), compared oxidized coal with brown coal and found these common properties: presence of humic acids, low carbon and high oxygen content, low heat value, excessive hygroscopicity, high content of volatile substances, high content of carbon dioxide in the primary gas, and high reactivity toward nitric acid. In characterizing the "age" of coals by ferric chloride and methylene blue adsorption, Pentegov and Nyankovskii (14) found that the coals had to be free from oxidation for a successful application of the test. This loss of reducing power of coal for ferric chloride was investigated as a measure of surface oxidation of coal by Vologdin and Kamendrovskaya (23) and by Grigor'ev (7). Ferric oxide was also used (27). Surface oxidation also brings about the formation of water-soluble material which will reduce potassium permanganate, as reported by Peters and Cremer (15), and also by Bunte, Brueckner, and Bender (3). Yohe (30) has shown that virgin coal surfaces, after exposure to air, exert a definite oxidizing effect on titanous chloride.

An oxidized coal surface shows a reduced reaction rate as the process proceeds. Bunte and Brueckner (2) measured the decrease in air pressure in a closed system and analyzed the remaining gas. Stansfield, Lang, and Gilbart (21) measured the amount of oxygen absorbed between the 24th and 96th hours of exposure to oxygen while the sample was being ground in a ball mill. Studies of rates of

mill. Studies of rates of oxygen absorption have been made by Winmill (29) and by Graham (6, 24). Schmidt and Elder (18) studied the effects of rank, extent of oxidation, temperature, and oxygen partial pressure on the rate. The rate of oxidation by chromic acid has been applied to commercially roasted samples by Howard and Schulz (3), who found a decrease in this rate as the roasting proceeded.

Lefebvre and Faivre(12) prepared oxidized coal samples so that the amount of oxygen fixed could be calculated, then they heated these to 350° C. and found that most of the fixed oxygen was evolved as carbon monoxide, carbon dioxide, and water. Karavaev et al. (10) and Schmidt, Elder, and Davis (19) reported an increase in the carbon dioxide in the gas during carbonization; the latter workers also reported a lowering of the total gas yield, as did Bunte and Brueckner (2).



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FIGURE 2. RATE OF OXIDATION OF POCAHONTAS COAL

None of these methods was developed to the stage of acceptable laboratory tests for determination of the extent of oxidation of coal. With the object of development of a quantitative method for determination of surface oxidation of coal, preliminary examination was made of a number of the properties of oxidized coal surfaces, using for this purpose a sample of Illinois No. 6 coal which had been oxidized by exposure to air in a drying oven at 105° C. for several weeks. Comparisons for both the oxidized coal and an unoxidized sample were made of: (1) sorption of electrolytes, (2) pH of aqueous suspensions, (3) sorption of basic organic compounds, (4) carboxyl group determination, (5) oxidationreduction potentials, (6) rates of oxidation, (7) rates of drying, and (8) nature of the thermal decomposition products of the surface complex. Even with this highly oxidized sample of coal, only the carboxyl group determination and nature of the thermal decomposition products of the surface complex gave evidence of being sufficiently sensitive to be of value. Both methods were, therefore, studied further and the results obtained are described below. As has also been reported by other workers, the authors noted the great difference in ease of wetting by water of the fresh and oxidized coal surfaces, the latter being much more readily wet, and it is possible that some sensitive method based on this phenomenon could be developed. Small but significant differences in the rate of loss of water from fresh and oxidized coal surfaces in an inert gas stream were observed.

Preparation of Samples of Oxidized Coals

Oxidized samples of three typical bituminous coals—Illinois No. 6, Pittsburgh, and Pocahontas No. 3—were prepared in the apparatus shown in Figure 1. A sample of -200-mesh coal, previously dried in vacuum at 75 °C. to 110 °C., depending upon the temperature of the run, weighing 50 to 60 grams, was placed in the vertical tube, A, which had a fritted-glass disk sealed in near the bottom to support the coal, and was immersed in a bath held at the desired temperature. Oxygen was circulated up through the coal sample by the mercury piston pump, F, and returned to the pump through absorption tubes B and C, carbon monoxide combustion tube D, and absorption tube E. Additional oxygen as required was supplied from buret K. Tube B was filled with indicating Drierite, tubes C and E with Ascarite and Drierite. Tube D was filled with powdered iodine pentoxide mixed with ground glass to prevent caking and was kept at 125 °C. by the electric heater. Through the manostat arrangement oxygen was supplied to the system as required. The pressure drop resulting from consumption of oxygen caused the mercury in the manometer, G, to actuate a relay, H, controlling the motor driving the screw elevator, I, which determined the height of the leveling bulb, J, causing oxygen to flow into the circulating system until the pressure was restored and the contacts on G opened again. A 100-ml. water-jacketed buret was employed in all runs except on Illinois coal, where at 125°C. one of 1000-ml. capacity was required. To fill the buret, tank oxygen was brought in through the Ascarite tube, L, through stopcocks V_2 and V_3 . For this purpose the holder of the leveling bulb, J, could be disengaged from the screw mechanism to lower it and to follow the level in the buret as it filled. V_1 permitted balancing the two sides of the manometer. All runs were at approximately atmospheric pressure.

In this apparatus the total mass of oxygen consumed and the amounts of water, carbon dioxide, and carbon monoxide formed could all be measured. Hence, the amount of oxygen fixed by the coal was readily calculated.

Data on the reaction of the three coals at 75°, 100°, and 125° C. are illustrated by the curves of Figures 2, 3, and 4. The nearly linear log-log relation between oxygen consumed and time has been pointed out by other workers (16) in this field. Satisfactory agreement between duplicate runs (open and solid circles) was obtained, except in the case of the Illinois coal at 125° C., where there was difficulty with temperature control, owing to exothermic character of reaction.

The equations for straight lines fitted to the data by least squares were: $\log M = b_1 + b_2 \log t$, where M is in millimoles of oxygen consumed per 100 grams of coal and t is in hours. The values of the constants are given in Table I.

The values of the intercepts, b_1 , show very definitely that the reactivities of the coals increase with decrease in rank. The form of the curves and the nearly constant values of the slopes for the various coals indicate hindered reactions and a relatively constant hindrance, irrespective of the reactivity of the coal and the temperature.

Data giving the distribution of the oxygen between the gaseous products and the coal surface are shown in Table II. Although total oxygen consumed varied more than tenfold with different temperatures and reaction times, the per cent distribution among the different products is surprisingly constant.

TABLE I. CON	ISTANTS	IN EQU	ATIONS FO	OR REA	CTION RA	TES
	75°	C.	100°	C.	125°	C.
	<i>b</i> 1	b2	61	b2	bı	ba
Pocahontas No. 3	-0.532	0.657	+0.069	0.638	+0.526	0.714
Pittsburgh	-0.613 -0.134 -0.095	$0.671 \\ 0.723 \\ 0.713$	-0.021 +0.398 +0.485	$0.683 \\ 0.750 \\ 0.672$	+0.550 +0.955 +0.090	0.711 0.761 0.695
Illinois No. 6	+0.333 + 0.233	0.615 0.655	+0.409 +0.893 +0.910	$\begin{array}{c} 0.731 \\ 0.592 \\ 0.651 \end{array}$	+1.815 +1.583	0.377

Determination of Carboxyl Groups

This procedure for determining the acidic groups on the surface of the oxidized coal is essentially the same as that



FIGURE 3. RATE OF OXIDATION OF PITTSBURGH COAL

described by Ubaldini and Siniramed (25) for determining the equivalent weights of naturally occurring "humic acids". In the Coal Research Laboratory this method has been used in obtaining the equivalent weights of "humic acids" prepared by the oxidation of bituminous coals. The procedure is based on the decomposition of calcium acetate by the acid groups and the determination of the resulting acetic acid by the liberation of carbon dioxide from calcium carbonate. The equations for the reactions are:

 $2\text{RCOOH} + \text{Ca}(\text{OAc})_2 \longrightarrow (\text{RCOO})_2\text{Ca} + 2\text{HOAc}$ $2\text{HOAc} + \text{CaCO}_3 \longrightarrow \text{Ca}(\text{OAc})_2 + \text{H}_2\text{O} + \text{CO}_2$

 $2\text{RCOOH} + \text{CaCO}_3 \longrightarrow (\text{RCOO})_2\text{Ca} + \text{H}_2\text{O} + \text{CO}_2$



FIGURE 4. RATE OF OXIDATION OF ILLINOIS COAL

Whether the reaction proceeds in one manner or the other, one mole of carbon dioxide is liberated for each two carboxyl groups. The reaction is carried to completion by refluxing the mixture and sweeping out the carbon dioxide formed with nitrogen. The apparatus used is shown in Figure 5.

Before this method was applied to oxidized coals its reliability was tested on a number of authentic samples of organic acids. Succinic, benzoic, o-phthalic, o-, m-, and phydroxybenzoic, and gallic acids were employed for this purpose. The simple carboxylic acids gave results for equivalent weight which were 1 to 2 per cent high-i. e., less than the theoretical amounts of carbon dioxide were evolved during the reaction. With the hydroxy acids the results were all low by about the same amount and carbon dioxide continued to be evolved slowly if the reaction time was increased. With the hydroxybenzoic acids the equivalent weights calculated on reaction of the carboxyl alone were too low by about 10 per cent when a reaction time of 4 hours was used. With gallic acid the values were almost exactly half that calculated for reaction of the carboxyl. That this excess evolution of carbon dioxide was due to reaction of the phenolic hydroxyls was shown by the fact that the methoxy compounds of these acids gave results agreeing with the theoretical values within 1 per cent. Since in a measurement of surface oxidation of coal it is immaterial what type of acidic group reacts, the procedure appeared suitable for the purpose desired.

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The finely ground sample was placed in flask D, the weight being adjusted to evolve a convenient amount of carbon dioxide: 1 gram of calcium carbonate and 100 ml. of 3 per cent calcium acetate were then added, the flask was attached to the reflux condenser, C, and the mixture was boiled with a microburner. Tank nitrogen purified by passage over hot reduced copper was used as a sweeping gas and passed through the sulfuric acid bubble counter, A, and Ascarite tube, B, down through the long tube in the center of the condenser and bubbled through the boiling mixture. The evolved carbon dioxide was swept out through the condenser, sulfuric acid bubble counter, E, and drying tube, F, filled with Anhydrone, into the weighing tube, G, containing Ascarite and Anhydrone. The nitrogen passed out through the guard tube, II, filled with soda lime, the trap, I, and the bubble counter, J, to the atmosphere. Under these conditions a manipulative blank of 1 to 2 mg. of carbon dioxide was supoblained. This blank could be reduced to 0.2 mg. by a short preliminary refluxing of the reagents before addition of the sample. With slightly oxidized coals difficulty in wetting was observed; part of the sample floated on the surface and was carried up the side of the flask out of contact with the bulk of the reagents. In such cases addition of 10 ml. of a 1 per cent solution of a wetting agent, such as Aerosol or Nekal BX, was found to improve the reproducibility of the procedure.

With the lightly oxidized samples of coal the amounts of carbon dioxide evolved by this procedure were only a few milligrams per gram of coal, so that it was necessary to use large samples, 5 to 10 grams, and to weigh the absorption tube on a semimicrobalance. Weights were recorded to 0.1 mg.

mg. The results of determinations of the acid groups on the prepared samples of oxidized coals are shown in Table III and Figure 6. The total acidity has been calculated in terms of carboxyl, since it seems probable that these groups are chiefly responsible for the reaction observed. In calculating carboxyl groups the amount of carbon dioxide evolved from the unoxidized coal was subtracted from the values for the different oxidized samples. The difference, multiplied by two, since each mole of calcium salt reacts with two carboxyl groups, yields the carboxyl groups formed in the oxidation. The amount of carbon dioxide evolved from the unoxidized Pocahontas coal corresponds to the presence of approximately 0.01 per cent of oxygen as carboxyl groups and the corresponding figures for Pittsburgh and Illinois are 0.10 and 0.13 per cent, respectively. In the case of the Pocahontas coal there was a somewhat smaller evolution of carbon dioxide from the sample which had been oxidized at 75° than from the original unoxidized samples. In Figure 6 carboxyl groups, in millimoles per 100 grams of coal, found

TABLE II	DISTR	BUTION OF O	XYGEN		IZED C	OALS
Temperature	Time	O: Used	H ₂ O	CO ₂	CO	Fixed
° C.	Hours	100 g.	%	%	%	%
		Pocahontas No	. 3 Coal			
7575100100125125	240 306 261 312 99 215	$ \begin{array}{r} 10.86\\ 11.40\\ 39.40\\ 40.90\\ 86.40\\ 143.0 \end{array} $	$\begin{array}{r} 30.85\\ 29.20\\ 31.60\\ 32.16\\ 29.85\\ 27.62 \end{array}$	$11.05 \\ 11.31 \\ 12.80 \\ 12.84 \\ 13.19 \\ 14.75$	$1.66 \\ 1.58 \\ 2.04 \\ 1.81 \\ 2.08 \\ 2.38$	56.43 57.90 53.50 53.13 54.85 55.25
		Pittsburgh	Coal			
75 75 100 100 125 125	223 319 240 52 43 212	$\begin{array}{r} 36.49 \\ 48.38 \\ 104.8 \\ 45.7 \\ 139.4 \\ 316.0 \end{array}$	$18.82 \\ 21.19 \\ 27.77 \\ 19.04 \\ 17.93 \\ 27.17 \\$	$14.44 \\9.06 \\12.50 \\10.06 \\15.06 \\18.77$	$1.70 \\ 1.59 \\ 2.10 \\ 1.53 \\ 2.01 \\ 2.47$	$\begin{array}{c} 65.03 \\ 68.15 \\ 57.63 \\ 69.35 \\ 65.00 \\ 51.62 \end{array}$
		Illinois No. 6	Coal			
75 75 100 100 125 125	246.5323.02606246148	$\begin{array}{r} 49.35\\ 68.27\\ 189.8\\ 106.9\\ 275.4\\ 327.4\end{array}$	18.2720.2133.1424.5034.7729.9	$13.31 \\ 12.15 \\ 18.07 \\ 13.84 \\ 16.22 \\ 19.16$	2.091.962.532.063.592.23	$\begin{array}{c} 66.32\\ 65.36\\ 46.26\\ 59.60\\ 45.38\\ 48.71 \end{array}$

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by this method, are plotted as a function of the amount of oxygen known to have been fixed in preparing the sample. It is evident that only a fraction of the total oxygen fixed reacts like a carboxyl group and that this fraction varies greatly with the coal, ranging from a few per cent for the Pocahontas up to 40 per cent for the Illinois. There is, however, for each coal a general linear relation between the oxygen found as carboxyls and the total fixed. The method is obviously less sensitive for high-rank coals. With a Pittsburgh seam coal, samples prepared containing 1.0 per cent by weight of "fixed" oxygen evolve approximately 1 mg. of carbon dioxide per gram of sample.

Thermal Decomposition of the Surface Complex

It is known that the gaseous products obtained from the thermal decomposition of partly oxidized coals contain larger proportions of the oxides of carbon than do those from virgin coals.

TABLE III. D	ETERMINATI	COALS	GROUPS	ON OXIDIZEI
Temperature of Oxidation ° C.	Time Hours	O2 Fixed —Mills	CO2 moles per 10	Carboxyl 0 grams-
	Pocah	ontas No. 3 Co	al	
75 75 100 100 125 125	0 240 306 261 312 99 215	6.13 6.60 21.1 21.8 47.4 79.0	$\begin{array}{c} 0.36 \\ 0.31 \\ 0.29 \\ 0.52 \\ 0.61 \\ 0.66 \\ 0.95 \end{array}$	0.32 0.50 0.60 1.18
	Pie	tsburgh Coal		
75 75 100 100 100 125 125 30	0 223 319 168 240 52 43 212 507	23.75 32.98 66.1 60.4 31.7 90.6 163.1	3.14 5.71 5.07 4.43 5.09 7.46 3.64	5.14 3.86 2.58 3.90 8.64 1.00
	Illin	nois No. 6 Coal		
75 75 100 100 125 125	$0\\246.5\\323.0\\260\\62\\46\\148$	32.73 44.83 87.8 63.7 125.0 159.6	4.28 11.02 12.56 8.95 14.98 15.32	13.58 16.56 9.34 21.40 22.08

In order to collect the gaseous products quantitatively, approximately 10 grams of the coal sample were placed in the bottom of a small molecular still, such as that shown in Figure 7. The still was evacuated through a small multiple-stage mercury diffusion pump which was in turn backed by a Toepler. The discharge tube of the Toepler delivered the evolved gases into a mercury-filled gas sampling tube. The collected gas was measured and analyzed in an Orsat apparatus and the volumes were calculated to standard conditions. It was found convenient to cover the coal sample with a 200-mesh nickel screen to prevent spurting when gas evolution became rapid. The condenser of the still was kept filled with a dry ice-ethylene chloride mixture to freeze out water and hydrocarbon vapors. Heat was applied to the still by means of an electrically heated aluminum block. Temperatures were controlled to $\pm 5^{\circ}$ C. The whole system was thoroughly evacuated at room temperature, 10^{-3} mm. of mercury, raised to 350° in 45 minutes, and maintained at that temperature for 3 hours with continuous evacuation.



The results are shown in Table IV and Figure 8. It is evident that this is a more sensitive procedure for determining surface oxidation of coal, since a much larger fraction of the oxygen appears as a measurable product, in this case oxides of carbon, than was the case in the carboxyl group determination. The particular experimental arrangements used did not permit the determination of water vapor. Modification of the analytical procedure to permit determination of the water evolved might increase the sensitivity considerably, since it seems probable that, as in the oxidation step itself, the larger fraction of the oxygen appearing as volatile products will be as water. Carbon monoxide appeared in all samples in small amounts.

Summary

A number of possible methods for determining the extent of surface oxidation of bituminous coals have been examined qualitatively. These were sorption of electrolytes; pH of aqueous suspensions; sorption of basic organic compounds; carboxyl group determination; oxidation-reduction potential; rate of oxidation; rate of drying; thermal decomposition of the surface complex. Of these, only two—carboxyl group determination and thermal decomposition of surface complex—showed sufficient promise to justify detailed



INDUSTRIAL AND ENGINEERING CHEMISTRY



SOA O POCAHONTAS COAL D PITTSBURGH COAL 43 A ILLINOIS COAL GRAMS Δ Š 22 MILLIMOLS N z EVOLVED 203

FIGURE 8. CARBON DIOXIDE FROM DECOMPOSITION OF COAL AS A FUNCTION OF DEGREE OF OXIDATION

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fixed oxygen was so evolved than in the above test, this is a more sensitive procedure for the measurement of the extent of surface oxidation, particularly in the case of high-rank coals.

More exact evaluation of the usefulness of these methods depends upon their application to naturally aged coal samples and correlation of the analytical results with carbonization tests.

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ABSTRACTED from a thesis by John A. Radspinner presented to the Graduate Faculty of the Carnegie Institute of Technology in partial fulfillment of the requirements for the D.Sc. degree, March, 1942.

TABLE IV. CARBON OXIDES EVOLVED IN VACUUM DECOMPOSI-TION OF OXIDIZED COALS

Total

varying periods and under such conditions that the extent of oxidation was definitely

Carboxyl group determinations showed that only a frac-

tion of the total oxygen fixed reacts like a carboxyl group, ranging from a few per cent for the Pocahontas coal up to

40 per cent for the Illinois. A general linear relation was found, however, between the oxygen as carboxyls and the total known to be present. Hence, this procedure, though

rather insensitive, can be used for the determination of the

Examination of the gaseous products obtained by thermal

decomposition of these oxidized coals in vacuum at 350° C.

also showed a linear relation between oxygen fixed and that

evolved as oxides of carbon, and since a larger fraction of the

°C.	Hours	Milli	imoles pe	r 100 gra	m8	Millimoles, 100 g. less blank
		Pocabont	as No. 3	Coal		
75 75 100 100 125 125	0 240 306 261 312 99 215	6.13 6.60 21.1 21.8 47.4 79.0	$\begin{array}{r} 4.90\\ 5.22\\ 5.56\\ 8.84\\ 11.61\\ 10.08\\ 22.33\end{array}$	2.393.003.295.375.669.2013.58	0.14 0.20 0.27 1.28	$\begin{array}{r} 0.677\\ 0.907\\ 2.99\\ 3.27\\ 6.87\\ 11.19\end{array}$
		Pittsb	urgh Co	al		
75 75 100 100 125 125	$\begin{array}{c} 0 \\ 223 \\ 319 \\ 168 \\ 240 \\ 43 \\ 212 \end{array}$	23.7332.9866.160.490.6163.1	$11.93 \\ 16.11 \\ 17.43 \\ 27.17 \\ 25.57 \\ 27.69 \\ 40.30$	$\begin{array}{r} 4.92\\ 8.71\\ 10.84\\ 15.24\\ 15.19\\ 17.14\\ 26.16\end{array}$	0.24 0.13 0.77 0.84 2.09	$\begin{array}{r} 3.79 \\ 5.92 \\ 10.32 \\ 10.27 \\ 12.22 \\ 21.24 \end{array}$
		Illinois	No. 6 C	onl		
75 75 100 100 125 125	$\begin{array}{r} 0 \\ 247 \\ 323 \\ 260 \\ 62 \\ 46 \\ 148 \end{array}$	32.73 44.83 87.8 63.7 125.0 159.6	$\begin{array}{r} 24.75\\ 41.20\\ 45.68\\ 61.00\\ 42.72\\ 65.70\\ 75.73\end{array}$	$\begin{array}{r} 13.72\\ 24.92\\ 20.78\\ 38.43\\ 24.96\\ 40.88\\ 47.90\end{array}$	$\begin{array}{c} 0.47\\ 0.89\\ 3.79\\ 1.90\\ 0.06\\ 4.96\\ 6.12 \end{array}$	$11.20 \\ 13.06 \\ 24.71 \\ 11.24 \\ 27.16 \\ 34.18$

570

known.

Temperature

extent of surface oxidation.

Determination of Halogen in Organic Compounds

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A method is described for the determination of chlorine, bromine, and iodine in organic compounds. The sample is decomposed by vaporizing it into a stream of combustible gas which is then burned at a jet. The products of combustion are collected in a suitable absorption medium, and the resulting alkali halide is determined by a standard method. This procedure has been employed with thirty-six different compounds, covering a wide range of physical properties from low-boiling liquids (gases) to high-melting solids, some of which contained more than one halogen. By the substitution of silver, lead, or copper for glass in certain parts of the apparatus, the method should be equally satisfactory for the analysis of organic fluoro- compounds. The suggested procedure is economical of time and equipment, and compares favorably with other methods in accuracy and precision.

THE literature of organic halogen determination has been surveyed in some detail recently (3), and need not be reviewed here. This paper presents a method of decomposing the sample and recovering the halogen in a form suitable for determination by any well-known standard method. The principal advantages offered over others in common use are the short time required for an analysis, the simplicity of the apparatus without sacrifice of accuracy and precision, and the ease with which such stable compounds as the chlorofluoromethanes are decomposed.

The nearest approach to the method described below is that of Cadenbach (1) for the determination of fluorine. Cadenbach vaporized or decomposed the sample in a stream of hydrogen in a silver tube, and burned the gas mixture at a jet, collecting the products through a silver funnel and tube in a standard solution of alkali contained in a gaswashing bottle.

A modification of the lamp method of determining sulfur in gasoline has been applied to the determination of small amounts of chlorine in gasoline (6). It is assumed that the chlorine emerges from the combustion process in the form of hydrochloric acid, and that it can be determined by absorption in a standard solution of alkali. This assumption may, perhaps, be valid when the chlorine content of the sample is very low, but if more than a trace of halogen is present, some of it is oxidized beyond the halide stage. The free halogen may be readily detected in the products of combustion. In order to ensure the quantitative recovery of the halogen as halide ion, the products of combustion must be collected in an alkaline solution containing a reducing agent which

will not interfere in the subsequent determination of the halogen.

The work of Hass and others (4) on the chlorination of methane required the determination of methyl chloride in a mixture with methane. They mixed the sample with an excess of air and passed it through a clay combustion tube at 1000° C., collected the products of combustion in wash bottles containing a solution of sodium carbonate and sodium arsenite, and titrated the chloride by the Mohr method. Their procedure was adapted from one described earlier by Martinek and Marti (5).



FIGURE 1. APPARATUS FOR SOLIDS AND HIGH-BOILING LIQUIDS

In the method of analysis proposed in this report, the sample is decomposed by burning it in a stream of halogenfree combustible gas at a small jet under a chimney through which the products of combustion are carried away in a stream of air drawn through a gas-washing bottle containing an absorption solution of sodium carbonate or hydroxide and sodium arsenite. After the combustion of the sample, the halide is determined in the absorption solution by a modified Volhard procedure.

Reagents and Solutions Required

The solution used in the gas-washing bottle to absorb the halogen was approximately 0.2 N with respect to sodium carbonate or hydroxide, and 0.1 N with respect to sodium arsenite. The

ate or hydroxide, and 0.1 W with respect to sodium arsenite. The sodium arsenite is readily obtained by dissolving the requisite amount of arsenic trioxide in a little sodium hydroxide. The final solution should be tested to be sure that it is free of halide. The inorganic halide ion in the absorption solution may be determined by any suitable method, but the Caldwell and Moyer modification (2) of the volumetric procedure of Volhard was become for its comparison in pairing a large number of data chosen for its convenience in making a large number of determinations. A 0.1 N solution of silver nitrate and a 0.05 N solution of potassium thiocyanate were prepared and standardized against pure sodium chloride and against constant-boiling hydrochloric acid. Other reagents needed are halogen-free concentrated nitric acid, nitrobenzene, and ferric sulfate.

Description of Apparatus

Two forms of apparatus are required, one for solid and highboiling (above 100° C.) liquid samples, and the other for lowboiling liquids and condensable gases.

Figure 1 shows the apparatus used for solids and high-boiling liquids. ABC is a U-tube made of 9-mm. glass tubing on the A side, and of 1-mm. capillary on the C side. It may be suspended by a wire loop from the stirrup hook of the balance, thus serving as the vessel for weighing the sample. Solid samples are introduced at A and shaken down to B. Liquids are best introduced at C by means of a medicine dropper drawn out to a fine capillary. If both legs of the U-tube are capillary, liquids boiling as low as 80° C. may be handled satisfactorily, but as a rule it is better to use this form of apparatus only with the higher-boiling substances. A large sample may be burned by increasing the size of the B portion of ABC.

D is an ordinary glass adapter commonly found in any laboratory, serving as a chimney in which the flame burns in a stream of air drawn through the absorber, E. If E is provided with a fritted-glass dispersion disk, a single absorber is sufficient. G is a stopcock to control the rate of flow of the air stream. F is a small crucible furnace used to melt and vaporize the sample. The heat of this furnace is controlled by means of a variable transformer. A thermometer, T, assists in regulating the temperature in the furnace. It is necessary that the C side of the U-tube be entirely within the furnace, in order to avoid condensation of the sample in the capillary. The whole apparatus, except the furnace, is mounted on one supporting ring stand, so that the assembly may be handled as a unit and lifted into or out of the furnace without interrupting combustion. The dimensions of the various parts are not very critical, and are determined largely by the materials at hand. It is suggested, however, that the absorber be of 200to 250-ml. capacity, and the dispersion disk of medium porosity.



FIGURE 2. APPARATUS FOR LOW-BOILING LIQUIDS

Figure 2 shows the apparatus used for low-boiling liquid samples. The weighed sample contained in the glass bulb, B, evaporates into A when the stem of the bulb is broken, and the vapor is swept out by a stream of combustible gas entering through the tube, C, and is burned at F under the chimney, D.

Some of the gas which burns at F is introduced through the side arm, L, in order to keep the flame burning when the mixture coming from A may be too rich to burn by itself. Screw clamps on the rubber tubing at J and K control the flow of gas. A slight file scratch is made on the stem of the sample bulb before it is introduced into A, and the stem is broken off by manipulation of tube C in the flexible rubber stopper, E. In the case of highly volatile samples, A must be cooled before the sample bulb is opened; and the less volatile samples must eventually be warmed gently to hasten evaporation. This may be accomplished by means of a suitable liquid bath surrounding tube A. The spark igniter, I, is not absolutely essential but it is very convenient and often saves a determination when the flame happens to go out when the sample bulb is opened. It consists of two pieces of Nichrome wire mounted through a piece of rubber stopper, M, and connected to an induction coil. The absorber and chimney are the same as in Figure 1.

The preparation of sample bulbs requires no great glass-blowing skill. A fine capillary, 0.5 to 1 mm. in diameter and 25 cm. in length, is drawn from Pyrex tubing in the usual manner, a thin bulb 6 or 7 mm. in diameter is blown on one end, and the stem is bent in the middle to an angle of 45°. After weighing the empty bulb, the open end of the capillary stem is put into the liquid to be sampled and the bulb is immersed in a cold bath. For some substances an ice-water bath is cold enough, but others will require a bath such as acetone and dry ice. A little liquid is drawn into the chilled bulb, but not enough to fill it. It is then withdrawn from the bath and warmed a little with the fingers, thus expelling more or less of the air. A second immersion in the cold bath will usually draw in a sufficient sample. In no case should the bulb be completely filled; it will burst on warming to room temperature unless there is some free space to allow for expansion of the liquid. When the proper amount of sample has been drawn into the bulb, the steam is scaled off at the bend while the bulb is still in the cold bath. The scaled off portion of the stem is passed through a flame to remove any liquid remaining in it, and the filled bulb and stem are weighed together after they have come to room temperature.

Details of Analytical Procedure

SOLID SAMPLES. Weigh the clean and dry U-tube (ABC, Figure 1) suspended from the stirrup hook of the balance by means of a wire loop. Introduce the appropriate amount of sample (usually 0.1 to 0.2 gram) through A, and shake it down to B. Weigh the tube and contents.

Assemble the apparatus as shown in Figure 1. Absorber E should contain approximately 50 ml. of the carbonate-arsenite solution, and cock G should have been previously adjusted to allow just enough air through the system to support the flame. Turn on the gas enough to give a flame 1 cm. high, ignite it at C, and at once put the chimney over the flame. Turn on the current in heater F and adjust it so that the temperature rises slowly toward the sublimation point or boiling point of the sample. The volatilization characteristics of various substances differ greatly, but experience soon teaches the operator the proper handling in each case. The character of the flame serves as a useful and convenient guide to the proper heat treatment of the sample. Some organic halogen compounds impart a fairly bright blue or green color to the nearly colorless flame of the city gas, while others make it brilliantly luminous with a white or yellow light, and if the vaporization rate is too great the flame usually becomes smoky and soot may be deposited in the chimney.

Soon after the sample has disappeared and the color of the flame indicates that it is all burned, turn off the gas, disassemble the apparatus, remove the chimney from the absorber, and rinse carefully into the absorption flask the inlet tube and dispersion disk and the inside of the cap. To the solution in the flask, add either from a buret or by means of a transfer pipet a slight excess of the standard 0.1 N silver nitrate solution. A sufficient excess of silver nitrate is indicated by the appearance of a yellow-brown precipitate of silver arsenite in the alkaline solution. Add 2 ml. of concentrated nitric acid, 0.5 gram of ferric sulfate (powdered solid), and 3 ml. of nitrobenzene for each 10 ml. of silver nitrate used. Stir the mixture vigorously until the precipitate has coagulated, and then titrate the excess silver with the standard 0.05 N thiocyanate solution. The author prefers to add both standard solutions from burets and to cross the end point several times in each direction.

HIGH-BOILING LIQUID SAMPLES. If the substance boils above 100° C., proceed as described above for solid substances, but introduce the sample at C by means of a capillary medicine dropper.

LOW-BOILING LIQUID SAMPLES. If the substance to be analyzed boils below 80° to 100° C., it probably cannot be weighed and burned in the apparatus shown in Figure 1 without losing some of the sample. It must, therefore, be sealed in a small glass bulb for weighing, and burned in the apparatus shown in Figure 2. The sample bulbs are made and filled as previously directed.

Make a small file scratch on the stem of the sealed bulb containing the weighed sample, 2 or 3 cm. from the bulb, and carefully insert the bulb into tube A (Figure 2). Replace tube C, taking care not to break the sample bulb or its stem. Open the screw clamp, J, until A is filled with the fuel gas or hydrogen. Then close J and open K, ignite the gas at F, and adjust K to give a flame 1 cm. high. The sample must then be cooled, if necessary, to bring it somewhat below its normal boiling point in order to prevent too rapid evaporation when the bulb is opened. This may be easily accomplished by immersing A in the same cooling bath that was used in sealing the sample bulb. If the boiling point of the sample is considerably above room temperature, no cooling will be necessary. Now assemble the absorber as described above, place the chimney over the flame, and break the stem of the sample bulb by manipulating C in the flexible rubber stopper, E. Open J a little and partially close K to maintain the flame at a height of 1 cm.

If the sample boils below room temperature, it will evaporate satisfactorily without further attention as A gradually warms up to room temperature. Less volatile substances will require the application of some heat to hasten the evaporation. This is best accomplished by means of a water bath around A, which is heated slowly toward, and eventually above, the boiling point of the sample. After the sample has all evaporated, close K and open J a little more, and allow the fuel gas to sweep through Afor a few minutes after the flame color indicates that the sample is all burned. Determine the halide in the absorption solution as described above for solid samples.

Discussion of Method and Results

The accuracy and precision of the procedures may be judged by the results listed in Table I. Some of these compounds were purified as indicated in the table, and in each case the halogen content was checked by the peroxide bomb method of decomposing the sample. The average results by the proposed method are in substantial agreement with those obtained by the older method, and the average deviation from the average value is not much over 0.1 per cent of the average value. This is the order of magnitude of the precision of ordinary analytical work. Further refinements in the technique would undoubtedly lead to a higher degree of precision. For the purpose of computing averages, one more figure is retained in the results than could ordinarily be justified.

- ALMANGER DESIG							
TABLE I. A	NALYSIS	OF	COMPOU	NDS OF	KNOW	IN HAI	LOGEN
			CONTERN	-			
Compound Analyzed	No. of Detns.		% Halog Theory	en Found	Devi Av.	ation Max.	Check Analysis
Methyl chloride b Dichloromono-	11	Cl	70.23	70.25	0.09	0.17	70.20
fluoromethane c	13	CL	68.90	68.87	0.07	0.13	68.89
n-Bromotoluened	14	Br	46.72	46.78	0.04	0.08	46.72
Chloral hydrate (12	CI	64 32	64.32	0.08	0.13	64.26
2-Chloro-2 3 3-tri-		100					
methylbutaner	16	CI	26 33	26.11	0.04	0.11	26.09
n-Bromoiodohan-	6	Br	28 25	28 19	0.04	0 08	28 20
zene ^g		I	44.86	44.76	0.07	0.12	44.76
^a Check analyses ^b Commercial pr ^c Commercial pr ^d Purified by fra	oduct, re oduct, re ctional cr	xide l distil distil ystal	homb met led; boild lled; boild lization;	chod. ed at -23 ed at 8.7° m. p., 26	.9° C., C., 73 .5° C. t	744 mr 8 mm. o 27.5°	n. C.
 Sublimed: m. 	p., 52° C	. to	53° C.				

/ Recrystallized from petroleum ether; m. p., 130° C. to 131° C. # Analyzed as received; m. p., 87° C. to 89° C.

One compound in Table I requires further comment. The *p*bromoiodobenzene should perhaps not have been included, since it was not so pure as the listed results would indicate. The values for bromine and iodine were calculated by assuming equivalent quantities of the two halogens and simply dividing the titration value by two. Actually, however, the combined silver halides were recovered and weighed in each case, and the true value of each halogen was calculated from the titration value and the weight of precipitate. This method of determining two halogens together is not very good, since small experimental

TABLE II. ANALYSIS OF VARIOUS ORGANIC HALOGEN COMPOUNDS

	No. of	_	-% Halo	gen	Average Devia-
Compound Analyzed	Detns.		Incory	rouna	tion
Dichlorodifiuoromethane.					
b30°	2	Cl	58.64	58.4	0.1
Ethyl chloride, b. 12°	2	CI	54.95	53.0	0.0
Ethyl bromide, b. 38°	9004 0	Br	73.33	73.1	0.1
Methyl iodide, b. 42.5°	3	I	89.41	89.4	0.2
Chloroform, b. 61°	3	CI	89.08	88.2	0.2
Carbon tetrachloride, b. 76-7°	2	Cl	92.19	91.9	0.2
n-Butyl chloride, b. 78°	7	CI	38.30	36.9	0.0
n-Amyl chloride, b. 108°	7	CI	33.26	33.0	0.1
Chloronierin, b. 112°	2	CI	64.70	63.7	0.0
Tetrachloroethylene, b. 121	3	CI	85.51	85.2	0.2
n-Amyl bromide, b. 128-9°	4	Br	32.89	51.9	0.2
Athylene chloronydrin, b. 129°	2	G	44.03	43.2	0.0
Chlorobenzene, D. 132	á	Ci	31.00	07.1	0.0
a Chloroothyl abloroformata	4	CI	27.10	21.1	0.0
b 61-2° at 21 mm	9	CI	10 60	.10 6	0.1
8-Chloroethyl sostate b 145°	3	či	28 03	30.0	0.0
Trimethylene bromide b 167°	3	Br	79 16	77 5	0.0
8 8'-Dichlorodiethyl ether		2.	13.10		0.0
h 178°	2	CL	49 58	19 6	0.0
Benzyl chloride, b. 179°	2	či	28.01	27.7	0.1
e-Bromophenol, b. 194-5°	3	Br	46.18	45.8	0.1
Chloral alcoholate, m. 56-7°	3	CL	54.98	54.7	0.0
Chloroacetophenone, m. 59°	2	Cl	22.93	23.1	0.0
Chlordácetić acid, m. 62-4°	2	Cl	37.52	37.3	0.0
p-Bromophenol, m. 63.5°	2	Br	46.18	46.3	0.0
p-Dibromobenzene, m. 87-8°	2	Br	.67.75	67.8	0.0
Iodoform, m. 119°, sublimes	2	I	96.69	97.0	0.1
Hexabromoethane, m. 148-9°,		ALLER			
aublimes	2	Br	95.24	95.2	0.0
Hexachlorobenzene, m. 227°,					
sublimes	3	Cl	74.70	73.9	0.0
Benzidine hydrochloride	2	CI	27.57	27.5	0.0
Phenylhydrazine hydrochloride,	2	CI	24.52	24.4	0.1
m. 240-1°					

errors are magnified in the final values, but it showed 31.4 per cent bromine and 39.6 per cent iodine, which is approximately the halogen content of a mixture containing 89.6 per cent bromoiodobenzene and 10.4 per cent dibromobenzene. The compound was left in the table, however, because the peroxide bomb method gave almost identical results, and because it shows that the method is satisfactory for recovering total halogen.

The proposed procedure was also applied to a wide variety of other organic halogen compounds (Table II). Most of these substances were taken from stock reagent bottles and come were obviously not pure. The agreement with theory is close enough, however, to indicate that these compounds can all be analyzed successfully by this method. The method should be applicable to any substance which can be vaporized without too much pyrolysis. Failure to obtain satisfactory analyses was experienced in the case of two solid compounds (3,5-dinitrobenzoyl chloride and 2,6-dibromoquinonechloroimide), both of which decomposed on melting and left a carbonaceous residue which apparently retained some of the halogen.

Hydrogen or some other combustible gas may be used to sweep out the vaporized sample, but the city gas supply is considerably more convenient to use if it shows a negligible blank.

Attempts were made to determine fluorine in several organic compounds, using the same apparatus as for the other halogens. The results were always low and were somewhat erratic. This was not surprising, however, because the glass of the collecting chimney and of the inlet tube of the absorption flask was severely etched. But neither the vessel where the sample was vaporized nor the absorption flask itself was etched, and in the light of Cadenbach's success with apparatus made of silver (1), there is no apparent reason why the fluoro- compounds could not be analyzed satisfactorily by the proposed method if the collecting chimney and the inlet tube of the absorber were made of a suitable material, such as copper, silver, or lead. This possibility is under investigation at the present time. Especially encouraging is the fact that the two chlorofluoromethanes and the o-chlorofluorobenzene listed in the tables vielded substantially correct values for the chlorine. This indicates that the decomposition of the samples containing fluorine is accomplished satisfactorily, and that the only remaining problem is that of recovering the fluorine quantitatively.

The time required for the analysis of a sample varies considerably, depending upon the physical characteristics of the substance. Excluding the time required for preparation of apparatus and standard solutions, but including the sampling and calculation of results, the analysis of a very volatile substance such as methyl chloride may be completed in 35 to 40 minutes, and may be turned out in a routine manner at the rate of one analysis every 15 minutes. Other substances may require as much as 30 to 45 minutes

for the vaporization and burning of the sample. Much also depends upon the experience of the analyst.

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Determination of Sulfur Residues from Sulfur Application on Citrus Foliage

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Elemental sulfur (98 per cent sulfur by weight) mixed with a sulfur-free spray oil was applied to lemon leaves and then stripped off with purified carbon disulfide. After removal of the solvent, the sulfur was oxidized to inorganic sulfate by alkali fusion, and the sulfate ion was determined gravimetrically by precipitation as the barium salt. No special apparatus was required, and 10 to 200 micrograms of sulfur per square centimeter of leaf surface were determined rapidly and accurately in field practice.

ELEMENTAL sulfur has long been used for the sup-pression of various insect and mite pests and diseases of agricultural crops. It has been applied to the plants by different methods and in various combinations with inert materials and with other insecticides. The practice of applying elemental sulfur and petroleum spray oils simultaneously has brought up the difficulty of rapidly determining this elemental sulfur quantitatively in the presence of low concentrations of an oil of low volatility.

The usual procedure (4, 11) has been to oxidize the elemental sulfur to sulfate, which is then precipitated with a soluble barium salt and weighed as barium sulfate. To simplify the procedure in work with spray residues, a preliminary extraction (3, 4, 8, 11) of the sulfur from the plant material, followed by an oxidation process, is the most logical method. If the whole sample is oxidized in an alkaline fusion (2, 12), the time element involved becomes prohibitive. This same objection applies, generally, to methods in which the elemental sulfur is reduced to sulfide (6).

Even when simplified as to size and heterogeneity of sample, the gravimetric methods are usually time-consuming. Several volumetric (7, 9, 10, 13, 14) and photometric (15)

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procedures for the estimation of the sulfate ion have been proposed, but these methods often require special equipment or are otherwise unsuited to the rapid determination of a small amount of elemental sulfur, in the presence of petroleum spray oils and spreading (wetting) agents, which are contained in a large amount of bulky material.

The present method is an outgrowth of a study initiated by Boyce et al. (1), who devised a sulfur-residue method involving a mechanical stripping of the sulfur from treated leaves in the absence of spray oils, and it combines the solvent extraction or stripping technique of Thatcher and Streeter (11) with an alkaline fusion similar to that of White (12). Wet-oxidation methods using nitric acid and bromine were found to give variable and incomplete oxidation (65 to 85 per cent) of elemental sulfur in the presence of a petroleum oil.

Experimental Procedure

The leaf sample to be analyzed (usually 125 average-sized

The leaf sample to be analyzed (usually 125 average-sized mature leaves) was collected in a 2-quart Mason jar, which was capped and stored at 0° C. Just before the analysis, the leaves were removed from the jar with specimen forceps, and their surface areas were measured photoelectrically (5). For the extraction of the sulfur, 100 ml. of recently redistilled carbon disulfide were added to the jar, and the sample was shaken vigorously for 2 minutes. After decantation of the supernatant liquid through a Büchner funnel, another 100-ml. portion of carbon disulfide was added; the sample was shaken for 1 minute, and the supernatant liquid was decanted through the same funnel into the same receiving flask. The filtrate was transferred to a 250-ml. volumetric flask, and the funnel and receiving flask were washed carefully with 50 ml. of fresh carbon disulfide. This wash solution was then added to the previous filtrate, and the volume was adjusted to 250 ml. with additional carbon disulfide. additional carbon disulfide.

In the meantime, a fusion melt consisting of 8 parts of pure In the meantime, a fusion melt consisting of 8 parts of pure potassium hydroxide, 1 part of potassium nitrate, and 0.3 part of distilled water (all parts by weight) was prepared. This melt was crushed while warm and stored in a bottle tightly stoppered with a rubber stopper. For each sample, 3 grams of this crushed melt were weighed into a 20-ml. silver crucible, and an accu-rately measured 5-ml. aliquot of the carbon disulfide extract was pipetted onto the melt in the crucible. The carbon disulfide was evaporated from the sample, under vacuum, by placing the cru-cible containing the sample on a thin iron plate; a bell jar con-nected to the laboratory vacuum line was placed over the sample, and the iron plate was warmed gently by means of a light bulb or very sensitive hot plate. (If the rate of evaporation was too high, spattering was likely to occur.) Under these conditions of evaporation, the carbon disulfide apparently did not react with fusion melt. the

When all the solvent had been removed, the sample was fused over a shielded microburner with constant stirring with either a silver or a platinum wire. Considerable care had to be exercised in increasing the temperature of the melt during fusion, since spattering was sure to occur if the temperature was raised too rapidly

After bubbling had ceased, even over a raised flame, the crucible was heated strongly until the black deposit disappeared and the melt became water-clear. After cooling, the melt was transferred to a 250-ml. beaker and dissolved in 10 ml. of distilled water, and the excess potassium hydroxide in it was neutralthe water, and the excess potsstum hydroxide in it was neutral-ized with 6 N hydrochloric acid, phenolphthalein being used as indicator. The resulting solution was filtered quantitatively into a 400-ml. beaker, and the filter paper was washed with four 50-ml. portions of distilled water. The combined filtrate and washings were brought to a volume of 300 ml. with distilled water, and 1 ml. of 6 N hydrochloric acid was added.

After the acidified solution had been heated to boiling, 0.1 N barium chloride solution was added dropwise from a buret, with constant stirring, until no new precipitate of barium sulfate formed when the mixture was allowed to settle for a minute and a drop of the barium chloride solution was added to a clear region of the sample solution. The solution was kept just at the boil-ing point during this addition. An excess of 10 ml. of the barium chloride solution was then added, and the sample solution was kept hot for 1 hour to allow time for complete precipitation of the barium sulfate. A watch glass was used to cover the beaker at all times.

A Gooch crucible was prepared in the usual manner and dried at 160° to 180° C. to constant weight. Immediately before filtering, the sample was again tested for complete precipitation. If precipitation was complete, the sample was filtered through the Gooch crucible, care being taken that no precipitate should adhere to the beaker or stirring rod. The precipitate was washed at least ten times with hot water, until the washings were free from chloride ion.

The crucible and its contents were dried approximately 1 hour at 160° to 180° C. to constant weight, and the sample was weighed as barium sulfate. Blanks were run on both untreated leaves and solvent, and any necessary corrections were applied.

Discussion

The method reported in this paper is a combination of several of the standard procedures for the determination of sulfate ion, modified to eliminate certain errors introduced by the extraneous materials commonly found in oil-spray preparations, and to expedite the oxidation of sulfur to sulfate.

About 30 minutes, exclusive of drying periods, are required for one complete analysis; this value includes the time required to measure the total surface area of the sample. By running series of samples simultaneously and progressively, the authors have had no difficulty in analyzing 15 samples per man per 8-hour day.

In all test analyses, a known weight of yellow dusting sulfur (98 per cent sulfur by weight), comparable to that found in actual practice in the field on a unit leaf surface, was added to a volume of a so-called "light-medium" sulfur-free spray oil comparable to that applied in actual field work. This oil-sulfur mixture was then applied to average-sized mature lemon leaves, the leaf surface areas were measured photoelectrically, and the sample was analyzed for micrograms of sulfur per square centimeter of leaf surface. A small correction factor from blanks run on the solvent (1.1 mg. of sulfur per 5 ml. of freshly distilled solvent) was applied; blanks run on untreated leaves indicated that a small correction factor (average value of 1.5×10^{-2} mg. of sulfur per sq. cm. of leaf as used in these test analyses) was usually necessary per unit leaf area, the magnitude of this correction factor depending upon the previous spray history of the sampled leaves. Blanks run on the oil indicated it to be sulfur-free. Results of analyses to show the accuracy and reproducibility of the method are presented in Table I.

TABLE I. ANALYSES OF ELEMENTAL SULFUR ON LEAF SAMPLES (125 leaves each, containing known quantities of pure sulfur and a sulfur-

free spray oila,	to show the accuracy	and reproducibility	of the method;
Sample	Sulfur Applied	Sulfur Recovered	(Corrected)
	Grams	Grams	% b
1	0.980	0,974	99.4
2	0.980	0.985	100.5
3	0.980	0.945	96.4
4	0.980	0.944	96.3
5	1.558	1.558	100.0
6	0.941	0.922	98.0
7	0.613	0.606	98.8

^a Each sample contained 0.5 ml. of a so-called "light-medium" spray oil which had previously been shown to contain no sulfur, as determined by the present method. ^b Coefficient of variation (per cent), 1.09.

It has been the experience of workers at the Citrus Experiment Station that a coefficient of variation of 1.69 per cent, as found in this method, indicates a low variability in methods to be applied to the removal of spray residues in field experiments.

This method has been extensively used at the University of California Citrus Experiment Station for the determination of sulfur residues resulting from field applications of various forms of sulfur in combination with other materials in control studies of the citrus thrips, Scirtothrips citri (Moult.), and the citrus bud mite, Eriophyes sheldoni Ewing. Greater precision, with a consequently increased time requirement, obviously may be attained in this method by increasing the number of extractions and thus the volume of extracting solvent. However, the degree of accuracy of the method as reported is thoroughly suitable for the purpose for which the method was devised.

Interfering Materials

The sulfur-free spray oil added to each sample (usually 0.5 ml. per 125 leaves) apparently did not interfere with the accuracy of this method. Excessive amounts of salts formed during neutralization, leading to coprecipitation, probably constitute the main source of positive error, while those forms of sulfur insoluble in carbon disulfide probably constitute the main source of negative error. Careful technique is essential in obtaining reproducible results with this method.

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Reductions with Nickel-Aluminum Alloy and Aqueous Alkali

Quantitative Determination of Halogens in Organic Compounds

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A RECENT publication (3) from these laboratories described the dehalogenation of organic compounds by a nickelaluminum alloy and aqueous alkali.

Reduction as a method for the dehalogenation of organic compounds has been known for many years. The application of reduction methods for the quantitative determination of halogen in organic compounds is based on the conversion of halogen into salts of the halogen acids and the subsequent estimation of the halogen by standard analytical procedures. For this conversion, molecular hydrogen developed, for example, from zinc and acid is not generally applicable, since only a limited number of organic halogen compounds quantitatively undergo the halogen displacement when treated in this manner.

The introduction of catalytically activated hydrogen as an analytical tool for the dehalogenation of organic compounds was first described by Busch and Stove (1), who used a palladinized calcium carbonate catalyst which was prepared by heating an aqueous suspension of freshly prepared calcium carbonate with palladium chloride. The organic compound was dissolved in alcohol or water and then shaken at room temperature with the catalyst and hydrogen and sufficient alkali to neutralize the halogen acid formed. Later, Kelber (2) reported a similar procedure using a reduced nickel catalyst. Recently, the simultaneous reduction and dehalogenation of chloro-substituted azo compounds were reported to occur in the presence of Raney's nickel catalyst and hydrogen at room temperature and pressures varying from 1 to 3 atmospheres (4). All these methods when adapted for analysis require the use of hydrogen gas, a reduction catalyst prepared especially for the reaction, and the usual apparatus for catalytic reduction.

It was observed that on treatment with aqueous alkali and a nickel aluminum alloy, quantitative dehalogenation of organic compounds takes place (3). This reduction method has been very advantageously used for the quantitative determination of halogen in many aliphatic, aromatic, alicyclic, and heterocyclic compounds. The simple procedure and the fact that only the usual laboratory apparatus is required in carrying out the analysis give it a definite advantage over the other reduction methods for the determination of halogen in organic compounds. In addition, the results obtainable with this reduction method (100 \pm 0.3 per cent) compare favorably in both accuracy and precision with those by any of the other reduction methods. Its advantages over the Carius method of heating with nitric acid in a sealed tube or the peroxide oxidation in a Parr bomb are obvious.

Procedure for Analysis

FOR ALKALI-SOLUBLE COMPOUNDS. A 0.3-gram sample of the substance is dissolved in 100 ml. of 5 per cent sodium hydroxide in a tall 500-ml. beaker. Using a watch glass to cover the beaker, 3 grams of Raney nickel-aluminum alloy, in three or four portions, are added in the course of 10 minutes. The beaker must be covered with the watch glass at all times during the reduction to prevent loss of the solution by the fine spray caused by the liberation of hydrogen. The alloy may be added by simply sliding the watch glass just over the lip of the beaker, dropping the charge into the solution, and restoring the watch glass to its original position. When the reaction has subsided, the solution is heated on a steam bath for 15 minutes, the condensate on the watch glass is quickly washed into the beaker, and the solution is heated for about one hour at 90° C. to 95° C. At this stage, the nickel settles out and a clear colorless solution is obtained. The condensate on the watch glass is again washed into the

The condensate on the watch glass is again washed into the beaker and the alkaline solution is decanted from the nickel into a 200-ml. volumetric flask. The residual nickel is washed three times by decantation with hot water, the solution and washings are combined, and allowed to cool, and the volume is adjusted to the mark. A 100-ml. aliquot, or a fraction thereof, is acidified to Congo red paper with 10 per cent nitric acid and the halogen determined by any standard procedure. If the halogen is to be determined gravimetrically, the acidified solution is cooled and filtered if necessary, and the halide is then precipitated.

FOR ALKALI-INSOLUBLE COMPOUNDS. The sample is weighed into a 250-ml. Erlenmeyer flask equipped with a condenser. After adding 10 ml. of 95 per cent ethyl alcohol and 3.5 grams of alloy, the condenser is set in place and the flask cooled in an ice bath. Seventy-five milliliters of cooled 10 per cent sodium hydroxide are added through the condenser and, after the initial reaction has subsided, the ice bath is removed and the flask heated with a low flame until all the alloy has reacted (1.5 to 2 hours). It is not advisable to heat the mixture too rapidly since the initial reaction is vigorous and solution may be lost through the condenser. Any excessive foaming, during the reflux period, is controlled by the addition of a few drops of octyl alcohol. When the reduction is completed, the condenser is washed down with water and the determination completed as described for the alkali-soluble compounds.

TABLE I. DETERMINAT	tion of Halogen	
Halogen Compound	Theory	Found
	%	%
3.5-Diiodo-4-hydroxyphenylacetic	62.84	62.15
acı(a β-(3,5-Diiodo-4-hydroxyphenyl)-α- phenylpropionic acida	51.40	51.61
α-(3,5-Diiodo-4-hydroxyphenyl)-β-	51.40	51.60
N-methyl-3,a-diiodochelidamic	56.57	56.54
acid ^α β-Bromopropionic acid	52.21	56.44 52.38 52.06
Dibromolevulinic acida	58.32	58.00
Bromobenzene	50.85	51.01
2-Bromopyridine	50.61	50.70
p-Bromoacetophenone	40.17	40.17
2-Bromocholestanone ^a	17.17	16.34
Cholesterol acetate dibromideª	27.35	27.56
w-Chlorobenzoic acid	22.67	27.36
		23.06
p-Nitrochlorobenzene	22.52	22.57
β-(p-Chlorobenzoyl)-propionic acid ^a	16.73	17.01
2-Chloropyridine	31.25	16.81 31.02
" Compounds prepared in the authors'	laboratory; others we	re Eastman

Summary

A simplified procedure for the determination of halogen in organic compounds is described. Quantitative displacement of halogen by catalytically activated hydrogen occurs when the organic compound is treated with a nickel-aluminum alloy in an alkali hydroxide solution. The halogen is obtained in the form of the alkali salt of the halogen acid and can easily be estimated

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by any standard procedure. The method is accurate, rapid, and adaptable to routine analysis, requiring only the simplest of laboratory glassware and no special reagents.

Acknowledgment

The authors wish to take this opportunity to thank Felix J. Pheiffer of the Analytical Division for his help with the preliminary work.

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Analysis of Ethanol for Minor Amounts of **Esters and Aldehydes**

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LTHOUGH often of a routine nature, the estimation of A esters and aldehydes in 95 per cent alcohol is fraught with difficultics. Furfural, acidity, and permanganate-time tests are rather readily made while specific gravity determination requires only careful attention to detail. Higher alcohols present some difficulties not considered here.

Esters

The ester content of pure ethanol usually lies between 1 and 5 parts per 100,000 volumes calculated as ethyl acetate on a 100proof basis. By the A. O. A. C. method for esters in distilled liquors (1) on a 50-ml. sample, this would be equivalent to 0.05 to 0.3 ml. of 0.1 N alkali. In distilled liquors except gin the amount is usually about 10 times that cited.

The usual chemical glassware is not sufficiently alkali-resistant to be used in the determination of such small quantities of esters. The alkali used to saponify the esters attacks the glass to such an extent that the alkali so consumed far exceeds that necessary to saponify the esters. Consequently the blank determinations are too high for accurate work. Furthermore, such blanks vary with the age of the glassware used.

A few pieces of old glassware were found in this laboratory which gave small blanks, probably owing solely to usage; they are used in pairs, giving similar blanks. An old expedient of using silver flasks involves washing out the contents into a clean flask after saponification and before titrating, using freshly boiled and cooled distilled water.

Recent studies of the chemical resistance of borosilicate glasses sold as Pyrex, Kimble, and Glasbake (3) show that dilute potassium hydroxide solutions attack such glass to a lesser degree than dilute sodium hydroxide solutions. Therefore, potassium hydroxide is used. Special alkali-resistant Pyrex, while not fully satisfactory, is preferable to the usual chemical glass.

PROCEDURE. Measure 50 ml. of 95 per cent ethanol and dilute to 100 ml. with freshly boiled and cooled distilled water. Exactly neutralize any free acidity with 0.02 N potassium hydroxide solution, using phenolphthalein as indicator. Add exactly 10.0 ml. of 0.1 N potassium hydroxide solution and reflux gently for 30 minutes. Wash down the condenser with menter the distilled water and exact the flex perturbation of the menter of the solution of the menter of the solution of the menter of the solution of neutral distilled water, stopper and cool the flask and contents in a water bath, remove the stopper carefully, and wash down. Add exactly 10.0 ml. of 0.1 N hydrochloric acid solution and titrate the excess acid with 0.02 N potassium hydroxide solution. Run a blank determination under identical conditions, substituting 100 ml. of freshly boiled and cooled distilled water for the diluted alcohol. Each milliliter of titration is equivalent to 0.00176 gram of ethyl acetate. The usual titration will therefore fall between 0.6 and 2.9 ml. of direct titration after subtraction of the blank.

Aldehydes

The volumetric A. O. A. C. method, involving titration of excess bisulfite with standard sodium thiosulfate, is simple and sufficiently accurate when used for one or two samples. As a special distillation is required for each sample for multiple determinations, a colorimetric method is preferred for economy of time.

In the most commonly used colorimetric method (2) aldehydefree alcohol is prepared by distillation from metaphenylenediamine hydrochloride. Unless freshly prepared with great care, error is easily introduced, and the alcohol is rarely completely aldehyde-free. This may be due in part to contact with air in redistillation and in storage, even in a cold, dark place. Redistilled synthetic methanol is consistently aldehyde-free and has been used largely to replace the ethyl alcohol in this determination for several years. While distilled liquors except gin are apt to contain 4 to 12 parts per 100,000 of aldehyde, the amounts in alcohol are of the order of 0.05 to 0.2 part per 100,000.

PROCEDURE. To 2.5 ml. of the alcohol sample add 2.5 ml. of water and 15 ml. of 50 per cent by volume redistilled synthetic methanol. Add 5 ml. of fresh Schiff's reagent prepared according to A. O. A. C. standards, and mix at once. All solutions must be at 60° F. and, after mixing, maintained at that temperature for 20 minutes to develop the maximum color due to the presence of alchedre. of aldehyde.

Prepare standards as follows: To 5 ml. of 50 per cent aldehyde-free alcohol add 15 ml. of 50 per cent synthetic methanol plus 0.02, 0.025, 0.03, 0.05, and 0.075 ml. of freshly diluted acetaldehyde solution containing 0.0001 gram per ml. Such small quantities can be measured with a sufficient degree of accuracy by using a 1-ml. pipet graduated in 100 parts. Vary these standards to suit specific needs. To each of the above add 5 ml. of the Schiff's regent, mix at once, and treat as with the sample. Pyrex test tubes (25-ml.), thoroughly cleaned with chromic acid-sulfuric acid solution and efficiently rinsed, are convenient comparison tubes

Compare the samples and the standards, all made at approximately the same time, after standing for 20 minutes at 60° F.

Summary

In the accurate determination of 1 to 5 parts per 100,000 of esters in 100-proof ethanol it is necessary to have either well-aged glassware which gives a small blank, or silver flasks. Many difficulties in the determination of 0.1 part per 100,000 of aldehyde are eliminated by substituting redistilled methanol for the major part of the aldehyde-free ethanol.

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Removal of Air from Powders in Density Determination

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N THE determination of the density or specific gravity of fine powders by the method of immersion in a liquid in a pycnometer, it is often difficult to remove the air from the spaces between particles, even though the sample be of a material that in coarser form is easily wetted by the immersion liquid. The air is commonly removed by keeping the open pycnometer, containing the sample and enough liquid to cover it well, in an evacuated space while the air comes off in rarefied bubbles. This process seldom goes through smoothly; the bubbling is spasmodic, sometimes coming in unanticipated bursts that throw part of the sample out of the bottle. The last bubbles of air hang on tenaciously, and considerable agitation is required to shake them out from the interior of the powder bed. This part of the work is commonly handled by alternate stirring and evacuation, which often proves to be a tedious operation.

Previous workers have introduced between the pycnometer and the pump a tube designed to catch any particles unavoidably thrown out from the pycnometer; the material thus caught was weighed and allowance made for it in the calculation (1). The advantages of using a suitable wetting liquid have been cited by Nutting (2). Where water is used to immerse organic crystalline compounds, it is often necessary to add a wetting agent.

With the setup described below the air can be removed smoothly by controlled agitation while the sample is under vacuum. The method has been used in this laboratory for several months.

The apparatus, shown in Figure 1, is simple and may be assembled from readily available elements. The source of agitation is a vibrator, V, of the type sold for massaging the face and scalp. In place of the original vibrator head is a special head, H, which holds the pycnometer flask, F; this head consists of a one-hole rubber stopper in which three nails are inserted at a slight angle to grasp the body of the flask. The vibrator is mounted head upward on a heavy base, B, which rests on a thick rubber sheet, G, covering the top of a wooden block, W. The rubber sheet serves as a gasket between the block and a vacuum bell jar, J, which covers that part of the assembly so far described. One or more air holes, A, are cut in the gasket to prevent the central portion from being lifted when the jar is evacuated. A round-bodied electric lamp cord (Type SJ) is run from the vibrator down through the gasket into the block and out at one side, the passage through the wood being bushed airtight with a rubber stopper, S. For convenience in handling there should be a coupling, C, in the line between the vibrator and the gasket.

Adjustment of the vibration intensity and of the pressure reduction is provided by the following arrangement: The apparatus is plugged into a continuously variable transformer, T, with voltage range from 0 to 115 or slightly above. The rubber tube from the bell jar to the house vacuum line has a branch connected to a manometer, M, and another branch left open at the end, E. With one hand on the adjusting knob of the transformer and the index finger of the other hand resting lightly over tube end E, the operator has fingertip control over vibration and vacuum at all times. If it is desirable to maintain a particular adjustment for some time without attention, the transformer may be set for the necessary voltage and the vacuum kept fairly constant by leakage through a screw pinchcock, P; or if the maximum vacuum is desired, the end of a cork stopper may be left resting against E.

A little practice will enable one to judge readily the optimum adjustments of agitation and vacuum, both of which may need considerable variation during the treatment of a given sample. The ideal is to maintain continuous but not violent bubbling, until not enough air is left to affect sensibly the measurement of the sample volume. A test for completeness of air removal in this sense is to observe whether the height of the liquid in the pycnometer changes on application or removal of vacuum. The test is most sensitive when the full vacuum is suddenly released, as by jerking the finger away from E, and when the bottom of the meniscus is nearly in line of sight with some letter or other marking on the flask.

When the last significant traces of air are persistent, two means are available for hastening their removal. One is to stir the sample with a stiff wire rod, R, extending through a flexible rubber stopper in the top of the bell jar. Another way, which is more convenient and may prove adequate, is to jerk the flask repeatedly by jiggling the electric plug that connects the transformer to the house line.

The current should not be left on longer than necessary, lest in its vacuum-jacketed condition the vibrator should become overheated. The time required for the whole operation of air removal is usually only a few minutes.

The density values obtained by this method are equivalent to those by the more common process, for in both cases the air removal is carried to the same end point as indicated by the expansion-contraction test. The saving of time by the method here described may be negligible or large, depending on the difficulty of manipulation of the given sample by the older method. The principal advantages, evident particularly with the more troublesome samples, are convenience and relative safety from loss of sample by spurting. The term



FIGURE 1

thus a means of safeguarding against accidents that otherwise are difficult to avoid.

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Determination of Sugars in Apple Tissue

ANALYTICAL EDITION

Some Modifications of the Usual Procedures

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N UMEROUS methods are available for extracting and determining the sugars found in plant tissues. Many of these have been reviewed recently by Browne and Zerban (5) in their excellent treatise on sugar analysis.

The Association of Official Agricultural Chemists recommends 50 per cent alcohol for the extraction of sugars from grain and stock feeds (2) and 80 per cent alcohol for the removal of sugars from plants (1). Jackson and McDonald (8) used the volumetric dichromate-ferrous ammonium sulfate-phenanthroline method for cuprous oxide and later reported (9) a study of Munson and Walker's tables for reducing sugars. Erb and Zerban (7) combined the Munson and Walker procedure for reducing sugars with the Jackson and Mathews (10) method for levulose, in a procedure for the individual determination of dextrose and levulose in a mixture containing sucrose. Erb and Zerban used a table of modified Munson and Walker values and calculated the variable reducing factors for different ratios of dextrose and levulose. Stegeman and Englis (12) compared several volumetric procedures for determining cuprous oxide with the gravimetric method and discussed briefly the possible use of diphenylamine with.dichromate in sugar work.

gravimetric method and discussed briefly the possible use of diphenylamine with dichromate in sugar work. The rupture of cell structure before extracting is advantageous. Kneen and Blish (11) heated wheat plants for 15 minutes in an oven held at 140° C. before extracting the sugars. The use of the Waring Blendor for sample preparation has already been described (θ) and its application is rapidly being extended.

Experimental

RECOVERY OF REDUCED COPPER. In an investigation of the sugars in apple tissue preliminary trials with several methods led the authors to consider the possibility of using diphenylamine with dichromate, for the recovery of reduced copper, as suggested by Taran (13). Table I shows the values obtained for the recovery of copper from varying weights of cuprous oxide by this procedure, the details of which are described later.

TABLE I.	RECOVERY OF REDU	CED COPPER
(From cuprous oxide di potassium die	ssolved in ferric sulfate s chromate and diphenyla	solution by titration with mine indicator)
Copper Added Mg.	Copper Recovered Mg.	Recovery %
$\begin{array}{r} 42.4\\ 64.5\\ 67.7\\ 82.2\\ 87.2\\ 89.7\\ 91.4\\ 98.8\\ 100.1\\ 107.9\\ 109.8\\ 121.9\\ 130.7\end{array}$	$\begin{array}{r} 42.6\\ 64.8\\ 67.7\\ 83.1\\ 87.7\\ 91.9\\ 98.6\\ 99.5\\ 107.1\\ 110.8\\ 121.9\\ 133.1\end{array}$	$ \begin{array}{c} 100.4\\ 100.5\\ 100.0\\ 101.1\\ 100.5\\ 99.7\\ 100.6\\ 99.8\\ 99.4\\ 99.8\\ 100.9\\ 100.0\\ 101.9\\ 100.0\\ 101.9\\ 101.9\\ 100.0\\ 101.9\\ 101.9\\ 100.0\\ 101.9\\ 101.9\\ 100.0\\ 101.9\\ 101.9\\ 100.0\\ 101.9\\ 101.9\\ 100.0\\ 101.9\\ 100.0\\ 101.9\\ 100.0\\ 101.9\\ 100.0\\ 101.9\\ 100.0\\ 101.9\\ 100.0\\ 101.9\\ 100.0$
100.0	130.1 Mea	$n 100.32 \pm 0.18$

In another series of trials varying quantities of cuprous oxide obtained by the Munson-Walker procedure were weighed, dissolved, and titrated directly by the dichromateferrous ammonium sulfate-o-phenanthroline-ferrous sulfate method of Jackson and McDonald and by the dichromateferric sulfate-diphenylamine procedure herein described. Table II gives the results of these trials.

TABLE II. COMPARISON OF JACKSON AND MCDONALD Dichromate-Ferric Sulfate-Diphenylamine Methods	AND
RECOVERY OF REDUCED COPPER	dise

	Contra the		Dichron	ate-Ferric S	ulfate-
Method of .	ackson and	McDonald	Diphe	nylamine M	ethod
Copper Added	Copper Recovered	Recov- ery	Copper Added	Copper Recovered	Recov- ery
Mg.	Mg.	%	Mg.	Mg.	%
29.7 50.0	30.2 49.5	101.7 99.0		CONTRACTORY - MAL	for the second
55.1	55.0	99.8	39.7	39.5	99.5
74.8	75.3	100.7	45.4	45.8	100.9
96.0	96.1	100.1	91.9	91.2	99.2
135.3	134.8	99.6	128.7	127.8	99.3
182.3	181.0	99.3	130.8	140.7	100.0
232.0	230.8	99.5	184.3	185.9	100.9
254.0	254.6	100.0	225.2	227.0	100.8
200.0	Mean 99	$.97 \pm 0.21$	010.2	Mean 100	$.03 \pm 0.25$

EXTRACTION. Several procedures were tried for convenience and thoroughness of extraction. Quadruplicate samples were analyzed raw and after being heated for 15 minutes in an ordinary convection oven set for 140° C. Although the differences were small, the heated samples averaged 7.06 per cent for reducing sugars and 1.66 for sucrose as compared with 6.71 and 1.63, respectively, for the unheated samples.

The slight gain in reducing sugars was attributed to a more thorough extraction of the heated sample. However, additional trials were run to ensure absence of pronounced changes in the distribution of the sugars present.

For this purpose triplicate samples of 70 to 80 grams each, of Rome Beauty tissue, in 10-cm. (4-inch) aluminum dishes with tight covers, were heated for periods of 5, 10, and 15 minutes in an ordinary convection oven set at 110°, 120°, and 140° C. A similar series was run with duplicate samples from a different stock sample of Rome Beauty tissue, but the heating was accomplished in a forced draft oven set for the same range' of temperatures and 15-minute heating periods only. Unheated samples were analyzed at the same time for comparison. The average values for both series are shown in Table III.

The original procedure used to extract the apple tissue with alcohol consisted in two hand grindings in a glass mortar, but trials showed that the operation could be accomplished TABLE III. SUGAR CONTENT OF HEATED AND UNHEATED TISSUE OF ROME BEAUTY APPLES

		Reducing	vection Ove	n	Forceo	i Draft Ov	en
Heating Period Vin	Temp.	sugar (as in- vert)	Sucrose (as in- vert)	Total sugar	sugar (as in- vert)	Sucrose (as in- vert) %	Total sugar
Not h	antad	7 59	1 52	0 11	7 99	1 00	0.76
5	110	7.54	1.71	9.25	****	1.00	9.70
10 15		7.73	1.55	9.28	7.82	1.97	9.79
5 10	120	7.68	1.61	9.29			
15		7.72	1.32	9.04	7.86	1.86	9.73
10	140	7.53	1.32	8.96			
15		7.49	1.44	8.93	7.93	1.79	9.72
The averag	ge water lo	oss in the for	ced draft o	ven was	0.56, 0.88, an	d 4.43 per	cent, re-

spectively, at 110°, 120°, and 140°, for 15 minutes; in the convection oven the losses were much less, ranging from 0.02 to 0.48 per cent.

more quickly and with equal efficiency by the use of the Blendor. With triplicate samples of Grimes Golden tissue, two extractions in the Blendor gave an average of 5.56 per cent total reducing sugars as compared with an average of 5.23 per cent for one extraction in the Blendor and 5.29 per cent for two extractions in the glass mortar.

CLARIFICATION. The need for clarification of alcoholic extracts of plant tissues is an open question and probably depends in considerable degree upon the nature

of the plant material from which the sugars are extracted.

In the present work triplicate or quadruplicate trials with alcoholic extracts of tissue of six varieties showed little or no appreciable difference in total reducing sugars between cleared and uncleared samples. The same was true for sucrose where this sugar was determined. On the other hand, one variety (Gravenstein) did show a higher value for reducing sugar in the uncleared sample (Table IV). In each instance the samples were cleared with neutral lead acetate and disodium phosphate and each lead precipitate was washed twice by centrifugation.

Several trials were made on the method of clearing alcoholic extracts or fresh juice when the cuprous oxide was determined by the dichromate-diphenylamine method (Table V). In all instances neutral lead acetate was used as the clearing agent. Comparisons were made of sodium oxalate, disodium phosphate and sodium carbonate as deleading agents, and of filtration and centrifugation of lead precipitates.

The clarification of alcoholic extracts of ground apple tissue proved to be slightly more difficult than that of apple juice and necessitated 2.5 ml. of lead acetate solution and 2.0 ml. of disodium phosphate solution. Trials were made to determine the effect of excess disodium phosphate and of alcohol in the clarified extracts. A 5-ml. excess of phosphate solution (total of 7 ml.) and 15 ml. of 85 per cent alcohol were without appreciable effect on the results obtained.

Information was desired concerning the sugar values obtained by combining the several steps tried individually, as compared with procedures already accepted as suitable for sugar work. For this purpose the combined procedure was compared with the A. O. A. C. (1, 2) methods mentioned.

A composite stock sample was made from 24 Rome Beauty apples and run through a food chopper. The material was mixed well and three lots were weighed out rapidly, in duplicate, for analysis. The first lot was extracted and analyzed in accordance with A. O. A. C. directions for plants, the second lot was extracted and analyzed in accordance with A. O. A. C. directions for grain and stock feeds, and the cuprous oxide values from both lots were determined gravimetrically after elarification with neutral lead acetate by filtration. The third lot was heated in aluminum dishes, comminuted and extracted in the Blendor, and clarified by centrifugation, and the cuprous oxide was titrated with dichromate and diphenylamine. The average values for this comparison are given in Table VI.

Finally, a series of six replications was made to test the reproducibility of the values obtained by the modified procedure. Dextrose and levulose were determined individually by the method of Erb and Zerban (7) and sucrose was determined by the A. O. A. C. (3) method after inversion with hydrochloric acid at room temperature. The results of these replications are shown in Table VII.

Discussion

Table I shows that copper in the form of cuprous oxide can be determined satisfactorily by dissolving in ferric sulfate solution and titrating with potassium dichromate with diphenylamine as an indicator, and Table II indicates that the values so obtained compare favorably with those obtained by the volumetric method of Jackson and Mc-Donald. In the former method the cuprous oxide dissolves readily, and the end point is distinct and with a little practice is easily recognized.

TABLE IV.	EFFECT OF	CLEARING ALC VARIETIES OF	COHOLIC E: Apples	XTRACTS FROM	Seven			
	Reducing Sugar Sucrose Month (as Invert Sugar) (as Invert Sugar) Applyred Not alarifad Clarifad							
Variety	Analyzed	Not clarified	Clarified	Not clarified	Clarified			
		%	%	%	%			
Gravenstein	September	6.95	6.76	1.70	1.70			
Grimes Golden	September	9.53	9.48	3.67	3.60			
Delicious	November	9.91	9.87	manal feel atten and				
Starking	December	9.34	9.32					
Stayman Winesap	December	6.99	6.97					
York Imperial	December	5.10	5.07	ALL SALANDER L	10/0 11/2/11/2			
Rome Beauty	April	6.97 7.53	6.94 7.53	i.89	1.86			

The heating of apple tissue prior to comminution and extraction may or may not be advantageous, depending somewhat upon the physical nature and degree of ripeness of the fruit. Hard, tough, or immature fruit is more easily prepared and extracted if first heated. This softens the tissue, ruptures the cells, and allows uniformity in sampling. It also destroys enzymes and, if carefully done, does not hydrolyze the sucrose present. Ripe fruit softened by maturity is not benefited by preliminary heating. Table III indicates that Rome Beauty apple tissue may be heated for periods of 5 to 15 minutes at temperatures of 110° to 140° C. without pronounced effect upon the values for reducing sugars and sucrose. In this instance the fruit was mature and the heating of little or no advantage. An interesting observation on the comparison of heated and unheated samples was the apparent greater amount of oxidation in the unheated samples as evidenced by their dark color in contrast to the lighter color of the heated samples. In storage at 3° C., the heated samples kept over a longer period than the unheated samples without appreciable change in sugar values.

The data relating to clarification are interesting (Table IV). Of the seven varieties tried, differences between clarified and unclarified extracts could perhaps be ignored in all cases except that of Gravenstein. Nevertheless, in no case did the value for reducing sugars in the clarified extract exceed that for the unclarified and the general trend is toward

TABLE V.	VALUES FOR REDUCING SUGARS IN APPLES AS AFFECTED BY	
	METHODS OF CLARIFICATION	

		Made to Volume before	No. of Washes	Mg. o as Inv Ali	f Reducin ert Sugar iquot of	ng Sugars in 5-Ml. Sample
	Method of	or after	for Each	Usr	Extract	Extract
Deleading Agent	Removing Ppt.	Clarification	Lead Ppt.	Juice	1	2
Sat'd Na-C-O.	Centrifugation	After	1	110.8		(approx)
	Centrifugation	After	None	105.5		and the second second
Sat'd Na-HPO4	Centrifugation	After	1	110.3		
States and the second second	Centrifugation	After	None	106.6		a line of the
Dry Na ₂ CO ₂	Filtration	Before			*83.3	6 10 0 m (1 0
Dry Na ₂ HPO ₄	Filtration	Before			82.5	
Sat'd Na ₂ HPO ₄	Centrifugation	After	3		84.5	
	Centrifugation	After	None		74.4	A COMPANY
Dry Na ₂ CO ₁	Filtration	Before			1011	75.0
Dry Na:HPO4	Filtration	Before				75.1
	Centrifugation	Before	200.00			75.6
Not clarified						75.5
					Contraction of the	

slightly higher values in the nonclarified material. It is possible that stage of maturity and relative amount of chlorophyll-bearing tissue are more important than varietal difference in this respect. It may or may not be significant that most of these trials were made during the winter and spring months, on apples taken from storage, whereas the largest differences between clarified and nonclarified extracts occurred in the analyses made earlier in the season. More data are needed on this point.

As indicated in Table V, sodium oxalate, disodium phosphate, or sodium carbonate may be used as a deleading agent in the ferric sulfate-dichromate-diphenylamine method. Since 5-ml. excess disodium phosphate did not disturb the values for reducing sugars it was accepted as a deleading agent. If the sugar solutions are made to volume after clarification it is necessary to wash the lead precipitates in order to avoid low values for sugar. If desired, the lead precipitates may be removed by centrifugation rather than by filtration, in which case it is convenient to make the solutions to volume, centrifuge in a closed tube, and omit the washing process.

Uncleared solutions may be somewhat less satisfactory to pipet, as particles may tend to gather in the tip or cling to the inside walls of the pipet, but where clarification can be omitted there is a very material saving in time. The results of these trials indicate that for ordinary work the clearing process may be omitted with apple extracts in most instances.

Table VI shows over-all values obtained from the modified procedure in comparison with those obtained by the two variations of the A. O. A. C. methods, and Table VII shows the values from six replications when dextrose, levulose, and sucrose were determined individually. These results indicate that the modified procedure is suitable for the analysis of apple tissue.

The Waring Blendor has been found to be very effective in reducing and mixing either raw or heated apple tissue in this work. Extraction of the tissue with alcohol, also, may be accomplished quickly and easily by use of the Blendor, the time required for two extractions in the blendor being approximately one half that required for two extractions by

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hand grinding in a mortar. Other time records show that omitting the time required to evaporate the extracts on the steam bath, which is similar in both methods, the time necessary for the determination of total reducing sugars on quadruplicate samples was 3.3 hours for the modified procedure herein proposed as compared with 5 hours by the A. O. A. C. procedure for feeds. Extraction in the Blendor, clarification in the centrifuge, and titration of the copper oxide by the dichromate-diphenylamine method each requires approximately one half the time necessary for extraction on the steam bath, clarification by filtration, and gravimetric determination of the copper oxide, respectively. Extraction by Soxhlet apparatus is still more time-consuming than extraction on the steam bath.

Procedure

PREPARATION OF EXTRACTS. Cut the sample into slices, weigh, heat in a tared aluminum dish with tight cover for 15 minutes in an oven set for 140° C. to soften the tissue, cool, and transfer the material to the tared Blendor cup with the aid of water. (The heating may be omitted with soft tissue which reduces readily in the Blendor cup.) Weigh the mixture in the Blendor cup to determine the amount of water added beyond the weight of the original sample before it was heated. The weight of water used for the transfer is usually about one third that of the sample taken for heating and the

or water used for the transfer is usually about one third that of the sample taken for heating and the small amount of water lost in heating is made up in the transfer to the Blendor cup. Comminute thoroughly and store as a bulk sample in the refrigerator. Heated apple tissue will remain unchanged for days or weeks and unheated tissue will keep for a somewhat shorter period.

Extract 20 to 30 grams in the Blendor with 1 or 2 grams of calcium carbonate and approximately 150 ml. of 95 per cent alcohol; this results in a mixture above 70 per cent alcohol and the separation of a flocculent precipitate. Filter the mass on a 9-cm. Büchner funnel into a 500-ml. suction flask, remove the paper and residue to the Blendor cup, and extract again with about 100 ml. of alcohol, again filter, combining the second filtrate with the first and washing the residue with alcohol until the total volume approximates 300 ml. Transfer the extract to a 400-ml. beaker with the aid of a little water, add a small amount of calcium carbonate, and evaporate on the steam bath to a volume of 5 to 10 ml.

If clarification is omitted, transfer the sirupy residue from the steam bath directly to a 100-ml. flask and make up to volume for analysis. If clarification is desired, add 2 ml. of saturated lead acetate solution to the flask and make to volume. Mix well, allow to stand a few minutes, and transfer all (or most) of the sample to a closed, dry centrifuge tube. Centrifuge until clear (5 to 10 minutes) and pour off into a second dry centrifuge tube containing an amount of dry disodium phosphate sufficient to precipitate all the lead present. Mix well, close the tube to prevent evaporation, and again centrifuge until clear.

Pour off and retain the clear liquid for analysis. A somewhat longer and possibly slightly more accurate procedure for clarification involves washing the lead precipitates twice or three times by centrifugation before making the sample to definite volume for analysis.

DETERMINATION OF SUGARS. Determine reducing sugars, dextrose, and levulose by the combined procedure of Erb and Zerban (7) and sucrose by the A. O. A. C. (4) method, after inversion with hydrochloric acid at room temperature. Filter the cuprous oxide on a loose-bottom (Caldwell) crucible, transfer the crucible to a 400-ml. beaker containing 50 ml. of ferric sulfate solution, dissolve the cuprous oxide, rinse, and remove the crucible and add 20 ml. of sulfuric acid. Add 3 or 4 drops of

ive	TABLE VI.	COMPARISO C. MITTUO	N OF THE MO	DIFIED PROCEDI	JRE WITH
nay lor,	A. O. P	edure	Reducing Sugars (as Invert)	Sucrose (as Invert)	Total Sugar %
by A by A M	. O. A. C. met . O. A. C. met Iodified proces	thod for plants thod for feeds ture	7.34 7.31 7.53	1.75 1.75 1.86	9.09 9.06 9.39
BLE VII.	SUGAR CO	ONTENT OF R	EPLICATE SAM	MPLES OF APPLI	E TISSUE
plication No.	Dextrose %	Levulose %	Reducing Sugars %	Sucrose (as Invert) %	Total Sugar %
1 2 3 4	$1.03 \\ 1.13 \\ 1.13 \\ 1.15 \\ 1.16$	$\begin{array}{r} 4.60 \\ 4.51 \\ 4.49 \\ 4.51 \\ 4.51 \\ 4.55 \end{array}$	5.63 5.64 5.62 5.66 5.71	$\begin{array}{c} 0.77 \\ 0.68 \\ 0.56 \\ 0.55 \\ 0.60 \end{array}$	6.40 6.32 6.18 6.21 6.31
6 Mean	1.25 1.14 ± 0.03	4.47 4.52 ± 0.02	5.72 5.66 = 0.02	0.62 0.63 ± 0.03 6.	6.34 29 ± 0.03

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diphenylamine indicator and titrate with dichromate solution until a darkening occurs. At this point add 5 ml. of phosphoric acid and 8 to 10 drops more of indicator. Add water to make the total volume about 250 ml. and complete the titration to the first permanent violet coloration.

REAGENTS. Reagents (Fehling's and Ost's) for reducing sugars are prepared according to A. O. A. C. (4) directions. Ferric sulfate solution is made by dissolving 60 grams of the

hydrated salt [Fe2(SO4)3.9H2O] in 1 liter of solution and filtering. The solution must be free from ferrous ions.

Potassium dichronate is weighed to give exactly 7.7135 grams per liter of solution. One milliliter is equivalent to 10 mg. of copper. Diphenylamine is used as 0.2 per cent solution in concentrated

sulfuric acid.

Sulfuric acid is a 1 to 7 aqueous solution.

Orthophosphoric acid is the usual 85 per cent U. S. P. sirup.

Lead acetate solution is a saturated solution of the neutral salt.

Disodium phosphate is used either dry or as a saturated solution.

Summary

In the analysis of apple tissue for sugars it is advantageous to heat the tissues in closed aluminum containers before grinding, to disintegrate, mix, and extract the heated tissue in a Waring Blendor, and to determine cuprous oxide by dissolving it in ferric sulfate solution and titrating with potassium dichromate in the presence of diphenylamine indicator. The procedure is rapid and easily manipulated and the results are sufficiently accurate for the determination of sugars in many plant materials.

In most instances it appears safe to omit clarification of the alcoholic extracts of apple tissue, with a corresponding saving in time. Where clarification is necessary this can be accomplished satisfactorily by addition of neutral lead acetate and centrifugation as described.

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Simple Device for Preparing Vapor-Air Mixtures

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N TESTING the efficiency of a combustion apparatus for chlorinated hydrocarbons in the atmosphere, the writer desired to introduce into the unit known amounts of solvent vapor at rates of 1 to 2 liters per minute. A simple method of doing so, and one most nearly meeting this need. was found in the experimental work of Olsen, Smyth, and



co-workers (1). However, a modification which would ascertain by successive weighings the amount of solvent used in each run seemed desirable. A very satisfactory method was finally devised which gave precise weighings and a wide range of concentrations and required very little manipulation.

Both ends of a two-way stopcock of about 8-mm. bore were cut off about 35 mm. from the base and one end was scaled. A short piece of glass tubing, 7 mm. in inside diameter, was drawn out, bent, and inserted in the two-hole rubber stopper as shown. The mixing chamber was a filter tube, the neck of which was bent at a right angle and connected to the combustion unit. The ap-

a right angle and connected to the combustion unit. The ap-paratus was mounted by means of a clamp on a ringstand. In operation, the solvent to be tested, trichloroethylene, was pipetted into the bulb and the stopcock closed and weighed by suspending it in the analytical balance (by means of a wire hook not shown in the diagram). The stopcock was then inserted in the rubber stopper, suction applied, and the stopcock opened to some fixed position, depending on whether a small or large concentra-tion was desired. A drop of phosphoric acid served as an efficient hubricant lubricant.

The vapor-air mixture was drawn through the apparatus for the desired length of time, after which the stopcock was closed, re-moved, and reweighed while pure air continued to flush residual vapor from the chamber. The difference in weight represented the amount of solvent which was carried over at a practically constant rate.

Since the experiments were conducted at room temperature, the evaporative loss was uniform throughout, amounting to about 1 mg. for each run. Experiments showed that at various openings of the stopcock and at raised or lowered positions of the inlet tube orifice a range of concentrations of from 10 to 500 p. p. m. was easily obtained.

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Systematic Polarographic Metal Analysis

Characteristics of Arsenic, Antimony, Bismuth, Tin, Lead, Cadmium, Zinc, and Copper, in Various Supporting Electrolytes

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The polarographic characteristics in nine supporting electrolytes of the metals listed in the title have been studied, and complete data are presented for their half-wave potentials and diffusion current constants. The utility of diffusion current constants in practical analytical work is discussed; the use of these constants eliminates the need for calibrating each particular dropping electrode with known concentrations of the substances to be determined.

PROGRAM has been started in this laboratory with the aim of developing systematic schemes of polarographic analysis that can be applied to the qualitative and quantitative analysis of any mixture of the commoner metallic elements. Soon after this program was initiated it became evident that its logical prosecution requires much more specific and quantitative information concerning the polarographic characteristics of the various metals than one can glean from the existing polarographic literature (6), and it was therefore decided to obtain such information before attempting to devise specific analytical procedures.

The present paper presents a compilation of the halfwave potentials, diffusion current constants, and other analytically pertinent characteristics of arsenic, antimony, bismuth, tin, lead, cadmium, zinc, and copper, in nine different supporting electrolytes. These metals were studied as a group because they are so commonly associated in nonferrous alloys and other commercial products, and also because, with the exception of zinc, they are usually separated as a group by hydrogen sulfide precipitation in common analytical schemes.

A simplified method of performing quantitative polarographic determinations, which eliminates the necessity of calibrating each dropping electrode with known concentrations of the substance being determined, is also described.

Experimental

A Model XI Heyrovský Polarograph, manufactured by E. H. Sargent and Co., Chicago, was used for recording polarograms according to the technique which has already been adequately described (6). The galvanometer of the instrument was cali-brated frequently by the usual method (6), and with sufficient care so that the sensitivity factor was known with an accuracy of ± 0.3 per cent. With the particular polarograph used the galvanometer deflection on the visual scale was 3.5 per cent larger than on the photographic paper for a given current, apparently because of a difference in the lengths of the two light paths, but both deflections were strict linear functions of the current (as re-quired) within the limits of accuracy of the readings. H-type cells like those described previously (6, 13) were used, with either a saturated calomel or mercury-mercurous sulfate reference working anode, and in all cases measurements were made with the cell in a water thermostat at 25.00° C. The im-portance of reasonably precise temperature control in polaro-graphic measurements has been stressed elsewhere (6). Dis-solved air was removed from the solutions by nitrogen which had been purified by passage over copper gauze at about 400° C. A Model XI Heyrovský Polarograph, manufactured by E. H.

been purified by passage over copper gauze at about 400° C.

The dropping electrode assembly was the same as that de-The dropping electrode assembly was the same as that de-scribed by Lingane and Laitinen (13), and the capillary proper consisted of a 9-cm. length of 6-mm. outside diameter Corning "marine barometer tubing" with a uniform internal diameter of approximately 0.03 mm. The *m*-value was determined and checked daily by means of the simple volumetric instrument previously described (10). At the time of this writing the *m*-value of this capillary has remained constant at 2.57 ± 0.01 mg. per second at 25° C. for over eight months; this is a good example per second at 25° C. for over eight months; this is a good example of the constant behavior that can be expected of such capillaries when they are accorded the simple maintenance care that has been recommended (δ). The drop time was in the neighborhood of 3.5 seconds, the exact value depending on the nature of the supporting electrolyte and the potential of the dropping elec-trode. In all cases the exact drop time was determined at the particular potential at which the diffusion current was measured. Stock solutions of the various metal salts were prepared from

reagent quality materials, and when necessary they were stand-ardized by the usual procedures. Particular care was taken in the preparation of the stock solutions of stannous tin to prevent the formation of stannic salt, because in some supporting elec-trolytes—e. g., dilute hydrochloric acid—stannic tin contributes to the diffusion current and hence its presence would lead to too high a value for the diffusion current constant of the stannous tin. A stock solution of stannous perchlorate in 1 N perchloric acid was prepared by dissolving pure tin in the acid solution in contach with a piece of platinized platinum wire to decrease hydrogen overvoltage: the solution was stored under a nitrogen atmosphere



		TA	BLE I. H	ALF-WAVE	E POTENTI	ALS			
(Values listed are	in volts z	s. the satur	ated calom	el electrode	at 25° C.	0.01% ge	latin is pres	ent in all	cases.)
Supporting Electrolyte	As	Bi	Sb	Sn(II)	Sn(IV)	Pb	Cd	Zn	Cu
0.1 N KCl 1 N HCl	-0.4	Insoluble -0.09	Insoluble -0.15	Insoluble -0.47	Insoluble -0.47	$-0.40 \\ -0.43$	$ \begin{array}{r} -0.60 \\ -0.64 \end{array} $	-1.00 a	+0.04 +0.04
1 N H2SO4	-0.7	-0.04	-0.32	-0.46	Insoluble	Insoluble	-0.59	a	-0.22 -0.00
1 N HNO3	-1.0 -0.7	-0.01	-0.30	-0.44	Insoluble	-0.40	-0.59	a	-0.01
1 N NaOH	N. R. b	Insoluble	-1.26	-0.73 °	N. R. b	-0.76	Insoluble	-1.53	-0.42
Acidic tartrate	-1.0	-0.29	-0.8	-0.20°	N. R. b	-0.48	-0.64	-1.23	-0.09
0.5 M sodium tar-	N. R.b	-0.7	-1.0	-0.33	N. R. b	-0.50	-0.64	-1.15	-0.12
Alkaline tartrate	N. R. b	-1.0	-1.2 - 1.32	-0.92	N. R. ^b	-0.75	-0.79	-1.42	-0.4d
$\frac{1 N \text{ NH}_{4}\text{Cl}}{1 M \text{ NH}_{3}} +$		Insoluble	Insoluble	-1.18 Insoluble	Insoluble	Insoluble	-0.81	-1.36	-0.24
^a Wave masked ^b Not reduced at	by final c	urrent incre ning electro	ease.						-0.50

^a Anodic wave. ^d See note under copper.



Figure 2. Polarograms of Arsenious Acid in 1 N Hydrochloric Acid in the Presence of 0.01 Per Cent Gelatin Concentrations of AssOs: (a) 0, (b) 0.196, (c) 0.385, (d) 0.742, and (e) 1.53 millimolar

in contact with excess metallic tin, and it was standardized by titration against a ceric solution at each time of use by the procedure already described (11). In all cases the concentrations were known with an accuracy of ± 0.3 per cent or better.

The supporting electrolyte solutions were also prepared from reagent quality materials, and in each case the purity of the solu-tion was checked by running a residual current curve. The concentrations of the components of the supporting electrolytes were known to within ± 10 per cent, which is a sufficiently rigorous tolerance as long as the concentration is large compared to that of the substance being determined.

The compositions of most of the supporting electrolytes are clearly shown in Tables I and II. The "acidic tartrate" solution (pH = ca. 4.5) comprised 0.4 *M* sodium tartrate and 0.1 *M* sodium hydrogen tartrate, and the "alkaline tartrate" solution (pH = ca. 13.0) was composed of 0.5 *M* sodium tartrate and 0.1 *N* sodium hydroxide. Goldin at a concentrative of 0.6

Gelatin, at a concentration of 0.01 per cent, was present in all cases as a maximum suppressor. A 0.2 per cent stock solution was used, and it was preserved effectively against mold growth and bacterial decomposition by addition of a few drops of toluene per 100 cc.

The residual current of each supporting electrolyte was determined and proper correction for it was applied in evaluating the diffusion currents (6).

Half-Wave Potentials and General Wave Characteristics

Table I contains a summary of the half-wave potential data that have been gathered in this study, the values being referred to the saturated calomel electrode at 25° C. The theoretical significance and practical utility for purposes of qualitative analysis of data of this kind have been discussed in detail elsewhere (6, 9).

The half-wave potential data of Table I are represented graphically in Figure 1, which is styled in accordance with

V. Majer's "polarographic spectrum" (3). This chart will be found more convenient than a tabular listing of data for purposes of orientation in planning analytical procedures. For example, suppose an alloy of antimony and lead is to be analyzed. A glance at Figure 1 shows that sodium hydroxide or alkaline tartrate would be the most suitable supporting electrolytes if antimony predominates, because in these media the lead wave precedes that of the antimony, but if lead predominates a hydrochloric acid medium should be used, so that the antimony wave will precede that of the lead.

The characteristics of the waves that are of analytical importance are discussed in the following paragraphs. These brief remarks are limited chiefly to new facts discovered in this investigation, and will serve to supplement previous descriptions (6).

ARSENIC. When present in the +5 state arsenic is not reduced at the dropping electrode under any conditions that have been tried to date.

Bayerle (2), Kacirkova (5), and Bambach (1) have shown that +3 arsenic produces complicated polarograms from strongly acid media. Some typical polarograms of arsenious



FIGURE 3. POLAROGRAMS OF ARSENIC

In (a) 1 N sulfuric acid, (b) 0.4 M sodium tartrate plus 0.1 M sodium hydrogen tartrate (pH = 4.5), and (c) 1 N sodium hydroxide. Concen-tration of +3 arsenie was 2.00 millimolar in each case, and 0.01% gel was present as a maximum suppressor.





acid obtained with 1 N hydrochloric acid as supporting electrolyte, and in the presence of 0.01 per cent gelatin, are shown in Figure 2.

The arsenic wave is seen to consist of two main parts with some semblance of a diffusion current plateau at -0.8 to -0.9 volt. The wave height at -0.8 volt is directly proportional to the con-centration of arsenious acid, and the diffusion current constant, $i_d/(Cm^{2/3}l^{1/6})$, is equal to 8.6 at 25° C. This value is almost twice as large as the corresponding values for antimony and bismuth (compare Table II), but since it is to be expected that the diffu-sion coefficient of the uncharged arsenious acid molecule will be larger than the diffusion coefficients of the chloro complex ions of larger than the diffusion coefficients of the chloro complex ions of larger than the diffusion coefficients of the chloro complex ions of antimony and bismuth, it seems reasonable to conclude that this wave corresponds to reduction of arsenious acid to the elemental state rather than to arsine. The poorly defined wave that starts at about -0.9 volt is probably due to reduction to arsine, as Kacirkova concluded; the height of the wave indicates that this reduction does not proceed completely. Curve *a* in Figure 3 is a typical polarogram of arsenious acid in 0.5 M sulfuric acid, and its character is similar to that obtained from hydrochloric acid. The development of the diffusion cur-rent is somewhat better than in hydrochloric acid, and it is linearly proportional to the concentration of arsenic. The wave obtained

rent is somewhat better than in hydrochloric acid, and it is linearly proportional to the concentration of arsenic. The wave obtained with 1 N nitric acid as a supporting electrolyte is virtually identi-cal in all respects with that obtained from dilute sulfuric acid. The data in Table II indicate that the diffusion cur-rent constants in 1 N sulfuric and nitric acids are practically identical with that in 1 N hydrochloric acid.

acid.

Curve c in Figure 3 demonstrates that arsenite ion in 1 N sodium hydroxide is not reduced at the dropping electrode.

Arsenite ion is not reduced from neutral or alkaline tartrate media, but a poorly developed wave is produced from an acidic tartrate supporting electrolyte, as shown by curve b in Figure 3. It is obvious that this wave is not suitable for analytical purposes.

BISMUTH. In agreement with the results of Bayerle (2), Kacirkova (5), and Page and Robinson (15), the author found that the +3bismuth wave is excellently defined in 1 N hydrochloric, nitric, or sulfuric acids, in the presence of 0.01 per cent gelatin as a maximum suppressor, as shown in Figure 4.

In 1 N hydrochloric acid $E_{3/4} - E_{1/4}$ was found to be 0.022 volt, compared to the theoretical value 0.019 volt (6). In 1 N nitric acid $E_{3/4} - E_{1/4}$ was equal to 0.026 volt, and in 1 N sulfuric acid it was equal to 0.050 volt. It follows from these data that the reduction of BiCl₄⁻⁻ from 1 N hydro-chloric acid proceeds reversibly, but the reduction of BiO⁺ from nitric or sulfuric acids is somewhat irreversible. However, all three supporting elec-trolytes are suitable for the determination of bis-

muth alone. In agreement with the conclusions of Page and Robinson (15) it was found that 1 N sulfuric acid is the best of these three supporting electrolytes for de-termination of bismuth in the presence of antimony (compare half-wave potential data in Table I).

Typical bismuth waves in acidic, neutral (pH =8.8), and alkaline tartrate media are shown in Figure 5.

The bismuth wave is well developed only in an acidic tartrate medium (pH smaller than about 7), and in tartrate medium (pH smaller than about 7), and in neutral or alkaline media (curves b and c) the waves are practically useless for quantitative purposes. Suchy (17) has stressed the use of a "neutral" tartrate supporting electrolyte, but since he added solutions of bismuth nitrate, which must have contained some free nitric acid, to a sodium tartrate solution, the solutions that he investigated must have actually had a pH value considerably smaller than that of a pure sodium tartrate solution. In the present experiments with "neutral tartrate" media the solutions were neutralized with sodium hydroxide to the pH of pure 0.5 M sodium tartrate (8.8 to 9.0) after the bismuth solution was added.

ANTIMONY. Antimony in the +5 state, like the corresponding compounds of arsenic, is not reduced at the dropping electrode from any of the supporting electrolytes so far studied.

Typical polarograms of +3 antimony in 1 N hydrochloric and 1 N nitric acids are shown in Figure 6 (see also Page and Robinson, 15). Both media are suitable for the determination of antimony in the absence of interfering substances, and, except for the peculiar irregularity near the top of the wave in hydrochloric acid, the wave forms are normal with excellent diffusion current plateaus.

The occurrence of the irregularity near the top of the wave (curve a, Figure 6) is dependent on the concentration of gelatin, and it disappears when the concentration of gelatin is increased above 0.01 per cent. It is significant that this ir-regularity was not observed by Page and Robinson (15), who used 0.1 per cent gelatin as a maximum suppressor.

The steep slope of the wave in 1 N hydrochloric acid corresponds closely to a reversible 3-electron reduction (probably of SbCl₄⁻), but the smaller wave slopes in nitric acid (and in sulfuric acid) indicate that the reduction of SbO⁺ is not perfectly reversible at the dropping electrode. Hydrochloric acid should be a









useful supporting electrolyte for determining antimony in the about supporting clocardy to the and other antimonial lead alloys—provided, of course, that interfering elements are either absent or have been removed. Page and Robinson (15) have shown that a hydrochloric acid medium is very suitable for determining antimony in various organic antimonial medicinals.

Polarograms of +3 antimony in 1 N sulfuric acid and 1 N sodium hydroxide are shown in Figure 7; the wave forms and diffusion currents in both media are very satisfactory.

The second small wave at -1.0 volt in 1 N sulfuric acid (curve a) may be due to partial reduction of the antimony to stibine; the smallness of this wave indicates that this reduction does not take place completely, and its presence precludes the determina-tion in the presence of antimony of other metals whose half-wave potentials in dilute sulfuric acid are more negative than about -0.8 volt.

The polarograms of antimony in tartrate media of various pH values, shown in Figure 8, demonstrate that only in an alkaline tartrate supporting electrolyte containing excess hydroxide ion is the diffusion current sufficiently well defined to be used for exact quantitative purposes (curve d), although

the wave in acidic tartrate medium (curve c) may be useful for semiguantitative work when other conditions preclude the use of an alkaline tartrate solution. The wave in neutral sodium tartrate solution in the absence of gelatin (curve a, pH about 9) is seen to comprise three distinct parts. Since reduction to oxidation states between +3and the metal is highly improbable, this triple wave probably corresponds to the existence of the +3 antimony in three different ionic and/or molecular states in a sodium tartrate solution, with the antimonyl tartrate ion predominating.

STANNOUS TIN. Excellently defined waves are obtained with 1 N hydrochloric acid, 1 N nitric acid, or 1 N sulfuric acid as supporting electrolyte when 0.01 per cent gelatin is present as a maximum suppressor, and as far as polarographic characteristics alone are concerned, all three media are equally suitable for the determination of stannous tin. In 1 N hydrochloric acid an indication of an anodic wave, corresponding to the oxidation of tetrachlorostannite ion to hexachlorostannate ion, was observed at about -0.1volt vs. the saturated calomel electrode, but the wave was too poorly developed to be of any analytical use.

Smrz (16) claimed that stannite ion in 1 N sodium hydroxide produced two cathodic waves at about -1.2and -1.55 volts, and that when a stannite solution was allowed to stand, the height of the first wave increased while that of the second decreased. He concluded that the first wave at -1.2 volts was due to the reduction of stannate ion produced by the slow disproportionation of stannite ion, but this conclusion is erroneous because stannate ion is not reduced at the dropping electrode (see below). The author's experience is considerably at variance with Smrz' results in other respects.

The polarogram of stannite ion in 1 N sodium hydroxide comprises a very well developed anodic wave at -0.73 volt, and only a single cathodic wave at -1.22 volts, as shown in Figure 9. The cathodic and anodic diffusion currents are exactly equal, and it is evident that the cathodic wave results from the reduction of stannite ion to the metallic

results from the reduction of stannite ion to the metallic state and the anodic wave corresponds to oxidation of stan-mite ion to stannate ion. The polarograms in Figure 9, and several others that have been obtained, show no indica-tion of the second cathodic wave at -1.55 volts that Smrz reported. From the fact that the anodic half-wave po-tential is -0.73 volt, whereas the reversible potential of the stannite-stannate couple is -1.21 volts vs. the S. C. E., it is clear that the oxidation of stannite ion proceeds irreversibly at the drop-ping electrode. The cathodic half-wave potential is several tenths of a volt more negative than one would predict from the reversible potential of the stannite-tin couple and a reasonable estimate of the free energy of formation of tin amalgam, from which it must be concluded that the reduction of stannite ion also takes place irreversibly. This irreversibility of the electrode reactions is of no importance in practical analytical work, since the diffusion currents are so well defined.

Stannite ion in 1 N sodium hydroxide is unstable to the extent of about 7.7 kcal. per mole with respect to disproportionation into Stannate ion and metallic tin (\mathcal{S}) , and therefore when it is used as a determining form of tin the solution must be freshly prepared and protected carefully from air oxidation. However the author observed no change in any of the characteristics of the stannite wave after a solution stood for one hour protected from atmos-pheric oxygen, and hence with pure solutions the disproportion-ation evidently takes place slowly. This may not be true with impure solutions, or in the presence of metallic tin.

The polarogram of stannite ion in sodium hydroxide medium is very similar to that of stannous tin in an alkaline tartrate solution (11), and the cathodic and anodic half-wave potentials in the two media are almost identical (compare Table I). Furthermore, inspection of the data in Table II shows that the diffusion current constant in an alkaline tartrate solution (2.86) is about midway



FIGURE 7. POLAROGRAMS OF 2.50 MILLIMOLAR +3 ANTIMONY In (a) 1 N sulfuric acid and (b) 1 N sodium hydroxide, in the presence of 0.01% gelatin

between the value in an acidic tartrate solution (2.41) and that of stannite ion (3.45). It may be concluded that a considerable proportion, although not all, of the stannous tin in an alkaline tartrate solution actually exists as stannite ion.

The characteristics of the stannous waves in various tartrate media have been discussed in a previous paper (1).

STANNIC TIN. Curve a in Figure 10 is a typical polarogram of stannic tin in 1 N hydrochloric acid; the character of the wave leaves much to be desired. Since the limiting current is not well developed, but increases uniformly with increasing negative potential, the wave cannot be recommended for exact quantitative work.

The small pre-wave starting at about -0.05 volt, whose height does not correspond to any integral electron requirement, indicates that in addition to the predominating SnCl6 - ion the solution also contains stannic tin in another form that is more easily reducible. Furthermore, the fact that two separate waves are obtained shows that the equilibrium between the two species is established very slowly. In view of the well-known tendency of stannic chloride solutions to hydrolyze slowly, even in the presence of a relatively high concentration of hydrogen ion, it is likely that the more easily reducible species is a hydrolysis product of some sort. The half-wave potential of the main stannic wave in a hydrochloric acid medium is identical with that of the stannous wave (compare Table I).

Stannic tin in either 1 N sulfuric or nitric acids is too greatly hydrolyzed, with the precipitation of basic salts, to permit the use of these media as supporting electrolytes.

Stannic tin is not reduced from its solutions in sodium hydroxide (curve b, Figure 10), nor from any of the three tartrate solutions. Although this is rather disappointing from the standpoint of determining tin itself, it will probably prove to be advantageous in connection with the determination of other metals, such as antimony, bismuth, or lead, in the presence of stannic tin.

LEAD. The lead waves from 0.1 N potassium chloride, 1 N hydrochloric or nitric acids, and 1 N sodium hydroxide are very well developed with excellently defined diffusion currents. All these media can be recommended for the determination of lead.

Normal well developed waves are also obtained from the various tartrate media, except that in an alkaline tartrate





a. 0.91 millimolar potassium antimonyl tartrate in 0.5 M sodium tartrate. b. Like a except 0.01% gelatin present. c. 0.86 millimolar potassium anti-monyl tartrate in 0.4 M sodium tartrate plus 0.1 M sodium hydrogen tartrate plus 0.01% gelatin. d. 0.71 millimolar potassium antimonyl tartrate in 0.5 M sodium tartrate plus 0.1 N sodium hydroxide plus 0.01% gelatin. Each curve starts at -0.3 volt.



FIGURE 9. POLAROGRAMS OF STANNITE ION N sodium hydroxide in the presence of 0.01% gelatin. Concentrations of tin: (a) 3.04, (b) 5.59 millimolar. In 1

solution the wave requires a fairly great voltage span (ca. 0.4 volt) for full development of the diffusion current.

CADMIUM. With either 1 N hydrochloric or nitric acid as supporting electrolyte the cadmium wave is excellently defined and both media are suitable for quantitative purposes.

The wave obtained from 1 N sulfuric acid can be recommended only for qualitative or rough quantitative measurements because the diffusion current does not reach a perfectly constant value, but increases gradually with increasing negative potential up to the potential of hydrogen discharge. It may be possible to obtain a better diffusion current in a more dilute sulfuric acid solution, but this has not been investigated.

With either an acidic or neutral tartrate supporting electrolyte the wave form is entirely normal with a very good diffusion current plateau, and both media can be recommended for the quantitative determination of cadmium.

On the other hand, an alkaline tartrate supporting electrolyte is not suitable for the determination of cadmium. In such a medium the wave itself is well enough defined, but the limiting current is abnormally small and it is not directly proportional to the concentration of cadmium. For example, in a typical series of experiments the quantity $i_d/(Cm^{2/3}t^{1/6})$ decreased from 1.36 to 0.33 when the cadmium concentration was increased from 1 to 18.6 millimolar. These data show that the limiting current is not diffusion controlled, and hence it has little analytical value.

The wave obtained from an ammoniacal supporting electrolyte is normal in all respects with an excellent diffusion current plateau.

ZINC. Zinc cannot be determined in the presence of a large concentration of hydrogen ion, because the wave is masked by hydrogen evolution.

The reduction of zincate ion from 1 N sodium hydroxide produces a well developed wave; the diffusion current is reached just before the discharge of sodium ion.

Well defined waves are also obtained from neutral or alkaline tartrate media. The voltage span of these waves is rather large (ca. 0.4 volt). from which it is evident that the reduction of the tartrate zinc complexes is not thermodynamically reversible, but in both cases a satisfactory diffusion current plateau





is developed. A distinct wave is also produced in an acidic tartrate medium, but the diffusion current is masked by hydrogen discharge and the wave can be used only for qualitative purposes.

The wave of the tetramminozinc ion from an ammoniacal supporting electrolyte is beautifully developed, and its slope corresponds closely to the value expected for a reversible 2electron reduction.

COPPER. Typical polarograms of cupric copper in 1 N hydrochloric, nitric, and sulfuric acids are shown in Figure 11.

The double wave in a concentrated chloride solution is similar to the characteristic double wave produced in the presence of ammonia, pyridine, and other substances that stabilize the +1 state of copper by complex formation (6, 9). In 1 N hydrochloric acid the first wave results from reduction of the +2 copper (probably present as CuCl₁⁻⁻) to the dichlorocuprite ion, CuCl₂⁻, and the second wave corresponds to further reduction of the dichlorocuprite ion to the metal. The exact half-wave potential of the first stage of the reduction in 1 N hydrochloric acid cannot be accurately measured, since it is more positive than the anodic dissolution potential (calomel electrode potential) of mercury, and the wave starts from zero applied e. m. f. From the instability constant of CuCl₂⁻ (2.9 × 10⁻⁶) quoted by Latimer (8) and the standard potential of the cuprous ion-copper amalgam couple (+0.144 volt vs. the S. C. E.), and by relations that have already been described (6, 9), the half-wave potential of the second wave should be -0.183 volt vs. the S. C. E. for the reversible reduction of CuCl₂⁻. The observed value (-0.22 volt) agrees sufficiently closely with the theoretical value to indicate that the reduction is reversible at the dropping electrode. From the character of the first wave, and also from a visible amalgam formation, it is evident that +2 copper is reduced by mercury in 1 N hydrochloric acid, and hence a separate anode, rather than a quiet pool of mercury as anode, should be used in practical analytical work in order to minimize contact of the solution with mercury. It is usually most convenient to measure the total height of the double wave. In both 1 N nitric and 1 N sulfuric acids the reduction of +2

In both 1 N nitric and 1 N sulfuric acids the reduction of +2 copper produces only a single wave, the reduction proceeding directly to the metallic state. The wave form in 1 N nitric acid is normal (curve b, Figure 11), but in 1 N sulfuric acid a peculiar semblance of a minimum is noted in the diffusion current (curve c, Figure 11) and this is followed by a gradually increasing current. Therefore, 1 N sulfuric acid cannot be recommended for the quantitative determination of copper, except when it is present at very small concentrations, nor for the determination in the presence of copper of more difficultly reducible substances.

In 1 N sodium hydroxide the +2 copper wave is perfectly normal and the diffusion current is very well defined. How-

ever, since the solubility of cupric hydroxide in 1 N hydroxide ion is small (ca. 0.001 M), sodium hydroxide possesses only limited usefulness as a supporting electrolyte for the determination of copper in practical analytical work.

The characteristics of the cupric wave in tartrate media have been discussed in a previous paper (11). The waves from acidic or neutral tartrate solutions are excellently developed. In an alkaline tartrate solution a small "pre-wave" occurs at about -0.4volt, and the diffusion current of the main wave at -1.6 volts is masked by the final increase in current from the reduction of sodium ion. It may be possible to eliminate the pre-wave by employing a more alkaline tartrate solution than that used in this study; if this is successful, it will provide a more convenient means than a prior chemical separation of eliminating the interference of copper in the determination of other metals in copper-base alloys.

Diffusion Current Constants and Their Application to Practical Analyses

An ideal polarographic procedure would permit the determination of a substance from a single

polarogram, or even from a single measured value of the diffusion current, without the necessity of calibrating the particular dropping electrode that is used with known concentrations of the substance in question. In addition to placing polarographic analysis on a relatively "absolute" basis, such a procedure possesses the important practical advantage of saving the considerable amount of time that must otherwise be spent in preparing standard solutions of each substance to be determined and in obtaining calibration polarograms. Chiefly as a result of the fundamental studies that were made by Ilkovič in Professor Heyrovský's laboratory in Prague (4), the factors which govern a polarographic diffusion current are now so well known that the application of this simplified technique to practical analyses is perfectly feasible, when certain fundamental data are available.

It was first demonstrated by Ilkovič (4), and later confirmed by others (6, 12), that the diffusion current is expressed completely and quantitatively by the following equation:

$$\dot{n}_d = kn D^{1/2} C m^{2/3} t^{1/6} \tag{1}$$

in which i_d is the diffusion current in microamperes, n is the number of electron equivalents per molar unit of the electrode reaction, D is the diffusion coefficient (sq. cm. per second) of the reducible or oxidizable substance, C is its concentration in millimoles per liter, m is the rate of mercury flow from the dropping electrode in mg. per second, and t is the drop time in seconds. The theoretical significance and general practical utility of this relation have been discussed in detail by Kolthoff and Lingane (6), and its validity has been definitely established, particularly as regards the linear dependence of i_d on C and on the quantity $m^2/t^{1/6}$. Since k, n, and D are independent of the characteristics of the dropping electrode capillary, the quantity $knD^{1/2}$, which is experimentally determinable as $i_d/(Cm^{2/3}t^{1/6})$, is a fundamental constant for any given substance, and is referred to below as the "diffusion current constant". This term has previously been applied to the ratio i_d/C (6), but since this ratio depends on the properties of the dropping electrode capillary—i.e., on $m^2/3t^{1/6}$ —it is recommended that this usage be discontinued in favor of the more fundamental quantity $i_d/(Cm^{2/3}t^{1/6})$.

According to theoretical considerations (6), constant k in Equation 1 should be equal to 605 at temperatures between about 15° and 40° C., when the other quantities are expressed in the units indicated above. The approximate correctness of this value has been verified experimentally in the few cases where sufficiently accurate values of diffusion coefficients are available to permit a comparison (6). In most cases, however, it is not possible to employ this theoretical constant to calculate diffusion

	т	ABLE II.	DIFFUSIC	N CURRE	NT CONST.	ANTS			
[Values listed are id/(Cm I	n all cas	t 25° C. Vi es 0.01% g	alucs in itali elatin was p	cs are uncer present as s	tain becaus maximum	e of poorly d auppressor.	lefined diffu }	sion cu	rents.
Supporting Electrolyte	Ав	Bi	Sb	Sn(II)	Sn(IV)	Pb	Cd	Zn	Cu
0.1 N KCl 1 N HCl 0.5 M H ₂ SO ₄ 1 N HNO ₃ 1 N NAOII Acidic tartrate 0.5 M sodium tartrate Alkaline tartrate 1 N NH ₄ Cl + 1 M NH ₈	8.6 8.4 8.8 N. R. b c N. R. N. R.	Insoluble 5.23 4.31 4.64 Insoluble 3.12 3.0 c Insoluble	Insoluble 5.54 4.94 5.10 4.54 <i>S.4</i> <i>S.9</i> 3.54 Insoluble	Insoluble 4.07 3.54 4.02 3.45 2.41 2.48 2.86 Insoluble	Insoluble 4.8 Insoluble N. R. N. R. N. R. N. R. N. R. Insoluble	3.80 3.86 Insoluble 3.67 3.39 2.37 2.30 2.39 Insoluble	3.51 3.58 2.6 3.06 Insoluble 2.34 2.34 d 3.68	3.42 a 3.14 2.30 2.65 3.99	3.23 3.39 2.12 3.24 2.91 2.37 2.24 a 3.75
^a Diffusion current ma ^b N. R., not reducible ^c No definite limiting	sked by current.	final curren	t increase (discharge of	hydrogen o	or sodium io:	n).		

current constants with any degree of accuracy, because diffusion coefficient data under the conditions existing in polarographic measurements are not to be found in the literature; therefore these constants must be determined experimentally.

Table II contains a summary of the diffusion current constants of the metals with which the present investigation is concerned. Except for the values in italics, which are more or less uncertain because of imperfectly developed diffusion currents, the values are believed to be generally accurate to ± 2 per cent. The values for lead, cadmium, and zinc in 0.1 N potassium chloride are taken from a previous compilation (6, 12), and that for copper in the same medium is based on the measurements of Kolthoff and Orlemann (7). All other values were determined in the present study.

The data in Table II can be applied directly to the analysis of unknown solutions of these metals in these particular supporting electrolytes. If we represent the diffusion current constant by I, then the concentration in an unknown case will be given by

$$C = \frac{i_d}{Im^{2/3}t^{1/6}} \tag{2}$$

In addition to a knowledge of the diffusion current constant, this method requires that the quantity $m^{2/3}t^{1/6}$ be known for the capillary that is used, but the determination of mand t by a technique that has already been described (10) requires only a very few minutes' time, and obviously it is much simpler than the preparation of a standard solution for each substance.

The reliability of this technique depends primarily on the existence of a linear relation between i_d and $m^{2/3} t^{1/6}$. Basing their opinion on the excellent work of Maas (14), Kolthoff and Lingane (6) have concluded that this relation is obeyed with an accuracy of at least ± 1.5 per cent. From more recent experience the author is convinced that with *m*-values in the usual range from about 1 to 3 mg. per second, and drop times between about 2 and 4 seconds, the accuracy of this relation is as good as the accuracy with which one can measure a diffusion current.

Although *m* is independent of the potential of the dropping electrode and the medium in which the mercury drops form, the drop time, and hence $m^{2/3} t^{1/6}$, changes appreciably with changing potential and also with the medium (6, 7). Therefore, *m* can be determined with the mercury drops forming in air (10), but it is essential that the drop time be determined in the same medium and at the same potential at which the diffusion current is measured (6, 7).

Although the diffusion current constant is independent of the properties of the dropping electrode, it does depend on temperature and on the composition of the supporting electrolyte, because the diffusion coefficient is a function of these factors (6). In most cases the temperature coefficient is in the neighborhood of 1.5 per cent per degree, which requires that the temperature be controlled to at least $\pm 0.5^{\circ}$, prefer-

ably at 25° C. Usually the composition of a supporting electrolyte is of more importance than its exact concentration, provided that the concentration is relatively large; in many instances the concentration can be varied by as much as a factor of 2, or even more, without seriously changing the diffusion current constant, although this should never be taken for granted without experimental verification. As a general rule the diffusion current constant of a substance is not influenced by the simultaneous reduction or oxidation of other substances at the dropping electrode, and the values listed in Table II are applicable to mixtures of the various metals.

Gelatin, which is commonly used as a maximum suppressor, frequently has a marked influence on the diffusion current constant, and hence its concentration must be controlled carefully and should not be larger than is actually necessary; 0.01 per cent is usually ample.

In addition to their practical analytical value, the data in Table II are also of theoretical interest because they lead directly to values for the diffusion coefficients, and hence constitute a measure of the apparent sizes, of the various ions. The diffusion current constants of cadmium, zinc, and copper are largest in ammoniacal medium, from which it follows that the ammino complex ions of these metals must be smaller, and perhaps also less subject to the restraining effects of interionic attraction, than the complexes present in the other media. The values for lead, cadmium, zinc, and copper in 1 N hydrochloric acid are only slightly larger than in 0.1 N potassium chloride, and the difference is of the same order of magnitude in each case.





In all cases, except that of copper, the diffusion current constants in the three mineral acids and in sodium hydroxide decrease in the order hydrochloric acid > nitric acid > sulfuric acid > sodium hydroxide, which indicates that the chloro complexes in hydrochloric acid are smaller than the aquo complexes that predominate in nitric and sulfuric acids, and that these in turn are smaller than the hydroxo complex ions present in sodium hydroxide solution.

The values in the tartrate media are smaller than in the other media, which is to be expected in view of the relatively large size of a tartrate complex ion. Furthermore, the diffusion current constants correspond to practically identical values for the diffusion coefficients of the tartrate complexes of the various metals. This leveling effect is doubtless due to the fact that the coordinating tartrate ions are so large compared to the size of the central metal ion, that differences in the size of the central ion, and even in the type and orientation of the bonds, have only a slight influence on the effective sizes of the different complexes.

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An Apparatus for Quantitative Catalytic Hydrogenation

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THE apparatus for catalytic hydrogenation recently described by Noller and Barusch (3) is very useful when not more than 50 ml. of hydrogen are to be absorbed; however, it is not suitable for the many occasions when it is necessary to meter with some degree of accuracy as much as several hundred milliliters of hydrogen. The apparatus pictured (Figure 1) fills the entire gap between a strictly micro apparatus and the standard Adams (Burgess-Parr) machine.

This apparatus is a combination, with certain modifications, of features previously reported. The buret system is similar to that described by Fieser and Hershberg (2) and the reaction flask together with the stirring device is a slight modification of the one used by Noller and Barusch (3). The 50-ml. buret is for small-scale work and the 500-ml. buret is used for larger runs. If more than 500 ml. of hydrogen are to be absorbed, the stirring is slackened or momentarily stopped while the buret is quickly refilled with hydrogen. All the stopcocks are the oblique-bore high-pressure type manufactured by Eck and Krebs, New York, N. Y., who fabricated the glass parts of this apparatus. For those who wish to construct their own apparatus, attention is called to the pressure stopcock recently described by Connelly (1). A somewhat less elegant, although reasonably satisfactory, method is to use rubber bands to keep the stopcocks seated firmly. Ordinary stopcocks with none of these precautions will leak hydrogen, especially if extra internal pressure is applied during the hydrogenation as described below.

Flasks of the three sizes indicated afford flexibility in the volume of liquid that can be used, and small coil springs keep the greased ground-glass joint tightly sealed. This joint is reversed to minimize the danger of contamination of the flask contents with grease. A critical dimension is the height of the apparatus, which should not be less than 1 meter, in order that the system may be subjected to either a vacuum or the pressure of an extra atmosphere without forcing mercury out of the manometer, Some experimenters will prefer using water or the solvent being employed in the hydrogenation as the displacing fluid instead of mercury, especially in view of the current limited availability of mercury. Increased accuracy can probably be obtained if the amount of dead space is reduced by using capillary tubing of about 3-mm. bore in place of the 10-mm. outside diameter standard tubing indicated for the manometer and connections. Unless care is exercised, the stirring may become vigorous enough to drive the stirrer through the wall of the flask, but encasing the iron core in a material such as Saran, instead of glass, may be at least a partial solution of this difficulty.

The air can be displaced from the apparatus by opening the flask stopcock and sweeping with hydrogen; however, unless care has been taken to trap hydrogen in the buret by closing the buret stopcock at the end of the previous hydrogenation, mere sweeping may leave a pocket of air in the buret. It is prudent, therefore, to open the buret stopcock, raise the mercury to a point near the top of the buret, close the screw clamp, and, with the flask stopcock closed, successively evacuate and flood the system with hydrogen three or four times by manipulating the three-way stopcock. Any addition of catalyst or compound after the system has been filled with hydrogen is made by washing the material through the cup into the flask with a little solvent after the internal pressure has been reduced by lowering the mercury in the buret. A small amount of solvent is allowed to remain in the cup, so that air is not admitted to the system. The sequence of addition of catalyst and reagents can be left to the discretion of the investigator; in many cases it is convenient to have the sample in the flask before attaching it to the buret system, but where a highly volatile substance is to be hydrogenated, it is preferable to introduce it through the cup after the sweeping or evacuation procedure has been completed. The catalyst can be reduced in the presence of the sample or the catalyst can be reduced first, a reading taken, and then the compound added through the cup. The former procedure provides a somewhat more active catalyst, whereas the latter has the advantage of eliminating the necessity of making a blank run to determine the amount of hydrogen absorbed by the catalyst.

Before the initial volumetric reading is taken, the height of the mercury in the buret is adjusted so that the pressure inside the system is equal to the atmospheric pressure, as evidenced by the same mercury level in both arms of the



FIGURE 1

manometer. A facile way of doing this is to raise the level of the mercury in the buret until the internal pressure slightly exceeds the atmospheric pressure and then vent the excess hydrogen to the atmosphere by momentarily opening the three-way stopcock. During the reduction, up to about one atmosphere pressure can be applied by raising the mercury level in the buret and closing the screw clamp, remembering that the internal pressure must be equalized with the atmospheric pressure before reading the volume.

The apparatus lends itself very easily to correction for changes in barometric pressure during the experiment, since with the aid of the manometer and leveling bulb a measured differential between the internal and atmospheric pressures can be created at will before making the final volumetric reading. For example, if the barometric pressure increases 5 mm. during the experiment, the mercury in the buret is adjusted so that the level in the right (open) arm of the manometer is 5 mm. below the level in the left (closed) arm before the volume is read. The absolute pressure in the system will then be the same as at the beginning of the experiment.

It is desirable to operate in a constant-temperature room but, in the absence of such a room, temperature changes during the experiment also can be compensated for by proper adjustment of the internal pressure in relation to the atmospheric pressure. If the temperature increases during the experiment, the mercury in the buret should be

adjusted so that the internal pressure is greater than the atmospheric pressure before making the final volumetric reading; and, vice versa, if the temperature decreases, the internal pressure should be adjusted so that it is less than the atmospheric pressure. Calculation shows that for this purpose a pressure differential of about 2.5 mm. of mercury corresponds to a change of 1° C. If both the pressure and temperature change, the algebraic sum of both corrections is used in adjusting the manometer levels:

$$\Delta P = P_i - P_f + (T_f - T_i) P_i/T_i$$

where ΔP is the increment which the internal pressure should be adjusted in excess of the atmospheric pressure at the end of the experiment-i. e., the number of millimeters the mercury level in the open arm of the manometer must be set above the level in the closed arm. P; is the initial barometric pressure minus the vapor pressure of the solvent at the initial absolute temperature, T_i ; P_f and T_f are the corresponding net pressure and temperature at the end of the experiment. Since these are all known, ΔP is easily calculated. In this way the final volume corrected to the initial temperature and pressure is read directly. The net volume of hydrogen absorbed is then corrected to standard conditions in the usual manner.

Although no rigorous comparison has been made with the rate of hydrogenation obtained when using a

shaking device, it can be shown that magnetic stirring affords reasonably rapid reduction. For example, reduction of 1.5 grams of nitrobenzene in ethanol solution was complete (900 ml. of hydrogen) in 1.25 hours although the Adams catalyst used (25 mg.) was over two years old.

Acknowledgment

The collaboration of W. Nudenberg, H. A. Fouche, R. E. Davis, and L. W. Butz of the United States Department of Agriculture is gratefully acknowleged.

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Photoelectric Photometer for Determining Carbon Disulfide in the Atmosphere

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FIGURE 1. PHOTOELECTRIC PHOTOMETER

THE problem of developing quick accurate methods for determining concentrations of toxic vapors has been receiving increased attention the past few years. Good analytical methods exist, generally based on colorimetry, for many vapors including carbon disulfide. Although these methods are usually very accurate, the large volume of air required for the sample precludes obtaining anything but an average concentration taken over a time interval that may run as high as 15 minutes or more.

Some of the methods of "grab" sampling for carbon disulfide have been developed to a degree which enables them to be used in continuous recording procedures $(\mathcal{S}, 4, \delta)$. These methods have all depended upon some secondary phenomenon, such as color produced by carbon disulfide vapor in

solutions of copper acetate and diethylamine in methyl Cellosolve; the conductivity produced in an aqueous solution of sulfur dioxide formed by burning carbon disulfide or the turbidity of a fog produced by first oxidizing the carbon disulfide to sulfur dioxide, and further oxidizing the sulfur dioxide to fog-producing sulfur trioxide. The color produced

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kins University, Silver Spring, Md. A photoelectric photometric method has been developed for measuring carbon disulfide in the atmosphere. The range of concentrations covered is 2 to 200 p. p. m. by volume. Time required for an individual determination is 1 minute or less, and the accuracy is 1 p. p. m. The apparatus may be run continuously with a resolving power of 5 to 10 seconds, and an accuracy of 4 p. p. m.

by the first reaction, the conductivity produced by the second, and the fog produced by the third all permit the use of accurate recording by electric or photoelectric devices. The accuracy remains high, but appreciable lag still exists between time of sampling and actual registry of contamination.

Obviously, a desirable method of recording is one which depends upon some primary property of carbon disulfide; in particular, some property which permits an almost instantaneous quantitative measurement on some form of meter. Such a method has been developed for other organic vapors. The apparatus consists of a simple, sensitive, and rapid ultraviolet photometer which was designed by V. F. Hanson, Electrochemicals Division, du Pont Co. (2). The present paper deals with the development of a very similar photom-



FIGURE 2. DIAGRAM OF APPARATUS

TUBE TO SAMPLING AREA



FIGURE 3. LAMP END OF ABSORPTION SYSTEM





eter, adapted to the specific problem of detecting carbon disulfide.

Optical Basis of the Instrument

Carbon disulfide has an intense absorption in the region of 3100 Accordingly, an absorption tube was set in front of a monochromator, and with a mercury arc for a light source the absorption coefficient for carbon disulfide at the mercury line 3132 was It was found that a column of carbon disulfide determined. actermined. It was found that a contain of carbon distinct vapor 1 cm, thick at 1 per cent concentration absorbed 5 per cent. Assuming Beer's law to hold, this indicates that an optical path 80 cm. long would be required for a concentration of 1 p. p. m. to produce an absorption of 0.02 per cent. The figure of 0.02 per cent was selected because it is the smallest change in light in the term that we be detected neurotecht with the present amplifier tensity that can be detected accurately with the present amplifier.

The absorption of carbon disulfide in this region is a matter of very good fortune, for none of the ordinary constituents of the atmosphere absorbs in this region-for example, Hanson's work on organic solvents showed extremely weak absorption at 3130 Å., although these materials absorbed very strongly at 2536 Å. [Ozone absorbs strongly enough at 3130 Å. to be measurable, as shown by Dobson (1); but it can be disregarded as a possible contaminant in ordinary processes which involve carbon disulfide.] Furthermore, none of the other contaminating vapors from the viscose process, such as hydrogen sulfide, absorbs in this spectral region. Theoreti-

cally, then, to determine the amount of carbon disulfide in the air, it is only necessary to set up an absorption tube some 80 cm. long, isolate the 3132 mercury line, and set up an amplifier capable of detecting sufficiently small changes in current.

Instrument Design

The instrument minus power supply is shown in Figure 1. The entire unit is mounted on a pneumatic-tired truck to permit easy transportation to the desired areas.

The apparatus is shown schematically in Figure 2. The light source is a G. E. AH-4 mercury lamp with glass envelope re-moved. Radiation from the lamp is rendered roughly parallel by condensing lenses of quartz, and reflected down the absorption

tubes by totally reflecting prisms of quartz. The lamp end of the absorption system is shown in Figure 3. The light is received by a pair of matched G. E. FJ-405 sodium photocells. The ends of the absorption tubes are closed with windows of Corex D glass. This glass in combination with the addition of the solution of sodium cells gives a system with about 60 per cent of its response due to 3132, 30 per cent due to 3650, 10 per cent due to miscel-laneous background, and 0 per cent due to 2536. No absorption has ever been found at 3650 for any samples of air drawn from various parts of the plant areas; accordingly the radiation of this line assumes the character of a constant background, divided equally between the two cells.

The electrical hookup is shown in Figure 4, and is very similar to the amplifier used by Hanson (2). The bias circuit is employed to establish a fiduciary zero in the plate circuit. Rough zero setting is obtained by the potentiometer, and accurate balance is obtained by the motion of the micrometer screws; these latter are ac-curately centered with 0.6-cm. (0.25inch) extension rods which travel vertically across the faces of the photo-cells. A vertical motion of 0.025 mm. cells. (0.001 inch) of either of the rods produces a change in light intensity of approximately 0.05 per cent. Micrometer 2 is equipped with a vernier dial to be used in calibrating absorption vs. concentration.

In addition to optical symmetry, current and voltage regulation is necessary to obtain the needed photo-metric accuracy. The constant-current constant-voltage circuit is shown in Figure 5. The voltage is held con-stant by a Sola 110-volt 125-watt voltage-regulating transformer. The

output of this transformer is fed into a resonance network whose characteristics were determined by trial and error after a pre-liminary rough estimate of the impedances. The present setup holds the current in the AH-4 lamp at about 0.25 ampere; the lamp perates very steadily, and may be expected to have a satisfactory life of some hundreds of hours before any unsteadiness sets in.

Operation of the Analyzer

The apparatus is first adjusted by setting switch B to the biasing position, and adjusting the bias rheostat, S, for a suitable



FIGURE 5. CONSTANT-CURRENT CONSTANT-VOLTAGE CIRCUIT

- C.
- R S
- 3.5 mfd. 2 henrics, 0.5 ampere 1000 ohms, 100 watts G. E. H-4 mercury lamp, envelope removed 110-volt, 125-watt Sola voltage regulator G. E. H-4 lamp transformer



plate current reading. B is then set to throw the photocells in the circuit; with the balancing rheostat, W, set near the middle and with the two micrometer screws set to give shadows about 0.9 cm. (0.375 inch) long on the cell windows, the lamp is adjusted to give about the same plate current reading as the bias. Final adjustment to this fiduciary zero is made with micrometer 1 and the potentiometer.

adjustment to this inducatly zero is induc when introduced a line the potentiometer. The air sample is introduced into the apparatus by means of a positive pressure pump. The outlet of the pump leads the air to the following train: (1) a can containing raw cotton to remove traces of pump oil, (2) a moisture trap containing magnesium perchlorate or anhydrous calcium sulfate, and (3) an Alfrax porous filter for removing dust particles. This purification train absorbs no carbon disulfide, and has proved satisfactory over several months' use.

A 4-way stopcock arrangement is provided for passing the sample through one absorption tube, and then through a bed of activated charcoal to the second tube. In this way the instrument always compares transmission through a contaminated column with transmission through an uncontaminated column, and very minute deviations from electrical balance can be detected. As the microammeter in the plate circuit deflects from the fiduciary zero, it is brought back by moving micrometer 2.

The time of reading, together with the time required to flush a new sample through the absorption train, is about 20 seconds. The accuracy is 2 p. p. m., taking the colorimetric method (3) as standard. The accuracy may be improved to 1 p. p. m. by using the reversing mechanism provided by the 4-way stopcock, which requires two readings for each determination. Figure 6 shows a typical calibration curve.

For purposes of reading rapidly changing concentrations,

the deflection of the microammeter itself may be calibrated, with the micrometer screws being left untouched throughout the run. The microammeter deflection is linear with carbon disulfide concentration up to more than 50 p. p. m., and the accuracy is 4 p. p. m.

The time variation in the carbon disulfide concentration at a fixed station in a purposely poorly ventilated mixing room is shown in Figure 7. The pump was run continuously, and readings were noted at intervals of 10 seconds. The general level at this station is shown at the beginning of the cycle and is around 5 p. p. m. During the run instantaneous readings as high as 50 p. p. m. A simultaneous check by the colorimetric chemical method gives values ranging from 14 to 18 p. p. m. Similar checks run at a number of locations show



FIGURE 7. CHART OF IMPROPERLY VENTILATED BARATTE



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that on the average the discrepancy between the two methods does not exceed 15 per cent for integrated runs.

Acknowledgment

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Yolk Nomograph for Mayonnaise and Salad Dressing

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IN CONNECTION with the determination of commercial egg yolk in mayonnaise and salad dressing, Cahn and Epstein (2) presented the equation

 $Y = \frac{2899P - 69N}{g - 12.2}$

where

- Y = per cent of commercial yolkP = per cent phosphorus pent-
- oxide
- N = per cent nitrogeng = per cent solids content of yolk

This equation, consistent with those of the Association of Official Agricultural Chemists (1)and based on the analytical data of Mitchell (3), can be solved conveniently and accurately by means of the accompanying nomograph. The use of the chart is illustrated as follows:

What is the percentage of commercial egg yolk, containing 43 per cent solids, in mayonnaise which tests 0.08 per cent phosphorus pentoxide and 0.11 per cent nitrogen? Following the key, connect 0.08 on the *P* scale with 0.11 on the *N* scale and note the intersection with the α axis. Connect this point with 43 on the *g* scale and read the percentage of egg yolk on the *Y* scale as 7.3.

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Improved Steam-Distillation Apparatus

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THE determination of nicotine by the conventional steam-distillation method (1) has long been known to have several decided disadvantages. The apparatus is bulky. Because bumping and foaming occur, considerable attention is required during distillation. Since a large volume of distillate must be collected, the time for distillation is rather long.



Kirk (2) has modified the Pozzi-Escot (3) apparatus in the construction of micro-Kjeldahl distillation apparatus. An adaptation (Figure 1) of this type of still has proved exceedingly satisfactory for the steam distillation of steamvolatile alkaloids on the macro scale. This modification requires the use of a separate steam generator.

The sample is placed in the inner chamber, A, paraffin and alkali are added, and the trap and condenser are connected at the glass joint, B, which is lubricated to prevent freezing. The initial volume of the sample and alkali should be as small as Initial volume of the sample and alkali should be as small as practical, preferably less than 25 ml. for an inner chamber with a total volume of 150 ml. Steam is driven in through C and passes into the inner chamber through D. The drain, E, is closed by rubber tubing and a pinchcock, and the distillate is collected at F. Where paraffin is added to prevent frothing, some will be carried over into the distillate; but in the case of alkaloids presented the adjust the distillate does be the distillate is collected at F. Where paraffin is added to prevent frothing, some will be carried over into the distillate; but in the case of alkaloids precipitated as silicotungstates and filtered through tared Gooch type crucibles this offers no objection.

This still has many advantages over the conventional apparatus. The compact construction allows for setting up batteries where large numbers of determinations are to be made. The heating of the distillation chamber by the steam in the outer jacket, together with the entrance of steam at the bottom of the inner chamber, eliminates the possibility of bumping. The apparatus is easily cleaned by drawing the spent sample into the steam jacket, rinsing well, and allowing the jacket to drain. The narrow inner chamber increases the length of liquid-vapor contact, thereby hastening the distillation. The ground-glass joint at the top of the distillation chamber affords a means for introducing the sample, alkali, etc., aids in cleaning, and makes the apparatus less rigid, thereby diminishing the danger of breakage. It is possible to take much smaller samples than are ordinarily used for analysis.

The volume of the distillate is dependent on the size of the sample used: 25 mg. of nicotine distilled quantitatively in 100 ml. of distillate and 50 mg. in 150 ml. The accuracy of the results obtained with the apparatus is shown in Table I. A nicotine solution was steam-distilled and titrated with a standard acid and compared with a direct titration of another portion of the same size.

The efficiency of the still depends on the time during which the liquid and steam are in contact. The inner chamber is heated by the steam held by the outer jacket, while at the same time the liquid-steam contact is much longer than in the conventional steam-distillation outfit. These two conditions much more than compensate for the absence of flame heating as in the usual apparatus. The efficiency is such that the nicotine may be distilled completely from a 2-gram sample of tobacco in 0.5 hour.

This apparatus has also been used satisfactorily for the determination of nornicotine and anabasine, both of which are much less volatile with steam than nicotine. The dimensions given were optimum for the distillation of tobacco samples. Modifications, such as using a larger condenser, increasing the length or the diameter of the inner chamber, or changing the type of trap, may be desirable for some applications.

TABLE I. COMPAN	RISON OF STE.	AM DISTILLATION	WITH DIRECT
	TITRA	ATION	
(Using 0	.02 N hydrochlo	rio acid against nicot	ine)
10 Ml. of Solution		5 Ml. of Solution	
Direct titration	distillate	Direct titration	distillate
Ml.	Ml.	Ml.	Ml.
7.58 7.57 7.57 7.58	7.57 7.56 7.57 7.57	3.77 3.78 3.78 3.78	3.78 3.80 3.80
Av. 7.575	7.57	3.773	3.793

Acknowledgment

The writers are indebted to O. A. Nelson for the glass blowing involved in making the apparatus described.

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Determination of Mercury in Rubber

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Iodine may be separated from mixtures of mercury and iodine, previous to determination of mercury by the Volhard method, by boiling with nitric acid under controlled

T HAS recently been necessary to determine small amounts of mercury (0.1 to 5.0 per cent) in natural and synthetic rubber compounds containing iodine. A survey of the literature showed that the method most often used for the determination of mercury in organic compounds containing iodine involves complete oxidation of the carbonaceous material by digestion with acid, followed by separation of the mercury from the iodine by reduction of the former to the metallic state and filtration (1, 6). In searching for a more convenient method of separation, it was found that this can be accomplished very simply by boiling with nitric acid under controlled conditions. Free iodine is expelled with but little loss of mercury, which can then be titrated with thiocyanate. The new method has been applied successfully to the determination of mercury in rubber samples containing iodine (see Table III).

Apparatus

The apparatus is shown in Figure 1. It consists of a 125-ml. Erlenmeyer flask with standard taper 24/40 joint connected to an air condenser 80 cm. in length and 1 cm. in inside diameter.

Reagents

STANDARD MERCURY NITRATE SOLUTION. Dissolve approxi-mately 0.5 gram of pure mercury in 10 ml. of nitric acid in a 1-liter volumetric flask. Add 25 ml. of water and cool to room temperature. Draw off most of the brown fumes and dilute to the mark with water.

STANDARD AMMONIUM THIOCYANATE SOLUTION (approximately 0.01 N). Dissolve approximately 1.8 grams of ammonium thio-cyanate in water and dilute to 2 liters. To standardize this solution, pipet 50 ml. of the standard mercury solution into a 125-ml. flask. Add 3 ml. of sulfuric acid, 5 ml. of nitric acid, and 0.2 gram of potassium sulfate. Color with permanganate and titrate as directed in the procedure.

FERRIC ALUM INDICATOR. Dissolve 30 grams of ferric alum (FeNH₄(SO₄)₂.12H₂O] in 95 ml. of water and add 5 ml. of colorless nitric acid.

Procedure

Weigh 20 to 100 mg. of the subdivided rubber sample and place in a dry 125-ml. Erlenmeyer flask with standard taper joint, taking care not to allow particles of the sample to cling to the walls or neck of the flask. Add about 0.3 gram of potassium persulfate ($K_2S_2O_8$) and tap the flask to collect the rubber parti-cles to one side of the bottom of the flask. Add 2 ml. of fuming sulfuric acid and cap tightly with a dry 80-cm. air condenser. (If the rubber sample weighs more than 50 mg. it is best to use 0.5 gram of potassium persulfate and 3 ml. of furning sulfuric acid.) Clamp the neck of the flask to a ring stand and tilt the flask so that the acid covers the rubber sample. Place in a hood and play a small flame from a Tirrill semi-microburner on the flask below the acid mixture. Heat gently to decompose the sample, taking great care to prevent loss of iodides

decompose the sample, taking great care to prevent loss of iolides of mercury. It is necessary to keep the flame low during the initial oxidation, so that evolution of white fumes from the tip of the condenser is not too vigorous. As the oxidation proceeds, the flame can be increased, until in the later stages the acid boils and bumps. Under no circumstances must the top half of the air condenser be allowed to get even warm. When destruction of the organic matter is complete, remove the flame and allow the flask to cool.

conditions. The method has been applied successfully to determination of small amounts of mercury in rubber samples containing iodine.

Wash down the walls of the condenser with 15 to 20 ml. of nitric acid (1 to 1). Detach the air condenser and wash the joint with water from a wash bottle. If the sample being analyzed contains less than 5 mg. of mercury, set the condenser aside. Cover the flask with a small watch glass, heat to gentle boiling on a hot plate (do not use a flame), and boil until all the iodine is expelled—i. e., until the solution and vapor are entirely free of color due to iodine and no insoluble iodides of mercury can be seen in the solution. After iodine is expelled, evaporate (rapidly if desired) to about 10 ml. (In case traces of organic matter remain in the solution, evaporate until white fumes begin to be evolved and then add 5 ml. of nitric acid, 1 to 1.) Cool and reserve.



FIGURE 1. DIGESTION APPARATUS

If the sample contains more than 5 mg. of mercury, replace the air condenser after washing the joint and expel the iodine as directed above, omitting the use of a watch glass. If some iodine collects in the condenser joint during boiling, cool the solution somewhat, break the joint, and allow the iodine to escape. Re-place the condenser and continue boiling. Wash down the sides of the flask (or flask and condenser) with water and remove the condenser if used. Dilute to 30 to 50 ml. with water and cool to room temperature. Add potassium per-mangenate (2 per cent solution) dronwise until a color is obtained

manganate (2 per cent solution) dropwise until a color is obtained which persists. Dispel the color with a drop or two of 3 per cent hydrogen peroxide. Add 0.5 to 1.0 ml. of ferric alum indicator solution and titrate carefully with 0.01 N ammonium thiocyanate solution until the first permanent brownish red color is obtained in the solution. Provide for blank correction:

MI. of NH ₄ CNS \times Hg factor \times 100	-	Der cent meraury	
Sample weight in grams	010	per cent mercury	

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Метнор						
	(After e	xpulsion of iodi	ne with nitric a	wid)		
No.	HNO: (1:1) Added <i>Ml</i> .	Hg Added Mg.	Hg Found Mg.	Error Mg.	Error %	
1° 2 3 5 6 7 8 9 10 11 12 13	10 10 20 20 20 20 20 50 50 50 50 50 25 50	1.13.75.15.05.65.710.112.811.719.270.0100.093.7	1.13.75.15.69.812.411.318.869.098.098.091.0	$\begin{array}{c} 0.0\\ 0.0\\ 0.0\\ +0.1\\ 0.0\\ -0.1\\ -0.3\\ -0.4\\ -0.4\\ -0.4\\ -1.0\\ -2.0\\ -2.7\end{array}$	2.0 1.8 3.0 3.1 3.4 2.1 1.4 2.0 2.9	
a 200 i	mg. of K2SO4 ad	ded with HgIs.				

Drampurst anton on Manarth

Discussion

Rubber samples containing mercury and iodine cannot be completely oxidized by treatment with sulfuric acid and 30 per cent hydrogen peroxide or by other mild methods of oxidation. After testing various methods it was found that the oxidation is best accomplished by the Kjeldahl method of Sloviter, McNabb, and Wagner (5). In view of the volatility of iodides of mercury and the ease with which they are mechanically carried out of the condenser by the escaping fumes of sulfur dioxide, the rate of digestion must necessarily be slow. Because of this, and in view of the fact that rubber samples containing mercury and iodine are difficult to oxidize, it is best to limit the sample size to 100 mg. or less. Oxidation of certain synthetic rubber samples such as Buna S and Butyl rubber may take several hours, even when the sample size is small. Attempts to decrease the time of oxidation by the use of selenium as a catalyst or by employing the Parr bomb were not successful, as low results were obtained.

With the conditions recommended in the procedure, some loss of mercury occurs during the expulsion of the iodine if the amount of mercury present is greater than about 5 mg. The loss may amount to as much as 2 or 3 per cent in some cases, but for many purposes this accuracy is satisfactory (see Tables I and II).

In preliminary work 30 per cent hydrogen peroxide was used to convert the iodide to free iodine. Very low results were obtained, however, when samples containing large amounts of mercury and iodine were analyzed. This probably resulted from the comparatively low acidity and the decrease in oxidizing strength of the solution as it is boiled. Nitric acid was found to be superior to hydrogen peroxide. The optimum concentration of the acid appeared to be about 1 to 1.

According to Hillebrand and Lundell (3) loss of mercury by volatilization as chloride is controlled, to a large extent, by the shape of the vessel and the concentration of the mercury in the solution. The same appears to be true in the present case. Thus, Tables I and II indicate that the loss of mercury increases with an increase in the amount of mercury present and is reduced appreciably by the use of a long reflux tube

While the actual loss of mercury increases with an increase in the amount of mercury present, the percentage loss first increases and then tends to decrease. The use of the air condenser appears to shift upward the concentration at which maximum per cent error is obtained. Finally, in the expulsion of the iodine, the more vigorous the boiling, the greater the tendency for loss of mercury.

In the determination of mercury in readily oxidizable organic materials, where nitric acid can be used as the oxidant, it may be possible to oxidize the sample and expel the iodine simultaneously. It is also probable that mercury can be separated from chloride or bromide by boiling with nitric acid.

During the development of the proposed method an attempt During the development of the proposed method an attempt was made to determine the mercury in the digestion mixture di-rectly by the Rupp method (4) without removing the iodine. Preliminary experiments in which known amounts of pure mer-curic iodide were analyzed for mercury by the Rupp method showed that low results were obtained when the amount of mer-cury exceeded about 2 mg. In agreement with Fitzgibbon (2) it was found that the addition of gelatin was beneficial. By adding 2 ml. of 1 per cent gelatin solution to the sample before reduction with formal debude correct results could be obtained on cusntities with formaldehyde correct results could be obtained on quantities of mercury up to 5 mg. With larger amounts low results were obtained and a black precipitate which is insoluble in standard iodine solution remained in the bottom of the flask.

iodine solution remained in the bottom of the flask. When mixtures of rubber and weighed quantities of mercuric iodide (< 5 mg. of mercury) were carried through the complete procedure very low results were obtained. The cause was finally traced to the presence of free iodine in the solution previous to reduction of the mercury with formaldehyde. This iodine was produced in the following manner: After complete oxidation of the rubber the condenser was washed down with 10 ml. of 5 per cent potassium iodide solution; bromine water was added drop-wise to oxidize the mercury and sulfur dioxide; when a slight permanent precipitation of iodine occurred the flask was stop-pered and shaken to oxidize all the sulfur dioxide; and after 5 pered and shaken to oxidize all the sulfur dioxide; and after 5 minutes the analysis for mercury by the Rupp method was made.

TABLE]	II. DETERMINA	TION OF MERCO METHOD	JRY BY THE	Volhar
(Afte	er expulsion of iodi	ne with nitric acid,	air condenses	used)
No.	Hg Added	Hg Found	Error	Error
	Mo.	Mg.	Mg.	%
1	0.7	0.7	0.0	Redda 6
2	2.7	2.7	0.0	
4	13.4	13.3	-0.1	1.1
5	31.6	30.9	-0.7	2.2
67	53.8	52.7	-1.1	2.0

Theoretically, free iodine should cause no trouble in the reduction of the mercury with formaldehyde, since the hypoiodite is reduced to iodide. Actually, however, when iodine is present the mercury is precipitated in a form that does not dissolve com-pletely in standard iodine solution. Black specks of undis-solved material and cloudy solutions are encountered and the results are very low.

Attempts to improve the results by titration of the free iodine in acid solution with sulfite or thiosulfate failed, as did also reduction of the iodine with hydrogen peroxide in alkaline solution. It was therefore concluded that the Rupp method could not be used for direct analysis of the mercury in the digestion mixtures.

TABLE III.	DETERMINATIO MERCURIC IC	ON OF MERCURY IN DDIDE MIXTURES	RUBBER-
No.	Hg Added Mg.	Hg Found Mg.	Error Mg.
1 2 3 4 5 6 6 7 6 8 9 4 10 * 11 *	$\begin{array}{c} 0.1 \\ 0.5 \\ 0.7 \\ 1.9 \\ 3.0 \\ 4.2 \\ 4.6 \\ 6.2 \\ 6.4 \\ 0.5 \\ 2.5 \\ 5.6 \end{array}$	$\begin{array}{c} 0.1\\ 0.5\\ 0.7\\ 1.9\\ 3.0\\ 4.2\\ 4.6\\ 6.1\\ 6.2\\ 0.5\\ 2.5\\ 5.6\end{array}$	$\begin{array}{c} 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0$
13.	5.8	5.7	-0.1

25 mg. of KI added with HgIs.
100 mg. of rubber, 0.5 gram of K₁S₂O₄, and 3 ml. of fuming H₂SO₄ used.
0.5 gram of K₁S₂O₄ and 3 ml. of fuming H₂SO₄ used.
50 mg. of KI added with HgIs.
Mercury determined by Rupp method.

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The only satisfactory procedure found was that in which the iodine was expelled by boiling with nitric acid, followed by complete expulsion of all nitrates, and finally, addition of potassium iodide, and analysis by the Rupp method in the usual way em-ploying gelatin. This method has been shown to be satisfactory for small amounts of mercury (see Table III), but because of its limited applicability and its complexity it does not compare with the Volhard method.

Experimental

Weighed quantities of pure mercuric iodide together with 3 ml. of sulfuric acid and various quantities of nitric acid (1 to 1) were placed in 125-ml. Erlenmeyer flasks. The iodine was then expelled and the mercury determined by the Volhard method as directed in the procedure, without use of the air condenser. Results are recorded in Table I.

The experiment was repeated using an 80-cm. air condenser. The mercuric iodide was treated with 3 ml. of sulfuric acid, 15 ml. of nitric acid (1 to 1), and 0.2 gram of potassium sulfate. The results are recorded in Table II.

Weighed quantities of pure mercuric iodide and 20 to 30 mg. of a mercury-free gum rubber stock were placed in 125-ml. Erlenmeyer flasks. The samples were then treated as directed in the procedure, using 0.3 gram of potassium persulfate and 2 ml. of fuming sulfuric acid. No air condenser was employed in the expulsion of the iodine. The results are recorded in Table III.

Summary

A very simple method has been developed for the separation of iodine from mixtures of mercury and iodine previous to the determination of the mercury by the Volhard method. The method has been successfully applied to the determination of small amounts of mercury in rubber samples containing iodine. The Rupp method has been investigated.

Acknowledgment

The author wishes to express his gratitude to B. L. Clarke and M. L. Selker of these laboratories, who read the manuscript and offered several valuable suggestions.

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Benzoin as Fluorescent Qualitative Reagent for Zinc

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CEVERAL reagents which give fluorescent compounds with zinc ions have been recorded in the literature. Lutz (3) has shown that urobilin and sterobilin, products of body metabolism, give a green fluorescence with zinc. However, cadmium, calcium, cobalt, copper, magnesium, nickel, potassium, and sodium give a similar fluorescence. The zinc precipitate with 8-hydroxyquinoline gives a yellow fluorescence but identical results can be obtained with other elements that precipitate with this reagent. The dyestuffs morin and cochineal (2) both fluoresce in the presence of zinc as they do with many other ions. Textbooks in qualitative analysis generally recommend dithizone, potassium ferri-cyanide with diethylaniline or Orange IV, mercury thiocyanate, or the Rinman's green test as confirmatory for zinc. Difficulty with these reagents is encountered due to lack of specificity, sensitivity, or indefinite results.

Yoe and Sarver (5) list some forty organic compounds that may be used as reagents for zinc. Of these the ones mentioned above are most widely used in qualitative analysis. Organic reagents which coordinate with the metallic ions often have a hydroxyl and a carbonyl group adjacent to or near one another. In testing compounds of this type for fluorescent reactions with the metallic ions it has been found that benzoin, C₄H₅.CHOH.CO.C₄H₅, serves as an excellent qualitative reagent for zinc.

Characteristics of the Reagent

Since benzoin is commonly made as a student preparation in elementary organic chemistry laboratories, it is readily available in large quantities. Benzoin is moderately soluble in 95 per cent alcohol and dissolves easily on warming. This

solution has a faint green fluorescence but when diluted in the test it offers no interference. It was found during the course of these experiments that a freshly prepared solution of benzoin gave better results than an older one. Since it is probable that this is due to oxidation of the benzoin, a reducing agent, sodium dithionite, Na₂S₂O₄, was added to the reaction mixture. With this present the age of the benzoin solution is immaterial. Other reducing agents were tried, but the dithionite gave the best results.

The fluorescence with zinc appears in an alkaline solution in the presence of magnesium hydroxide. This latter material was used in a series of experiments to see if it would absorb fluorescent compounds, as it does titan yellow in the common test for magnesium ion. In this particular case it was highly successful. Subsequent tests showed that the zinc-benzoin fluorescence on the magnesium hydroxide was much more lasting when a small quantity of silicate was present. It is probable that the adsorbing agent is a basic magnesium silicate.

Procedure for the Test

The test solution containing 0.1 mg. or more of zinc ion is made neutral or slightly alkaline with sodium hydroxide. If one is proceeding through the usual scheme of analysis and zinc is precipitated as the sulfide, this is dissolved in hydrochloric acid and boiled until all the hydrogen sulfide is removed. The solu-tion is then made just sufficiently alkaline with sodium hydroxide to dissolve the zinc hydroxide. Any hydroxides insoluble in to dissolve the zine hydroxide. Any hydroxides insoluble in sodium hydroxide are removed by filtration. The volume of solution should be between 5 and 15 ml. Approximately 1 ml. of each of the following reagents is added in successive order. Medicine droppers delivering about 1 ml. are sufficiently accurate for the measurement.

1. Sodium hydroxide-sodium silicate solution, prepared by mixing 100 ml. of 2.5 N sodium hydroxide with 0.6 ml. of 35 per

cent sodium silicate. The sodium silicate is unnecessary if immediate observations are to be made.

2. Sodium dithionite solution, made by dissolving 1 gram of sodium dithionite in 25 ml. of water. This solution must be pre-pared fresh daily and the quantity is so approximate that the "1 gram' may be measured in a porcelain spoon.

3. Benzoin solution, prepared by dissolving 0.3 gram of ben-zoin in hot 95 per cent ethyl alcohol.

4. Magnesium nitrate solution, prepared so that 1 liter of colution contains 2 grams of magnesium ion. After addition of these reagents the solution is shaken and after

a minute or two observed under an ultraviolet lamp. A green fluorescence between 4650 and 5700 Å. is a positive test. The G. E. H-4 lamp with a blue-purple bulb is most satisfactory as a source of ultraviolet radiations. If there is much visible light present, it is helpful to make the observation through a piece of green cellophane. For concentrations of zinc less than 0.1 mg, a blank should be run at the same time, because the contrast makes the test more pronounced. The fluorescence increases for the first few minutes after the solutions are mixed and then fades very slowly until it entirely disappears in several hours.

Interferences

Since the zinc test is carried out in a sodium hydroxide solution and all insoluble hydroxides are removed by filtration, it is only the amphoteric cations and certain anions that are likely to cause interference. Beryllium and boron both give a fluorescence with benzoin. The beryllium color range is in the yellow green from 4930 to 5700 Å. and the boron from 4710 to 5700 Å. Both fluoresce before the magnesium hydroxide is added and if the solution is examined under the lamp at this point they will not be confused with zinc. After the magnesium hydroxide is added, zinc can be distinguished from beryllium by comparing to a standard. The boron fluorescence is not apparent in concentrations under one part in 100,000. The only other element causing any difficulty is antimony, which gives a purplish fluorescence that will completely mask the green of the zinc. Since boron and beryllium are seldom found in general qualitative analysis mixtures, and antimony is removed in a previous group, these interferences are not considered serious.

Of the other cations left in solution after a sodium hydroxide treatment only the platinum metals, mercury, silver, and gold, cause difficulty. The ions of these elements are reduced to the metal by the dithionite and a black precipitate results. Consequently they must be removed before the zinc test is applied. Anions causing an interference on being reduced by the dithionite are those of molybdenum, vanadium, tellurium, and selenium. The colored anions such as chromate, permanganate, and the iron cyanides mask the color of the zinc fluorescence and cannot be tolerated. Colorless anions and anions not reduced to precipitates or colored forms by dithionite do not interfere.

All the usual cations and anions were tested as individuals except radium, hafnium, rhenium, and the rare earth group where lanthanum, cerium, praseodymium, and neodymium were the only ones available; the remainder were tested as a group using monazite sand extracts. Some anions, while not causing a fluorescence when alone or with other elements, seem to intensify that of the zinc. In descending order of effectiveness these are: silicate, phosphate, carbonate, and arsenate. Since this order is in fair agreement with the list of adsorbing agents used in chromatographic analysis as given by Strain (4), it is believed that the increase in fluorescence is due to the character of the adsorbing agent.

Unknowns containing various mixtures were run following the usual qualitative procedures, and zinc was determined by the fluorescent test outlined above with perfect results in all cases.

Sensitivity of the Test

This test is sensitive to 10 micrograms of zinc ion or to a concentration of one part in a million. This is not so sensitive as dithizone, which Feigl (1) claims is good to 0.1 microgram. It is, however, a very pronounced test with a high specificity where results are easily identified.

Discussion

It has not been possible to isolate the fluorescing material for analysis. Unsuccessful attempts were made to remove this from the magnesium hydroxide by means of organic solvents. Nor was it possible to get an indication of the composition of the substance by analyzing for the zinc and benzoin removed from the solution. Tests showed that the zinc was adsorbed from the solution even though benzoin was absent. The quantities involved indicated that 8×10^{-1} mole of magnesium adsorbed 8×10^{-6} mole of zinc from the alkaline solution. If a greater quantity of zinc was used, it was not completely removed. Much of the adsorbed zinc can be easily washed from the magnesium with 2.5 N sodium hydroxide; however, some remains after several washings. Benzoin is not adsorbed by the magnesium hydroxide, and even with the zinc present it seems impossible to have all the benzoin retained. Under the conditions of the experiment. it required only 1.4×10^{-7} mole of benzoin to produce a fluorescence with 7×10^{-7} mole of zinc, and yet after treating with magnesium and filtering, some of the benzoin but none of the zinc passed into the filtrate. The benzoin was tested for by its fluorescence with boron; this property will be described in detail in a later paper. A lesser quantity of benzoin does not produce a fluorescence but can still be detected in the filtrate after the magnesium hydroxide treatment.

No conclusions as to the formula of the zinc-benzoin complex could be obtained. From the formula of benzoin, it would be expected that the zinc replaces the hydroxyl hydrogen and coordinates with the ketonic oxygen, forming a complex of the type [Zn(C₆H₅CO.CO.C₆H₅)] +. In the filtrations mentioned above the zinc-benzoin complex remains on the filter paper as a highly fluorescent material which loses its fluorescence on drying.

Other adsorbing agents were tried in place of the magnesium hydroxide, but none were successful. Among these were spot test paper, activated alumina, and the hydroxides of cadmium, thorium, and zirconium.

The intensity of the fluorescence varies with the concentration of zinc; however, the differences are not sufficient for quantitative measurement. By comparison to a standard, concentrations differing by 10 micrograms at lower concentrations can be distinguished.

Summary

Benzoin in the presence of alkali and magnesium ion reacts with zinc to produce a green fluorescent compound having a spectral range from 4650 to 5700 Å. The reagent is highly specific for zinc; interference is given only by beryllium, boron, and antimony. While the test is not as sensitive as the one using dithizone, it is pronounced and easy to observe.

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Semimicrodetermination of Phosphorus in **Organic Compounds** CLITECHNIKI

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THE analytical procedure presented below for the determination of phosphorus in organic compounds makes use of the Parr sodium peroxide bomb described previously (4). The phosphate is determined volumetrically, the alkalimetric procedure used in steel analysis (2, 3, 6) being found applicable with little modification. The precipitate of ammonium phosphomolybdate is collected in a cylindrical filter funnel with fritted-glass disk. The decinormal carbonate-free alkali is standardized empirically against pure potassium dihydrogen phosphate in order so far as possible to exclude uncertainty caused by deviation of the composition of the precipitate from the theoretical. The titration is completed without boiling (3).

Reagents

Molybdate Solution. The familiar acid solution (1, 6) is used: 118 grams of ammonium molybdate $[(NH_4)_4M_07O_{24}.4H_2O]$ are dissolved in 400 ml. of water, 80 ml. of concentrated am-monium hydroxide are added, and the solution is poured into a mixture of 400 ml. of concentrated site and 600 ml. of 000 ml.

monium hydroxide are added, and the solution is poured into a mixture of 400 ml. of concentrated nitric acid and 600 ml. of water, with agitation by passing a current of air through the solution. After several hours the solution is filtered. If there-after a precipitate of molybdic acid appears the reagent must be filtered before use. Decinormal Sodium Hydroxide, carbonate-free, standardized against pure potassium dihydrogen phosphate by the procedure described for the analysis. It is convenient to prepare a standard solution of potassium dihydrogen phosphate—e. g., 8.5 grams per liter (0.135 N), and to add a 10-ml. aliquot to a solution of 9.0 grams of sodium nitrate, 0.2 gram of potassium nitrate and 1 to 2 ml. of concentrated nitric acid in 50 cc. of water, completing the standardization as described in the procedure starting with the standardization as described in the procedure starting with the third paragraph.

Decinormal Hydrochloric Acid, standardized against the alkali solution by titration with the latter, using phenolphthalein indicator.

Procedure

If the substance to be analyzed is a solid, transfer to the bomb cup an accurately weighed sample of such size (usually 10 to 30 mg.) that the phosphorus present will lead to consumption of 10 to 20 ml. of decinormal alkali. Add powdered sucrose in such amount that the combined weight of sample and sucrose is 0.2 gram. Introduce 0.2 gram of powdered potassium nitrate and 4.0 grams of sodium peroxide. If the substance to be analyzed is a nonvolatile liquid (the only kind tested), intro-duce first into the cup the sucrose, potassium nitrate, and so-dium peroxide, and then add the sample from a Lunge-Rey pipet (the delivery tip of which is drawn out to a fine opening so as to obtain small drops), determining the weight of sample by difference. difference.

Lock the bomb cover in place, mix the charge, ignite, and extract the cooled melt in water, using the manipulations de-scribed in procedures for determination of sulfur (4) and of the scribed in procedures for determination of sulfur (4) and of the halogens (5). Acidify the alkaline extract by addition of 10 ml. of concentrated nitric acid. The volume at this point should be about 60 ml. The liquid should be clear or nearly so. A small amount of dark carbonaceous material may be without signifi-cance, but if the amount is large this may indicate that the decomposition was incomplete, and it may later obstruct the filtration or reduce some ammonium phosphomolybdate. With the liquid at a temperature of about 40° C. (3) (ordi-narily the neutralization will warm the liquid to about this tem-perature) introduce from a pipet 50 ml. of the molybdate re-agent. Allow the solution to stand for 2 hours or overnight (1). Using light suction (to minimize danger of loss of ammonia by volatilization) filter the mixture through a filter funnel with

sintered-glass disk (a funnel of 15-ml. capacity and 22-mm. in-side diameter, and with a disk of "medium" porosity, is suit-able), mounted in a Witt suction filtration apparatus. Clear the able, incurted in a witt suction intration apparatus. Clear the beaker of the last traces of precipitate by rinsing with 1 per cent potassium nitrate solution, and scrubbing thoroughly. Wash the precipitate on the filter with 10-ml. portions of 1 per cent potassium nitrate solution, applied as a fine stream from a wash bottle. The total volume of the wash solution used in these operations should be 75 ml. Rinse the under side of the filter with user to prove the prior to the solution to the solution of the solution. filter with water to remove any adhering traces of acid. Place under the filter funnel (in the Witt apparatus) a 250-ml.

Erlenmeyer flask containing 5 drops of 1 per cent phenolphthalein indicator. With suction interrupted measure decinormal sodium hydroxide into the funnel from a 25-ml, or a 50-ml, buret. using enough to dissolve the precipitate, an operation which may be assisted by manipulation with a glass rod. Draw the solution into the flask with suction; if the liquid remains colorless measure from the burct and through the funnel enough additional decinor-mal alkali to produce a red color. Wash the filter with water. Titrate with decinormal acid to discharge the color, and add a slight excess of acid. Finally titrate with decinormal alkali to a "permanent" pale pink color.

TABLE I. DETERMINATION OF PHOSPHORUS IN ORGANIC

COMPOUNDS						
	Sodium Hydroxide			Pho	phorus	
Compound	Sample		mality4	Founds	Lated	
Compound	Mg.	Ml.	manuj	%	%	
n-Butyl phosphate, b. p. 161-163° at 16 mm.	$41.61 \\ 41.05 \\ 38.15$	32.86 32.90 29.71	0.1091	11.63 11.80 11.47 Av. 11.6	11.65	
Tri - p - tolyl phos- phate, m. p. 75.1°, corrected	$\begin{array}{r} 40.75\\ 30.44\\ 31.33\\ 16.59\end{array}$	27.79 20.73 21.32 7.95	0.0913 0.1279	8.39 8.38 8.37 8.26 Av 8.37	8.42	
Sodium Fglycerophos- phate, Eastman Ko- dak Co. No. 644 ^c	6.57 11.17	4.06 6.79	0.1259	10.55 10.40	10.37d 10.42d 10.39d 10.45 • 10.46 •	
				Av. 10.5	Av. 10.42	
Triphenyl phosphite, b. p. 240° at 21 mm.	$8.37 \\ 9.83 \\ 16.62$	4.83 5.66 9.77	0.1279	9.95 9.93 10.13	10.00	
in this is a spinite factor				Av. 10.0		
Tri - m - tolyl phos- phite, b. p. 249-251° at 11 mm.	$15.93 \\ 18.29 \\ 27.24 \\ 22.42$	8.29 9.13 13.54 11.33	0.1279 0.1289	8.97 8.67 8.65 8.78	8,81	
	0.000	Constant of	Posta des	Av. 8.78		
Tri - p - tolyl phos- phite, b. p. 260-261° at 10-11 mm.	30.56 9.11 13.07 10.78	$ \begin{array}{r} 15.37 \\ 4.66 \\ 6.74 \\ 5.63 \end{array} $	0.1279	8.67 8.81 8.89 9.00 Av. 8.83	8.81	
Triphenylphosphine, m. p. 80.6° correc- ted	15.19 14.97 16.96	10.26 10.16 11.80	0.1279	11.64 11.70 11.99 Av. 11.8	11.83	

Normality in terms of phosphorus as required by the ratio P @ 23

^a Normality in terms of phosphorus as required by the ratio $P \simeq 23$ NaOH. ^b These values are given as calculated, but obviously are valid to not more than three significant figures. ^c Eastman Kodak Co. designation is "sodium glycerophosphate.5Hr0 (52% alpha)". The results obtained indicate a composition midway be-tween the pentabydrate (10.13% P) and the tetrahydrate (10.76% P). ^d Results by umpire method: sample decomposed by nitric and sulfuric acids, and phosphoric acid determined as Mgr.PsO; following double pre-cipitation with magnesia mixture. In test analyses of pure KHrPO, this procedure gave 22.78% P; calcd. is 22.79%. ^e Results by umpire method: decomposition as above, and phosphoric acid determined as Mgr.PsO; following precipitation as ammonium phos-phomolybdate and then double precipitation with magnesia mixture. In test analyses of KHrPO, this procedure gave 22.83% P; calcd. is 22.79%.

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Results obtained by this procedure applied to seven organic compounds are given in Table I.

The compounds analyzed were all specimens obtained from the Eastman Kodak Company. Sodium glycerophosphate and tri-p-tolyl phosphate were analyzed as received. Triphenyl phosphine was twice crystallized from ethanol. The phosphorous esters were distilled under reduced pressure. They all contained some of the corresponding phenols (odor; fore-run during distillation), and when distilled in vacuo they underwent considerable change in the flask, an orange-colored turbidity appearing in the liquid in each case. As small amounts of these materials passed into the distillates, it was necessary to repeat the distillations. In all cases the specimens finally obtained were perfectly clear, and boiled within narrow temperature ranges, but the residual liquids were opaque and much discolored.

Samples were weighed on a semimicrobalance.

Acknowledgment

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Determination of Total Sulfur in Rubber

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A new volumetric method has been developed for the determination of sulfate sulfur. The sulfate is reduced to sulfide by treatment with hydriodic acid and the hydrogen sulfide is distilled off and titrated iodometrically. The new method has been applied to the determination of total sulfur in natural and synthetic rubber.

WITH the recent increase in research on natural and synthetic rubber there has arisen a need for a rapid method for the determination of total sulfur in rubber samples where only a semimicrosample can be spared for analysis.

The usual methods in which the rubber is oxidized by digestion with acid, followed in some cases by fusion to complete the oxidation, and the sulfur is precipitated and weighed as barium sulfate, yield good results on semimicrosamples but are time-consuming because quantitative precipitation of the sulfate cannot be attained unless the solution is allowed to stand overnight before filtration. Several volumetric methods, most of which depend upon the precipitation of the sulfur as barium sulfate, have been described, but none is very satisfactory in the determination of small amounts of sulfur.

St. Lorant (2) has proposed a volumetric method for the determination of microsamples of sulfate, in which the sulfate is reduced to sulfide with hydriodic acid, and the hydrogen sulfide is distilled off and determined colorimetrically. The author has recently developed a modification of this method which has proved to be very satisfactory in the analysis for sulfur in small samples of rubber. The procedure consists essentially of oxidation of the rubber in the usual manner, reduction of the sulfate to sulfide, separation of the hydrogen sulfide by distillation, and titration of the latter iodometrically.

The new method is very rapid (20 to 25 minutes for the distillation and titration) and is not subject to the errors of

adsorption, occlusion, and solubility encountered in the gravimetric barium sulfate method, or to difficulties in detection of the end point encountered in some of the volumetric methods. It possesses the distinct advantage over some of the gravimetric methods, that it is applicable to the analysis of rubber containing barium, lead, and calcium. The only serious objections to the method from the standpoint of general use are that hydriodic acid is expensive and that the applicability of the method is somewhat limited because of the fact that no more than about 5 mg. of sulfur can be handled conveniently. This means that the sample size must be small when analyzing rubber high in sulfur; and when small samples are used there is always the danger of error due to unequal distribution of sulfur in the sample.

Apparatus

The apparatus is shown in Figure 1. It consists of a 125-ml. Erlenmeyer flask with standard taper 24/40 joint, a distillation head with capillary pressure regulator, and a 300-ml. Erlenmeyer flask with standard taper 24/40 joint. The capillary tubing is 2 mm. in inside diameter and extends to within 2 to 4 mm. from the bottom of the 125-ml. flask.

Reagents

NITRIC ACID-ZINC OXIDE-BROMINE MIXTURE. Dissolve 10 grams of zinc oxide in 100 ml. of nitric acid and saturate with bromine.

ACID MIXTURE FOR DISTILLATION. Place 160 ml. of hydriodic acid (specific gravity 1.70), 160 ml. of hydrochloric acid, and 45 ml. of hypophosphorous acid (50 per cent) in a 500-ml. Erlen-meyer flask. (If the hydriodic acid contains hypophosphorous acid as a preservative use only 40 ml of hymophosphorous acid.) acid as a preservative use only 40 ml. of hypophosphorous acid.) Add a few grains of silicon carbide and boil vigorously without cover for 5 minutes. Cool in an ice bath to room temperature. Keep stoppered in a 500-ml. brown glass-stoppered bottle to

avoid oxidation of the hydriodic acid. AMMONIACAL CADMIUM CHLORIDE SOLUTION. Dissolve 10 grams of cadmium chloride dibydrate in water. Add 500 ml. of ammonium hydroxide and dilute to 5 liters.

STANDARD POTASSIUM IODATE SOLUTION (0.01 N). Recrystal-lize c. p. potassium iodate from water twice and dry at 180° C. to constant weight. Weigh 0.7134 gram of the pure potassium iodate and dissolve in water. Add 2 grams of sodium hydroxide and then 10 grams of potassium iodide (free from potassium



FIGURE 1

iodate). After complete solution of all salts adjust to room temperature and dilute to 2 liters in a volumetric flask.

STANDARD SODIUM THIOSULFATE SOLUTION (0.01 N). Dissolve about 5 grams of sodium thiosulfate pentahydrate in 2 liters of freshly boiled and cooled distilled water. Store in a clean Pyrex bottle. To standardize this solution, pipet 25 ml. of the standard potassium iodate solution into a 300-ml. Erlenmeyer flask. Add 200 ml. of water and 20 ml. of hydrochloric acid. Allow to stand 1 minute and then titrate with the thiosulfate solution. As the end point is approached add 10 ml. of 0.2 per cent starch solution and titrate carefully until the solution is colorless. The thiosulfate solution should be restandardized every 15 days.

STARCH SOLUTION. Add a cold aqueous suspension of 2 grams of soluble starch to 1 liter of boiling water. Cool to room temperature and store in a clean bottle.

Procedure

Place 0.050 to 0.100 gram of the rubber sample, which has been either "crumbed" or cut into as small pieces as possible, in a 125ml. Erlenmeyer flask with ground-

ml. Erlenmeyer flask with groundglass joint. (The method as written is applicable to the analysis of semi-

microsamples of rubber. If an analysis of larger samples is desired ap-

propriate increases in the amounts of reagents must be made. It is best, however, to limit the amount of sulfur in the sample to 5 mg. or less.)

(When highly saturated material such as Butyl rubber is to be analyzed, it is desirable to limit the sample size to 0.05 to 0.10 gram in order to decrease the time of oxidation and danger of explosion with perchloric acid. In general, oxidation of difficulty oxidizable material is more rapid and convenient with the perchloric acid method than with the A. S. T. M. method.)

Proceed by either of the following methods:

A. S. T. M. METHOD. Add 4 ml. of nitric acid-zinc oxidebromine mixture. Cover and heat on a steam bath or low-temperature hot plate to decompose the sample. When rapid solution ceases add 3 ml. of fuming nitric acid. Cover, and, while swirling the flask to prevent ignition of the sample, heat on a hot plate with surface temperature maintained at 180° to 200° C. When danger of ignition is past, allow the solution to boil gently until most of the organic matter is destroyed and the acid is all but expelled. With difficultly oxidizable samples such as Buna S and Butyl rubber it may be necessary to add more fuming nitric acid and take down to near dryness 2 or 3 times before enough of the sample has been oxidized to make it safe to continue. Finally, remove the cover and bake over a Tirrill flame until the zinc nitrate is converted to zinc oxide and most of the brown fumes are expelled. Return the flask to the hot plate to cool and to allow the remaining fumes to be expelled. Cool to 30° C. Wash down the sides of the flask with 5 ml. of hydrochloric acid and boil without cover to expel about half of the acid. It is essential that all nitrates be expelled in order to avoid interference in the titration described below. Cool to room temperature and reserve the solution for the distillation.

PERCHLORIC ACID METHOD. Proceed as directed in the A. S. T. M. method. When most of the readily oxidizable organic matter has been oxidized, and all but 1 or 2 ml. of the acid has been expelled, add 5 ml. perchloric acid (60 per cent). Cover and boil gently at a hot-plate temperature of 180° C. to 200° C. until white perchloric acid fumes appear. During this boiling it is essential that the flask be completely covered with a watch glass. With difficultly oxidizable material such as Butyl rubber considerable amounts of organic material may remain after expulsion of the nitric acid. If this occurs, the oxidation with perchloric acid should be allowed to proceed only to the point where the sample begins to char. At this point add more fuming nitric acid and repeat the evaporation. Repeat if necessary. Finally, when most of the organic matter is destroyed, the sample can safely be heated until fumes of perchloric acid appear without danger of ignition or explosion. Fume vigorously on a flame without cover to expel all but about 2 ml. of the acid. Cool to room temperature and reserve for the distillation.

After oxidation of the sample, add about 5 grains of silicon carbide (12-mesh grains that have been boiled in hydrochloricacid) to prevent bumping, and 35 ml. of the acid mixture and immediately cap with the distillation head. Place on a hot plate with surface temperature of 375°C. to 400°C. and boil for 5 minutes, catching the distillate in 150 ml. of ammoniacal cadmium chloride solution in a 300-ml. Erlenmeyer flask with ground-glass joint. The boiling should be timed from the moment fumes of ammonium chloride are first seen in the 300-ml. flask.

Remove the small flask from the plate and detach the distillation head. (If difficulty is encountered in removing the head, cool the joint and then run hot water on it.) Cool the distillate rapidly in an ice bath to 10° C. (In the analysis of samples containing over about 5 mg, of sulfur, add an excess of potassium iodate to a 125-ml. flask containing 20 ml. of hydrochloric acid and 20 ml. of water. Pour this solution in one stroke into the flask containing the sample. Stopper immediately and shake to oxidize all the sulfide in the flask. Wash the remains of the iodine into the large flask and back-titrate with thiosulfate as directed.)

Add 20 ml. of hydrochloric acid and swirl once to mix thoroughly. Titrate immediately and rapidly with potassium iodate solution, using a rapidly flowing buret—(i. e., a 50-ml. buret which will empty by gravity in 60 to 70 seconds)—until an excess of about 1 or 2 ml. has been added, as indicated by the yellow color. Cap immediately with a ground-glass stopper and shake vigorously to entrap any hydrogen sulfide in the atmosphere in the flask. Allow the potassium iodate buret to stand 1 minute after the titration before reading it. Add 10 ml. of starch solution and titrate with standard sodium thiosulfate solution (0.01 N). Carry a blank through the whole procedure. The blank should not be greater than 0.1 ml. of potassium iodate solution (0.01 N):

 $\frac{[(Ml. of KIO_3 - ml. of Na_2S_2O_1 \times KIO_3 factor) - blank] \times 0.01603}{\text{Sample weight in grams}} = \text{per cent sulfur}$

Discussion

The proposed volumetric method for the determination of sulfate yields satisfactory results when the amount of sulfur to be determined is less than about 10 mg. although slightly low values are obtained when the amount of sulfur present exceeds about 1 mg. (see Table I). With quantities greater than about 5 mg. special precautions must be taken to avoid loss of hydrogen sulfide during the titration.

Low results are obtained if the hydrogen sulfide is allowed to escape during the distillation or titration, if the temperature of distillation is too low, if the concentration of hydriodic acid is too low, and if nitrates in quantities greater than traces are present at the distillation. High results may be obtained

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TABLE I.	DETERMINATION OF BY THE PROPOSED V	SULFUR IN POTASS OLUMETRIC METHO	IUM SULFATE D
No.	Sulfur Present	Sulfur Found	Error
	Mg.	Mg.	Mg.
1	0.06	0.07	+0.01
34'	0.13	0.13	±0.00
4	0,25	0.25	±0.00
5	0,62	0.61	-0.01
65	0.62	0.62	±0.00
.7	1.25	1.24	-0.01
80	1.25	1.22	→0.03
95	1.25	1.23	-0.02
100	1.25	1.22	-0.03
Ild	1.25	1.22	-0.03
12.	1.09	2 10	-0.01
13	3.12	3.10	-0.02
15	8 92	8 16	-0.07
166	6.23	6.20	-0.03
 Titrated No HClo 0.2 gram 0.05 gram Different 	with KIO: using CCl. as O: present in acid mixture of BaCl:.2H1O present. n of PbCl: present. t K1SO: solution used.	indicator.	

unless a blank correction for the reagents is made. Because of the danger of exceptionally heavy contamination of the hypophesphorous acid with sulfur compounds, it is necessary to resort to a preliminary distillation of the acid mixture in order to reduce the blank to a reasonable figure.

In preliminary work the usual distillation apparatus for the evolution method for sulfur in steel was used. This proved unsatisfactory because the variation in the diameter of the neoprene rubber stoppers and the neck of the Erlenmeyer flasks was so great that the distance between the bottom of the flask and the end of the capillary pressure regulator could not be conveniently controlled. In the apparatus finally chosen the rubber stopper was replaced by a standard taper ground-glass joint.

When hydrogen sulfide is titrated directly with standard iodine using starch as indicator the end point is very poor, owing to the appearance, in the solution, of a permanent reddish color which obscures the blue of the end point. The color is probably caused by the adsorption of some compound of iodine and sulfur on the starch molecule. As evidence of this it is noted that very little free sulfur appears during the titration of those solutions which contain starch. Experiments indicated that the red color is more pronounced the colder the solution and the greater the salt concentration, especially if the salt is an iodide. It was found that in the titration of hydrogen sulfide in solutions containing but that in the titration of hydrogen suffice in solutions containing but small quantities of salts the red color could be almost completely eliminated by adding about 0.5 mg, of mercuric iodide or mercuric chloride to the solution or by titrating at 35° C. to 40° C. Un-fortunately, the addition of mercury caused the results to be slightly low, probably because of the conversion of part or all of the mercury to sulfide. Because of this, and the fact that the use of mercury salts is not very effective in the presence of appreciable quantities of salts, the problem was not considered further. further.

The best method for titrating hydrogen sulfide is that in which an excess of iodine is added, followed by back-titration with thio-sulfate using starch as indicator. This method has the advantage sulfate using starch as indicator. This method has the advantage that the end point is good and the danger of loss of hydrogen sulfide can be greatly reduced by rapid overtitration with iodine using a fast flowing buret.

Ising a last howing buret. It will be seen in the procedure that no extra iodide is added to the solution previous to titration, as is sometimes done in direct titrations of sulfide with iodine. This addition is unnecessary and in fact is purposely omitted in the method because a con-siderable amount of hydriodic acid comes over with the hydrogen sulfide, and any further addition of iodide is detrimental to the starch-iodine end point.

The two gravimetric methods most often used for the determination of sulfur in rubber stocks which are free from barium and large amounts of lead and calcium are those of Wolcsensky (3, hereinafter called the perchloric acid method), and Kratz, Flower, and Coolidge (1, hereinafter called the A. S. T. M. method). In the analysis of representative samples of natural and synthetic rubber stocks these two methods give results which are in good agreement. In like manner it was found (see Table II) that results obtained by the proposed volumetric method and the perchloric acid method check very well, although as would be expected from the data in Table I, the volumetric method gives somewhat lower results.

In agreement with Wolesensky it was found that great care must be taken to prevent loss of sulfur during the digestion of rubber samples with nitric and perchloric acids. The loss is negligible if the sample is digested slowly in a longnecked Kjeldahl flask. When a small Erlenmeyer flask is used, however, the loss may amount to 1 or 2 per cent (when the new volumetric method is used for the final determination), unless the digestion is slow and the flask is kept completely covered with a watch glass until all organic matter is expelled. In the procedure an attempt has been made to minimize this loss by delaying the addition of the perchloric acid until most of the readily oxidizable material has been oxidized. After oxidation of the organic material the sample can be taken to copious fumes of perchloric acid without loss of sulfur, providing an excess of zinc is present. This suggests that the sulfur, which is lost during the digestion of the organic matter, has not been oxidized to sulfate. No loss of sulfur is encountered when the A.S.T.M. method is used.

TABLE II. DETERMINATION OF TOTAL SULFUR IN NATURAL AND SYNTHETIC RUBBER USING PROPOSED VOLUMETRIC METHOD

		Per (Cent Sulfur F	ound
No.	Rubber Sample	HClO4 method	HClO4 oxidation	A. S. T. M. oxidation
12	Buna S gum stock	0.19	0.19	
3	Gum rubber 1	0.63	0.62	0.63
5	Gum rubber 2	1.88	1.87	1.85
78	Gum rubber 3	3.55 3.55	3.52 3.48	3.50
9		3.55	3.47	3.48

Experimental

A standard solution of potassium sulfate was prepared by dissolving 0.6780 gram of the pure dry salt in water and diluting to 1 liter in a volumetric flask. Aliquot portions of the solution were evaporated to dryness in 125-ml. Erlenmeyer flasks. The samples were then analyzed for sulfur as directed in the procedure, except that an acid mixture of the following proportions was used: 100 ml. of hydriodic acid (specific gravity 1.70), 100 ml. of hydro-chloric acid, 25 ml. of hypophosphorous acid (50 per cent), and 25 ml. of perchloric acid (60 per cent). The results are shown in Table I Table I.

Four representative types of rubber stocks (containing no barium, lead, or calcium) were analyzed for sulfur as directed in the procedure. Results were obtained using both the A. S. T. M. and the perchloric acid methods of oxidation. The samples were also analyzed by the gravimetric perchloric acid method. The results are given in Table II.

Acknowledgment

The author wishes to express his gratitude to B. L. Clarke and M. L. Selker of these laboratories, who read the manuscript and offered several valuable suggestions.

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Determination of Combined Formaldehyde in Organic Compounds and in Cellulose Formals

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Combined formaldehyde can be determined in organic compounds and in cellulose formals by a method that omits distillation and determines formaldehyde in the hydrolyzate by Blaedel and Blacet procedure adapted to photoelectric colorimeter.

STANDARD methods for the determination of formaldehyde usually require distillation with acid in order to isolate the formaldehyde. Organic compounds containing combined formaldehyde yield formaldehyde quantitatively when hydrolyzed in the presence of sulfuric acid. In the method presented distillation is omitted and the formaldehyde is determined in the hydrolyzate by the Blaedel and Blacet (1) procedure adapted to a photoelectric colorimeter in which a magenta color is developed by use of Schiff's reagent. Correct results may be obtained even in the presence of considerable amounts of other aldehydes. Amounts of formaldehyde between 0.01 and 0.10 mg, may be determined in 5 ml. of solution. Thus the method is applicable to large samples containing low concentrations or to small samples containing high concentrations of formaldehyde (Table I).

TABLE I. TYPICAL ANALYTICAL DATA

contraction formation offering secured 5.00	Formald	ehyde	
Compound	Theory	Found	Error
	%	%	%
Trimethylene-d-mannitol, m. p. (corr.) 232° C., C ₄ H ₁₄ O ₆	41.29	41.2	-0.2
Diacetyldimethylene-d-mannitol, m. p.		20.3	+0.5
(corr.) 164-5° C., C12H1108 Dimethylene-d-dulcitol, m. p. (corr.)	20.69	20.8 29.1	+0.5 -0.1
248-9.5° C., C.H14Os Discetyldimethylene-d-dulcitol ^a , m. p.	29.13	29.0 20.0	-0.4 -3.3
(corr.) 256-62° C., CizHisOs	20.69	20.0	-3.3
204-6° C., CoH1400	41.29	40.9	-0.9
Trioxymethylene, CalleOa	100.0	100.3	+0.3
Ethylal, CsH12O2	28.84	28.4	-1.6
Cellulose formal (1)	0.355	0.34	-2.9 -2.9
Cellulose formal (2)	1.965	1.99	+1.5
β-Methylethylidene glucoside, m. p. (corr.)	and a state of	1.55	71.0
186-8° C., C ₉ H ₁₆ O ₆ Cellulose	0.0	0.0	0.0
Formaldehyde, 14 mg. per liter + 200 mg. of	100.0	100.3	+0.3
Formaldehyde, 14 mg. per liter + 200 mg. of	100.0	100.0	1010
propionaldehyde	100.0	100.3	+0.3
Acetaldehyde (200 mg.)	0.0	0.0	0.0
riopionaluenyue (200 mg.)	0.0 ,	0.0	0.0

^a Compound probably impure. Haskins, Hann, and Hudson (2) give m. p. (corr.) of 264-265⁵ C ^b Values obtained by distillation followed by dimedone precipitation method.

With 12 N sulfuric acid, a constant maximum yield of formaldehyde is reached in 16 hours or less from cellulose formals at room temperature, but 16 days are required to attain theoretical yields of formaldehyde from trimethylened-mannitol and similar compounds. For lower concentrations of acid longer time is required. However, on heating at 90° C. these latter compounds, as well as cellulose formals, yield formaldehyde quantitatively in 2 hours (Table II). Further heating of cellulose formals with 12 N sulfuric acid produces darkening of the solutions and gives lower values. For this reason, heating for 2 hours at 90° C. is recommended as a general procedure, but for cellulose formals (samples analyzed contained less than 2 per cent of formaldehyde) overnight treatment with 12 N sulfuric acid at room temperature is satisfactory.

	Formaldehyde					
Material	Theory	2 hours	5 hours	8 hours	16 hours	24 hours
Trimethylene-d-mannitol	41.20	41.4	40.9	40.8	41.2 40.7	41.9
Dimethylene-d-dulcitol	29.13	29.1 29.0	29.0 28.9	29.2	28.8 28.6	28.6
Cellulose formal	1.52	1.53	1.40	1.28		

The size of sample is selected to yield a concentration of formaldehyde of approximately 0.05 mg. in 5 ml. of the hydrolyzate. It is desirable to set up a series of standards containing amounts of formaldehyde ranging from 0.01 to 0.10 mg. in 5 ml. and to develop the color in them at the same time as in the unknowns by adding 6 ml. of 10 N sulfuric acid and 10 ml. of the fuchsin-sulfite reagent. This reagent (1) is prepared by dissolving 0.5 gram of fuchsin (rosaniline hydrochloride) in 500 ml. of water, adding 5.15 grams of sodium acid sulfite, allowing to stand 15 minutes, adding 17 ml. of 6 N hydrochloric acid, and allowing to stand at least 3 hours before using. The reagent is stable for at least a month. The tubes are allowed to stand from 2 to 2.5 hours, during which time the color given by higher straight-chain aldehydes and their polymers fades completely, though fading of the color given by formaldehyde is not appreciable (1). The transmission is then determined and plotted against milligrams of formaldehyde to give a curve like the one shown in Figure 1. The formaldehyde solution used for the preparation of the standards is standardized by dimedone (5,5-dimethylcyclohexanedione-1,3) precipitation according to Yoe and Reid (4).

When color is developed by adding fuchsin-sulfite reagent to known amounts of formaldehyde, a definite and reproducible curve rather than a straight line is obtained when either the transmission or the logarithm of the transmission is plotted against the concentration. Other color reagents for formaldehyde, such as phloroglucinol in basic solution and phenylhydrazine hydrochloride in either acid or basic solution, also fail to give straight lines and the curves are not so nearly reproducible as those obtained with fuchsin-sulfite reagent.

Experimental

Crystalline formals of known composition were prepared from the corresponding alcohols by the method described by Haskins, Hann, and Hudson (2). They were purified to constant melting points by recrystallization and their identities were further verified by carbon and hydrogen determinations. The ethylal was purified by distillation.

purified by distillation. The data presented in Table I were obtained by weighing accurately 20 to 40 mg. of the crystalline compounds, transferring to 1-liter volumetric flasks, and dissolving in and making to volume with 12 N sulfuric acid. Portions of the solution were poured into glass-stoppered 250-ml. Erlenmeyer flasks, stoppered tightly, and placed in a constant-temperature oven at 90° C. After 2 hours the flasks were removed and cooled, and 5-ml. aliquots were pipetted into matched tubes of an Evelyn photoelectric colorimeter, provided with filter No. 565 (Corning Glass Co.). To each were added 6 ml. of water (6 ml. of 10 N sulfuric acid to the stand ards) and 10 ml. of the fuchsin-sulfite reagent. After addition of the reagent, the tubes were allowed to stand from 2 to 2.5



FIGURE 1. TYPICAL WORKING CURVE

hours and the transmission was determined. Spectrophoto-metric curves of the color developed indicated that filter 565, whose transmission limits are 550 to 585 m μ , is the correct filter to use

In the case of cellulose formals, about 0.1 gram of the material was accurately weighed and placed in 250-ml. glass-stoppered Erlenmeyer flasks. Exactly 100 ml. of 12 N sulfuric acid were added to each flask, and the flasks were placed in a constant-temperature oven at 90° C. for 2 hours or allowed to stand overtemperature oven at 90° C. for 2 hours or allowed to stand over-night at room temperature. Formaldehyde was determined on 5-ml. aliquots of the solution as described above. Solution of the sample was not necessary for correct results. Since cellulose formals of known composition were not available, the results obtained by the method described here were compared with the values determined by distilling the formaldehyde by the method (S) followed by determined for of formaldehyde in an of Wood (3), followed by determination of formaldehyde in an

aliquot of the distillate by dimedone precipitation according to Yoe and Reid (4).

The data in Table I show that acetaldehyde or propionaldehyde did not interfere with the determination. β -Methylethylidene glucoside and cellulose, both of which produce aldehyde groups but no formaldehyde on acid hydrolysis, gave zero values. Good agreement was obtained between the analysis of cellulose formals by the colorimetric and dimedone gravimetric methods.

In order to determine how small a sample it was practical to use, 5.840- and 6.207-mg. samples of trimethylene-d-mannitol were weighed on the microbalance, placed in 250-ml. volumetric flasks, and made to volume with 12 N sulfuric acid. The flasks were placed in a constant-temperature oven at 90° C. for 2 hours and cooled. Using 5-ml, aliquots and the above-described colorimetric procedure, values of 40.6 and 41.0 per cent formalde-hyde were obtained. Samples of 0.062 and 0.127 mg, smaller than those commonly used for microanalysis, were weighed on that those commonly used for microanalysis, were weighed on the microbalance, placed in matched tubes of the colorimeter, and 5-ml. portions of 12 N sulfuric acid were added with a pipet. The stoppered tubes were heated at 90° C. for 2 hours and the color was developed, giving values of 39 and 40 per cent of formalde-hyde, respectively. Considering the very small samples used, these values are in satisfactory agreement with the theoretical value of 41.29 per cent.

Acknowledgments

The authors are indebted to the following members of this laboratory: James H. Kettering, Lamont Hagan, and J. David Reid for the cellulose formals; Richard E. Reeves for the β -methylethylidene glucoside; and Robert T. O'Connor for the spectrophotometric curve of the color developed.

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NOTE ON ANALYTICAL PROCEDURE

Stability of the Nickelous-Ammonia Color System

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IN DEVELOPING a colorimetric method for the determination of nickel in steel with ammonia Ayres and Smith (1) found no change in the color of the system after 150 hours. In a spectrophotometric study of this method the senior author of this paper found that there was no evidence whatever of fading or other color change over a period of 4 weeks (2).

For the purpose of further study the six solutions which had been used in this test (2), containing 100, 200, 300, 500, 1000, and 1500 p. p. m. of nickel in 1.5 M ammonium hydroxide, were allowed to stand 55 weeks longer in glassstoppered Pyrex bottles in diffuse light. Spectral transmission curves were then made with the self-recording photoelectric spectrophotometer at Purdue University, and, when compared with the curves given by the corresponding freshly prepared solutions, were found to be very similar. From the transmittancy at 582 mp, the wave length of maximum absorption for this system, the percentage error in the apparent concentration of nickel was calculated (2) by use of the special color slide rule.

The range of apparent change in concentration of the nickel was from -0.7 to +7.1 per cent (average 3.0 per cent), thus showing that the color of the system is practically unchanged after 59 weeks. The percentage error is less in the more concentrated solutions (3). Such marked stability makes possible the use of a series of permanent standards, which must, however, be kept tightly stoppered to prevent loss of ammonia. The action of ammonia on the glass is reduced to a minimum when Pyrex containers are used.

Acknowledgment

The writers wish to thank M. G. Mellon of Purdue University, in whose laboratory this work was done, for the privilege of using the Purdue spectrophotometer.

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SCIENTIFIC APPARATUS BORATORY EQUIPMENT

Electro-Stripper

The efforts to reduce the thickness of tin coating applied to steel sheet have necessitated new methods of analysis in the laboratory, as errors inherent in older methods are proportionately higher when the thickness of the tin coating is reduced. The Bendix ElectroStripper has been developed for the determination of tin coating according to the method developed by Bendix, Stammer, and Carle [IND. ENG. CHEM., ANAL. ED., 15, 501 (1943)] and is available from the Wilkens-Anderson Co., 111 North Canal St., Chicago 6, Ill. With it one operator may handle 200 determinations in one day.

Multiple-Unit Combustion Furnace

Incident to the stepped-up production of high-octane aviation gasoline essential to the war program, the Universal Oil Products Co., Chicago, Ill., has developed a multiple-unit electrically heated combustion furnace offering several novel features. The equipment is manufactured by the Precision Scientific Co., 1750 North Springfield Ave., Chicago.

Although designed specifically for the determination of carbon on cracking catalysts used for producing high-octane aviation gasoline, the equipment is modifiable to handle a wide variety of organic combustions within the temperature limit of 540° C. (1000° F.).

Briefly, the equipment comprises (1) oxygen-purification system for combustion gases; (2) oxygen pressure-regulating column; (3) electrically heated furnace 24 inches long, with four combustion tubes 1 inch in diameter and 30 inches long. Heating intensity for each half of each tube is independently controlled, and temperature of any tube can be readily observed by means of an indicating pyrometer; (4) conventional absorption trains with calcium chloride for absorption of moisture and Ascarite for removal of carbon dioxide.





BOOK REVIEWS

Frontiers in Chemistry, Volume I. The Chemistry of Large Molecules. Edited by R. E. Burk and Oliver Grummitt. xii + 313 pages. Interscience Publishers, Inc., New York, N. Y., 1943. Price, \$3.50.

This is a collection of the substances of 12 lectures, presented by six outstanding American chemists at Western Reserve University early in 1942.

In the first chapter, by H. Mark, the mechanism of polymerization reactions is ably discussed, with emphasis on the kinetic theory equations on which the interpretation of such reaction mechanisms is based and on the assumptions underlying them. In the second chapter, Professor Mark presents a clear and useful summary, in nontechnical language, of the results of x-ray investigations of high polymers.

E. O. Kraemer contributes an interesting discussion of the viscosity of solutions of macromolecules and of the diffusion of these molecules in such solutions. He then presents an authoritative critical account of the application of the ultracentrifuge to the study of the sizes and shapes of large molecules.

A. Tobolsky, R. E. Powell, and H. Eyring, in an outstanding chapter on "Elastic-Viscous Properties of Matter", first outline, with the appropriate mathematical equations, a general procedure for the semiquantitative theoretical treatment of properties involving flow; they then apply this procedure, and others involving statistical methods, to the interpretation of various properties of systems containing giant molecules. Rubberlike elasticity and the viscosity and thermodynamic properties of solutions of long-chain polymers are especially considered.

R. M. Fuoss presents an excellent treatment of "The Electrical Properties of High Polymers", showing how the variation of dielectric constant and loss factor with temperature and with frequency is related to the polymer structure.

C. S. Marvel gives a fine discussion of the "Organic Chemistry of Vinyl Polymers", dealing especially with the evidence, obtained by classical organochemical methods, regarding the sequence of groups in vinyl polymer chains.

E. Ott, in the final chapter, contributes an admirable summary of the "Chemistry of Cellulose and Cellulose Derivatives", correlating the chemical properties of these substances with their structures.

Western Reserve University, the publishers, the editors, and the authors are all to be congratulated on this interesting and useful addition to the literature on giant molecules.

MAURICE L. HUGGINS

Inorganic Qualitative Analysis. H. A. Fales and Frederic Kenny. First edition. ix + 237 pp., 39 figures, 14 × 21 cm. D. Appleton-Century Co., New York, N. Y., 1943. Price, \$2.65.

The announced purpose of this book "is to present some important fundamental principles of chemistry and to use as a framework for the study of these principles well-tried and well-established qualitative analytical procedures".

The principles, covering seven chapters and including a total of 155 numerical problems, deal with general considerations, types of compounds, strong and weak electrolytes, hydrolysis of salts, solubility product, complex ions, and oxidation-reduction theory. This presentation seems adequate for a professed one-semester book. A schedule is included to correlate the class and laboratory work.

Laboratory directions, for work on a semimicro scale, cover 74 pages. Conventional procedures include 23 cations, but, as usual, the alloying metals in steel are slighted. The anions are limited to four—chloride, nitrate, sulfate, and carbonate. Obviously, real qualitative analysis of complicated unknowns is not contemplated. Each group of procedures includes supplementary experiments designed to illustrate the fundamental principles emphasized.

As a whole, the book reflects the careful writing characterizing the authors' previous text on quantitative analysis. It is clear, concise, and conservative. To the reviewer, it looks teachable in the kind of course for which it was written.

M. G. MELLON

Methods for Tungsten Analysis

The Bureau of Mines has published a report on methods of analyzing tungsten ores, particularly those from low-grade deposits now being explored because of a great wartime demand for the steel-hardening metal.

Analyses of the tungsten content of low-grade ores often have varied widely and have led to confusion. Dependable methods of analysis applicable to all types of these ores are essential, to determine which are worth treating and to regulate the method of treatment to assure the best recovery. To fill this need the report describes in detail three methods tried and proved in the Bureau of Mines laboratory at Salt Lake City: the standard cinchonine method, the tannic acid-antipyrine method, and a third method combining the first two.

The combination method was found most suitable for all types of low-grade tungsten ores and now is in use at the laboratory. The time required for analysis is less, the amount of cinchonine needed is reduced, and the final precipitation of tungsten invariably is complete.

A procedure for recovering the cinchonine, a reagent not readily available, also is outlined.

A copy of Report of Investigation 3709, "The Determination of Tungsten in Low Grade Ores", by H. E. Peterson and W. L. Anderson, may be obtained from the Bureau of Mines, Department of the Interior, Washington, D. C.

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