INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

VOLUME 18, NUMBER 12 **ISSUED DECEMBER 18, 1946** **CONSECUTIVE NUMBER 24**

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We acknowledge with thanks the action of J. T. Baker Chemical Co. in releasing the front cover of this issue for editorial purpo ses.

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Published by the American Chemical Society at Easton, Pa. Editorial Headquarters: 1155 16th Street, N. W., Washington 6, D. C.; telephone, Republic 5301; cable, Jiechem (Washington). Chicago Editorial Branch: Room 819, 25 East Jackson Blvd., Chicago 4, Ill., telephone, Wabash 7376. Houston Editorial Branch: 413 West Building, Houston 2, Texas; telephone, Capital 6516. New York Editorial Branch: 60 East 42nd Street, New York 17, N. Y., telephone, Murray Hill 2-4662. San Francisco Editorial Branch: 24 California Street, San Francisco, Calif., telephone, Exbrook 2895. Business Office: American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C. Advertising Office: 332 West 42nd Street, New York 18, N. Y., telephone, Bryant 9-4430.

Entered as second-class matter at the Post Office at Easton, Pa., under the Act of March 3, 1879, as 24 times a year—Industrial Edition monthly on the 1st, Analytical Edition monthly on the 15th. Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

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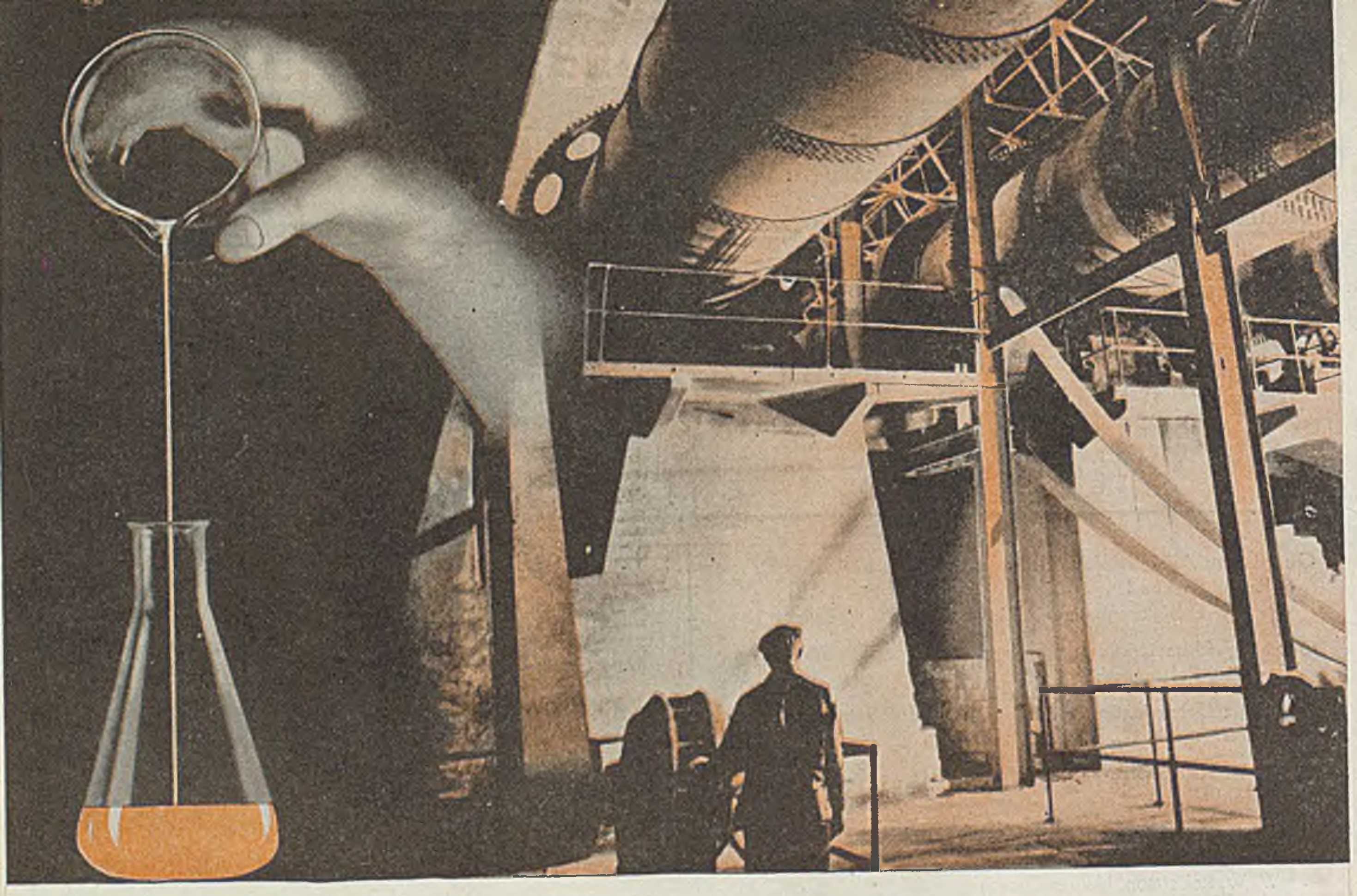

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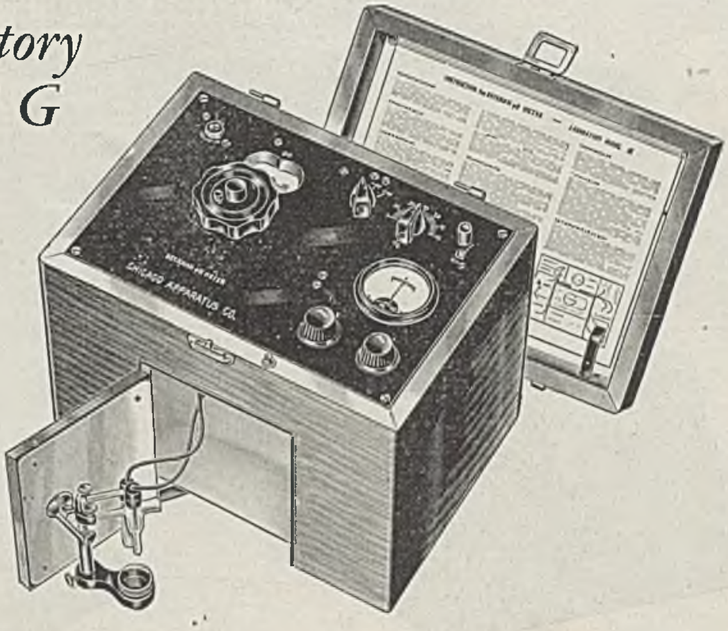

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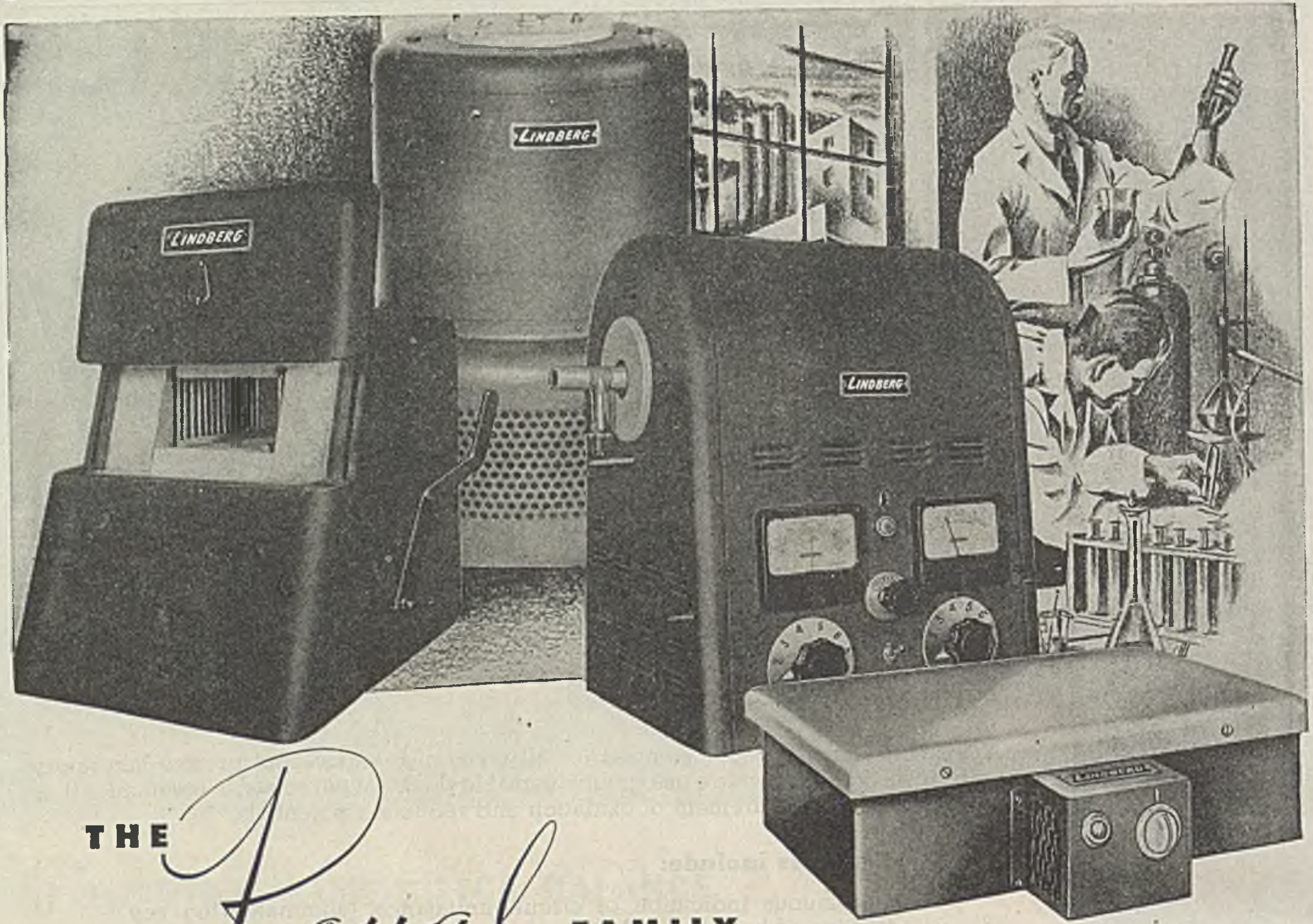

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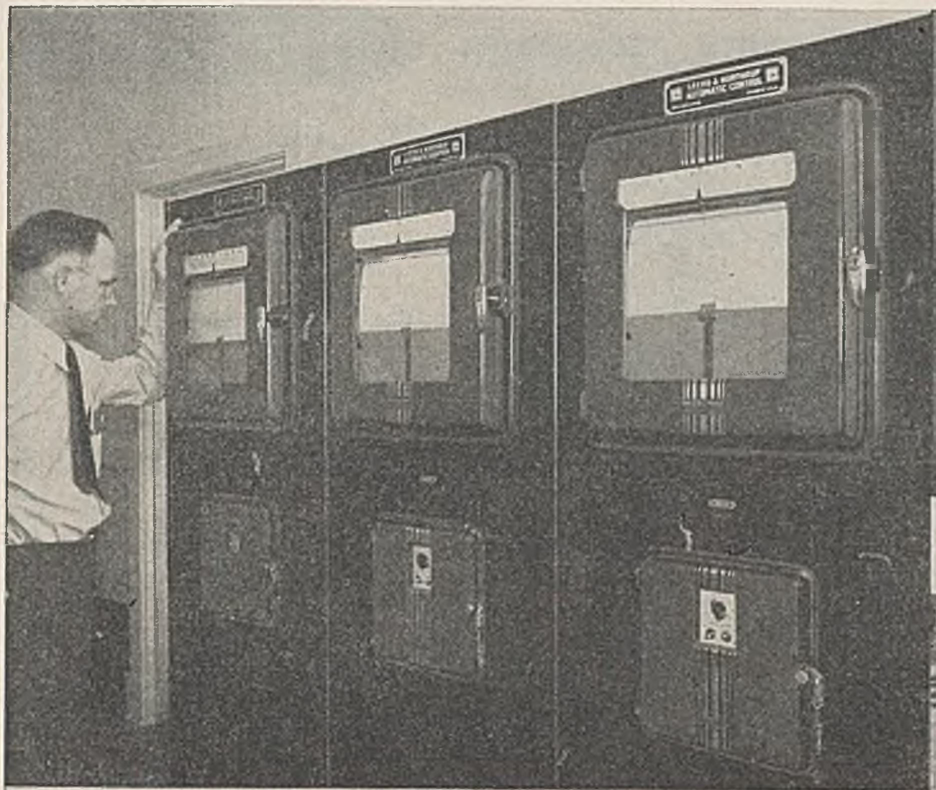

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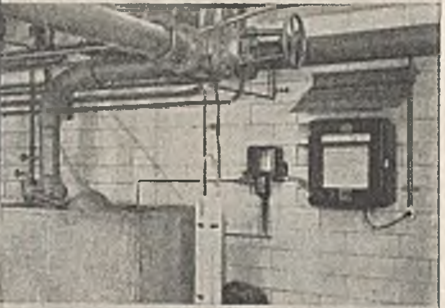

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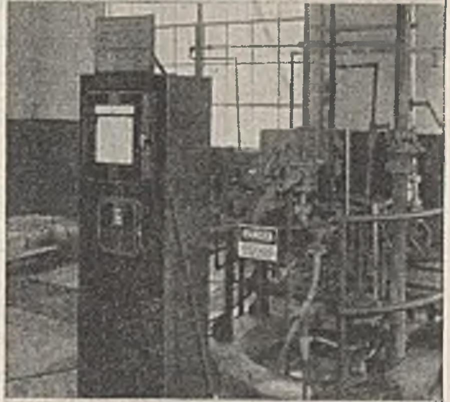

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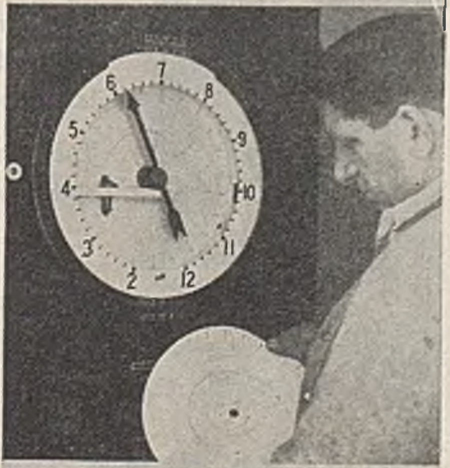

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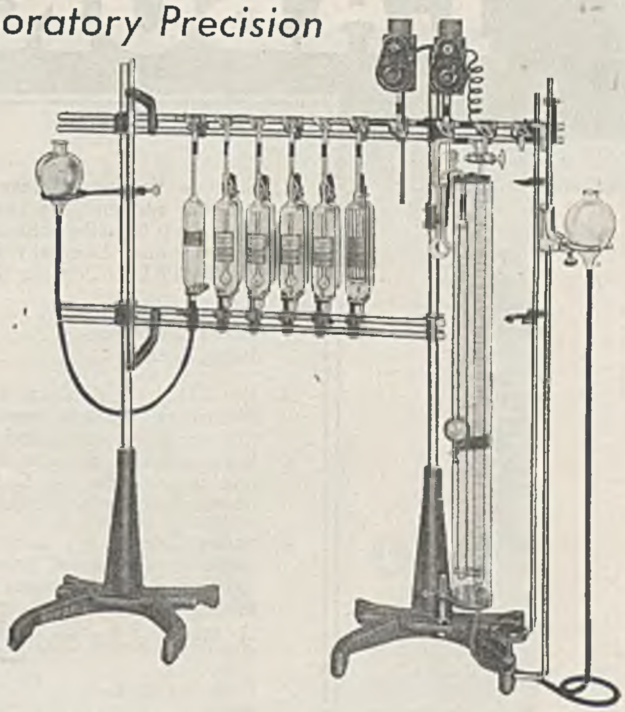

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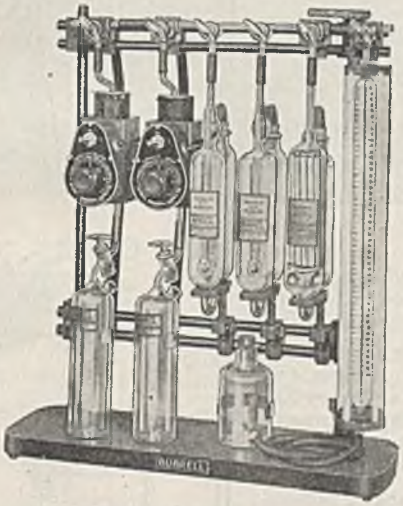

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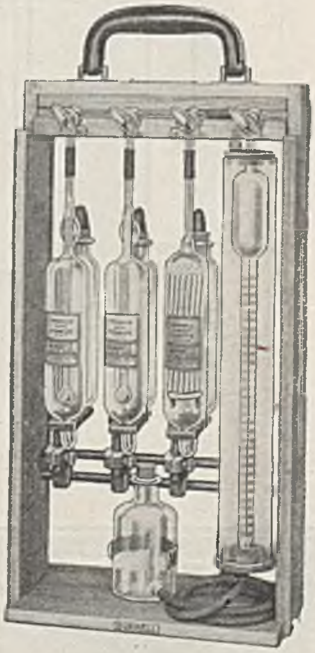

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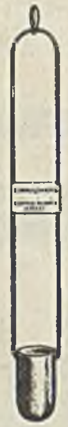

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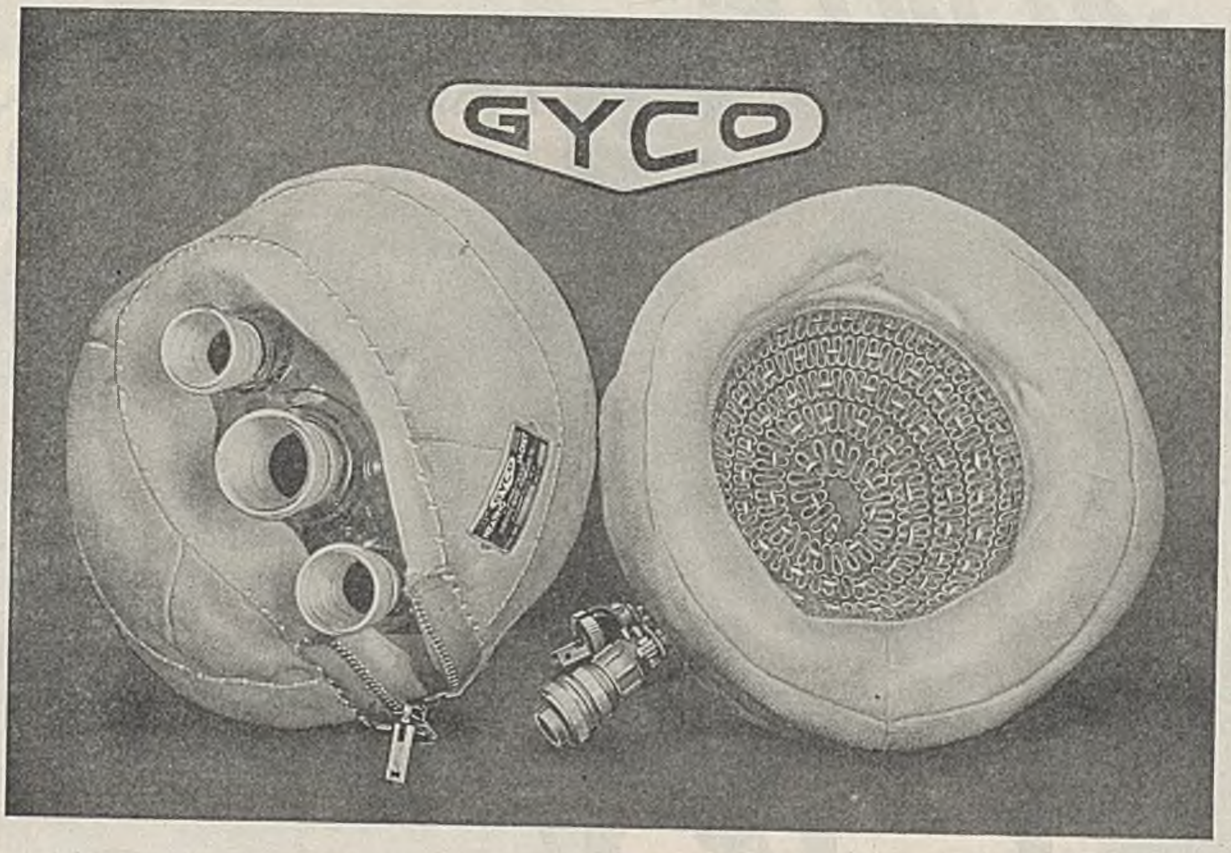

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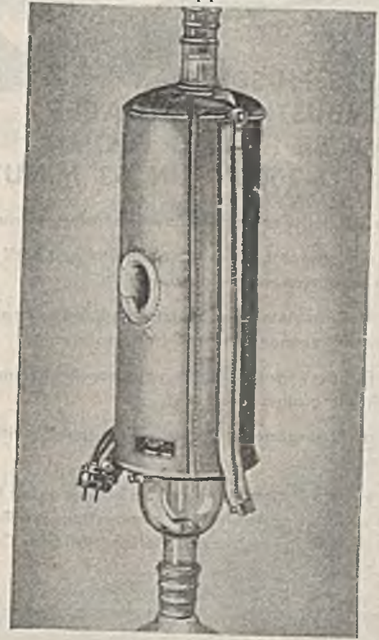

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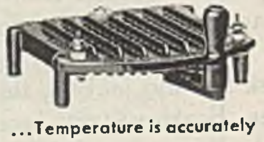

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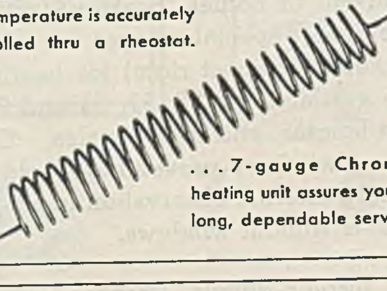

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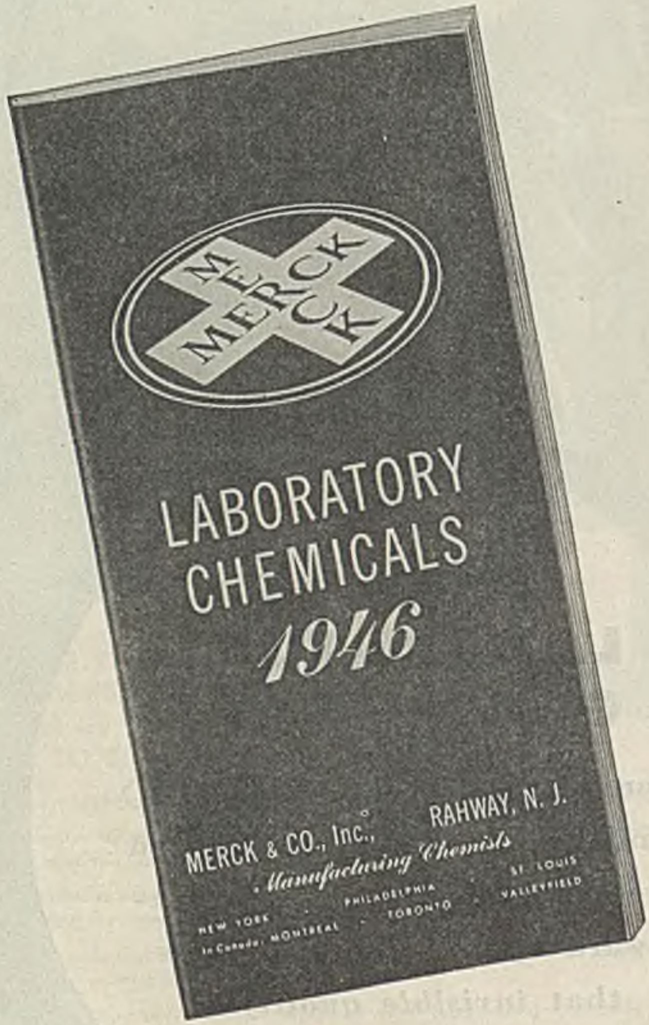
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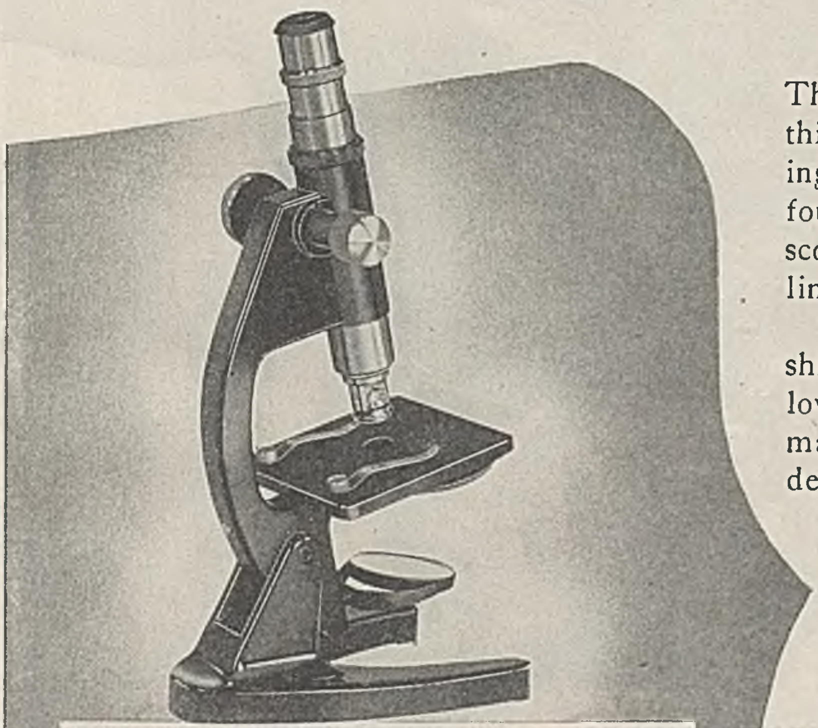

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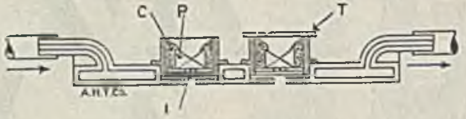

Cross-section of Nichols Refractometer, indicating water circulation within jacket. P, prisms; C, cement; L, engraved line; and T, cover glass

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A determination consists of a simple measurement under the microscope of the distance between two lines and reference to a calibration graph — prepared in accordance with the method outlined below — which permits conversion of the distance directly into n_D without further calculations. The two lines observed in the microscope are refractions of the single line L, 0.0001 inch wide, engraved on the glass base of the cell beneath the prisms and are produced because of the difference between the refractive index of the prisms and that of the sample placed in the cell.

The n_D of solids can also be determined by indirect methods as described in the directions for use.

The instrument is offered in two models, i.e. Macro and Micro, each having a nickel plated brass water jacket, 76 × 38 × 4.5 mm, to permit precise temperature control and two cells marked n_D 1.52 and n_D 1.72, respectively, to provide for convenient measurement of a wide variety of liquids. Each model is supplied with two cover glasses to prevent evaporation of liquids with high vapor pressure.

Macro cells are 11 mm outside diameter and require 100 to 200 cu. mm (2 to 4 drops) of sample; Micro cells are 5 mm outside diameter and require only 6 to 8 cu. mm of sample, of which 5 to 6 cu. mm can be recovered, depending upon the physical properties of the liquid.

Method of Calibration. To calibrate the instrument in accordance with the individual characteristics of the cell and microscope set-up used, the cell is filled with a liquid of known refractive index, covered with a cover glass and placed under a microscope with a magnification of approximately 100×. Then, using the special eyepiece micrometer disc on the diaphragm of the microscope eyepiece, the distance between the two lines observed is measured. This is repeated for each of the five standard liquids supplied with the outfit, and a graph prepared on cross section paper by entering the refractive indices as ordinates and the measured distances in scale divisions as abscissae. The points plotted for the standard liquids will form a line which is nearly straight and from which observed distances for liquids of unknown refractive index can be converted directly into terms of refractive index provided the conditions of test are identical.

8664.	Refractometer, Nichols, Improved Macro Model, complete outfit, as above described, with cells 11 mm outside diameter, with two cover glasses, eyepiece micrometer disc and set of five standard liquids, n_D 1.4000, 1.4500, 1.5500, 1.6500 and 1.7000, respectively, in leatherette velvet-lined case, with detailed directions for use. .	75.00
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Analytical Edition
PUBLISHED BY
THE AMERICAN CHEMICAL SOCIETY
WALTER J. MURPHY, EDITOR

Quantitative Analysis of Hydrocarbon Mixtures by Means of Raman Spectra

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BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

THE subject of hydrocarbon analysis by physical methods has become increasingly important in recent years. Of these methods, two make use of the fact that the set of molecular vibrational energy levels is a unique property of each compound. In the method of infrared absorption spectra, a beam of continuous radiation from a hot body is passed through the sample and the transmitted radiation is examined to learn what has been taken out of it. This information provides the raw data for the analysis of the sample. In the method of Raman spectra, essentially monochromatic light is sent into the sample and the scattered light is examined for lines of modified wave length. The analysis of the sample is based on the position and intensity of these modified lines. The literature on this subject is extensive. The following are typical references: (*1*, *2*, *4*, *8*).

Each method has advantages and disadvantages. The present paper describes the authors' technique for applying Raman spectra to the analysis of certain hydrocarbon mixtures and indicates the type of results obtained.

The method described here is not presented as a fully developed method which can be applied with standard equipment directly to routine analysis. However, it is a relatively simple procedure which leads to useful results with liquid hydrocarbon mixtures.

The Raman spectrum of a typical hydrocarbon in the gasoline range consists of a relatively small number of lines whose sharpness depends on the structural type of the hydrocarbon. When two or more pure hydrocarbons are mixed, the Raman spectrum of the mixture is a superposition of the spectra of the individual components without any frequency displacement. The only type of interference which does occur is the accidental overlapping of lines arising from different compounds. With a spectrograph of sufficient dispersion, this is not a serious difficulty for mixtures containing four or five components, and in almost all cases such a mixture can be analyzed by use of Raman lines which are not overlapped. So far as is known, for constant illumination of the sample, the intensity of light scattered by a hydrocarbon in a mixture is directly proportional to the concentration of the hydrocarbon.

Most Raman spectra are accompanied by an appreciable amount of background scattering, caused either by a continuum from the light sources (mercury arcs) or by fluorescence from a minute amount of fluorescent contamination in the sample. The continuum from the mercury arcs can be reduced or practically eliminated by the use of suitable optical filters, or better still, by a choice of mercury arc which emits relatively little continuous radiation. The fluorescence of the sample can often be greatly reduced by a simple bulb-to-bulb distillation without fractionation, or, in more difficult cases, by a distillation over metallic sodium. However, even when efforts have been made to minimize the background, it is usually present to some extent. The only way to overcome this difficulty is to make a suitable correction for the background when the spectrum is subjected to quantitative evaluation.

The method of internal standards has been used, in both emission and Raman spectroscopy, to reduce the effect of variations in the intensity of illumination. A known quantity of some suitable substance is added to the sample and the blackening of the analysis lines is measured relative to that of the lines of the standard. For example, Rank, Scott, and Fenske (*6*) have described the use of 2 cc. of carbon tetrachloride in 25 cc. of sample as an internal standard. The chief objection to this procedure is the undesirable contamination of the sample, which is often needed for other types of work. Even in moderately complicated mixtures there is a considerable probability that the useful lines of the internal standard would be overlapped. The authors have therefore not used internal standards.

The standard procedure of quantitative photographic photometry involves a calibration of the photographic material used by a graded series of exposures of known relative intensity on each plate or film. When the resulting spots are microphotometered, the optical density (defined as the logarithm of the ratio of the light incident on a spot to the light transmitted through the spot) can be graphed as a function of the logarithm of the intensity of the light used for the exposure (for constant exposure time). Then when the density of an analysis line is read from the microphotometer curve for a sample, the corresponding intensity can be read from *D*–log *I* curve. This procedure is rather time-consuming.

It has been found possible to evade a great deal of the awkwardness inherent in the photographic method without too much loss of accuracy by a semiempirical procedure involving a calibration for each system based on a few mixtures of known composition made up from compounds of high purity. This procedure also makes it possible to take into account the mutual interference of close-lying Raman lines. Once the calibration has been carried out, the calculations involved are brief and very elementary.

EXPERIMENTAL

The Raman spectra described here were obtained with a Steinheil spectrograph with three glass prisms whose dispersion varies from 6 Å. per mm. at 4000 to 20 Å. per mm. at 5000 Å. (*7*). The spectrograph is enclosed in a thermostated plywood box. The light source used for the earlier part of this work was the GE Type H-2 mercury arc. When this arc operates at its normal temperature, it emits a heavy continuum, which can be reduced by cooling the arc until part of the mercury condenses on the walls. However, under these conditions the light output is annoyingly sensitive to small changes in the temperature of the arc. The General Electric Co. kindly supplied an arc similar to the H-2 but with the mercury content reduced to such an extent that the maximum potential drop is 40 volts. These arcs, desig-

Table I. Calibration for Analysis of Four-Component Sample Using Known Mixtures

Raman Line Frequency, Cm.$^{-1}$	Compound	I_e°	Mixture 1 I_e	P	$P_{av.}$	P_c	R_1	Mixture 2 I_e	P	$P_{av.}$	P_c	R_2
818	*p*-Ethyltoluene	0.554	0.517	93.3	...	...	..	...	...	...	...	..
806	*p*-Ethyltoluene	0.530	0.527	99.3	92.1	58.1	0.97	...	...	...	...	..
644	*p*-Ethyltoluene	0.421	0.353	83.8	...	...	..	...	...	...	...	..
744	Pseudocumene	1.38	...	...	...	...	..	0.132	9.6	10.0	5.6	0.56
557	Pseudocumene	1.13	...	...	...	...	..	0.118	10.4	...	...	..
520	*m*-Ethyltoluene	0.398	0.215	54.0	54.0	34.1	1.14	0.450	113.0	113.0	63.9	1.07
576	Mesitylene	2.22	0.273	12.3	12.3	7.8	0.78	1.20	54.0	54.0	30.5	1.02
	Totals				158.4	100.0				177.0	100.0	

			Mixture 3				R_3	Mixture 4				R_4
818	*p*-Ethyltoluene	0.554	0.089	16.1	...	...	...	0.265	47.8	...	...	...
806	*p*-Ethyltoluene	0.530	0.079	14.9	15.1	10.1	1.01	0.306	57.7	51.4	32.8	1.09
644	*p*-Ethyltoluene	0.421	0.060	14.3	...	...	..	0.205	48.6	...	...	..
744	Pseudocumene	1.38	0.476	34.5	32.5	21.8	0.73	1.12	80.8	84.8	54.1	0.90
557	Pseudocumene	1.13	0.344	30.5	...	...	..	1.01	88.8	...	...	..
520	*m*-Ethyltoluene	0.398	...	...	...	...	..	0.082	20.6	20.6	13.1	1.31
576	Mesitylene	2.22	2.26	101.6	101.6	68.1	1.13	...	...	...	...	..
	Totals				149.2	100.0				156.8	100.0	

	R_1	R_2	R_3	R_4	$R_{av.}$
p-Ethyltoluene	0.97	..	1.01	1.09	1.02
Pseudocumene	..	0.56	0.73	0.90	0.73
m-Ethyltoluene	1.14	1.07	..	1.31	1.17
Mesitylene	0.78	1.02	1.13	..	0.98

Raman Line Frequency, Cm.$^{-1}$	Compound	I_e°	$R_{av.}$	I_c
818	*p*-Ethyltoluene	0.554	1.02	0.565
806	*p*-Ethyltoluene	0.530	1.02	0.540
644	*p*-Ethyltoluene	0.421	1.02	0.429
744	Pseudocumene	1.38	0.73	1.01
557	Pseudocumene	1.13	0.73	0.825
520	*m*-Ethyltoluene	0.398	1.17	0.466
576	Mesitylene	2.22	0.98	2.17

nated as Type H-11, are operated with the mercury completely vaporized and consequently are not appreciably temperature-sensitive. They have proved to be excellent sources for exciting Raman spectra. Six of them are arranged concentrically about the tube containing the sample.

For most of the Raman spectra under consideration here, the Raman tube had a volume of approximately 15 cc.; for the remainder, the sample volume was approximately 6 cc. When the amount of sample available permits, the use of the larger size tube has two advantages: the alignment of the tube with respect to the spectrograph is less critical, and the spectral lines obtained are longer, which makes it easier to select the portion of the lines suitable for microphotometering.

The known aromatic mixtures for calibration were made up from material which was especially synthesized or purified for this purpose. The purities as determined by the freezing point method were all 98% or better and most of them were above 99% (*3*). The usual exposure time for aromatic samples is 75 minutes on Ansco Fluorapid film; for paraffinic samples this is increased to 3 hours because paraffins are poorer scatterers than aromatics. A slit width of 0.1 mm. is used.

The particular Raman lines used for an analysis are those strong lines which have no close neighbors and which show the least overlapping with lines of the other compounds present. Which lines are best often depends on the composition of the sample. It is, of course, necessary to use lines which are neither under- nor overexposed—i.e., lines whose density lies in the linear range of the D-log I curve of the photographic emulsion.

The microphotometer curves required are obtained on a Leeds & Northrup recording microphotometer. The optical density of each Raman line used for analysis is read from the curve as well as the density of the background near each line. The antilogarithm of the background density is subtracted from that of the line density to give an effective intensity of the Raman line (I_e).

The sequence of thought leading to the method adopted for obtaining effective intensities from the microphotometer record was as follows:

1. The exposure of a given line on the negative is assumed to be proportional to the concentration of the corresponding compound in the mixture with constant total illumination.
2. Along the linear portion of the characteristic curve ($D = \gamma \log E$), γ, the gradient, depends only on the emulsion and the development conditions used.
3. Following Pierce and Nachtrieb (*5*), it is desirable to make the background correction in terms of E rather than D. If $\gamma = 1$, then E = antilog D. Since the combination of emulsion and development conditions used gave a value of nearly 1 for γ, this relation was the simplest one to try. The authors have since found that even with somewhat different values of γ they get satisfactory results, presumably because the calibration and the analysis are carried out under the same conditions. A much more rigorous method is the construction of the E *vs.* D curve as Pierce and Nachtrieb have done. In view of other possible sources of inaccuracy, it was not considered worthwhile to adopt their procedure.

Table II. Analysis of Four-Component Mixture

Raman Line Frequency, Cm.$^{-1}$	Compound	I_e	P	$P_{av.}$	P_c	P_{known}	Deviation
818	*p*-Ethyltoluene	0.348	61.6	..	..	..	...
806	*p*-Ethyltoluene	0.352	65.2	61.8	25.5	25	+0.5
644	*p*-Ethyltoluene	0.251	58.5	..	..	..	...
744	Pseudocumene	0.578	57.2	59.0	24.5	25	−0.5
557	Pseudocumene	0.502	60.9	..	..	..	...
520	*m*-Ethyltoluene	0.290	62.1	62.1	26	25	+1
576	Mesitylene	1.244	57.4	57.4	24	25	−1

If the exposure conditions and the photographic processing were strictly reproducible and the assumptions made were valid, the effective intensity as used here could be expected to be a linear function of the concentration, provided the blackening of the Raman lines is kept between the proper limits. Because the actual conditions used are rather far from ideal, even when an effort is made to reach a high degree of constancy, use is made of an empirical averaging process and of the fact that intensity ratios are less affected by variations in exposure and development

Table III. Analysis of C_8 Aromatics

Sample No.	*o*-Xylene Raman analysis	*o*-Xylene Deviation from known composition	*m*-Xylene Raman analysis	*m*-Xylene Deviation from known composition	*p*-Xylene Raman analysis	*p*-Xylene Deviation from known composition	Ethylbenzene Raman analysis	Ethylbenzene Deviation from known composition
R 298B	19	−1	30	0	26	1	25	0
R 393	5	0	10	0	11	1	74	−1
R 395	9	−1	9	−1	76	1	6	1
R 392	77	2	9	−1	5	0	9	−1
R 396	10	0.5	69	−2.5	11	1.5	10	0.5
R 398	4.5	−0.5	4.5	−0.5	5	0	86	1
R 400	22.5	−2.5	55	0	22.5	2.5	..	...
Maximum deviation		−2.5		−2.5		2.5		−1
Av. deviation		1		1		1		1

Table IV. Analysis of C_9 Aromatics

Sample No.	*p*-Ethyltoluene Raman analysis	*p*-Ethyltoluene Deviation from known composition	*m*-Ethyltoluene Raman analysis	*m*-Ethyltoluene Deviation from known composition	*o*-Ethyltoluene Raman analysis	*o*-Ethyltoluene Deviation from known composition	Mesitylene Raman analysis	Mesitylene Deviation from known composition	Pseudocumene Raman analysis	Pseudocumene Deviation from known composition
R 845B	30	0	14.5	−0.5	37	−0.5	18.5	1	..	...
R 812A	25.5	0.5	26	1	..	...	24	−1	24.5	−0.5
R 815A	9	−1	..	...	..	...	63.5	3.5	27.5	−2.5
R 846B	12.5	0.5	..	...	44.5	0.5	43	−1	..	...
Maximum deviation		−1		1		0.5		3.5		−2.5
Av. deviation		0.7		0.8		0.5		1.6		1.5

conditions than absolute intensities. The justification for the procedure is ultimately found in the analytical results obtained with it.

The calibration is carried out, as illustrated in Table I, in the following way:

> For each known mixture used for calibration, the effective intensity, I_e, of each Raman line suitable for analytical purposes is divided by the intensity, I_e°, of the same line in the spectrum of the corresponding pure compound photographed under the same conditions. The resulting "percentages", P, for each compound obtained from each of its useful Raman lines are averaged, $P_{av.}$ For each mixture the averages $P_{av.}$ are proportionally corrected to give corrected percentages, P_c, which add up to a total of 100%. The ratio, R, between each of the corrected percentages and the corresponding known percentage is obtained and the ratios for each compound are averaged over the mixtures, $R_{av.}$ Then the intensity of each of the analysis lines of each pure compound is multiplied by its averaged ratio, $R_{av.}$, to give a quantity, I_c, which is the intensity of the line corrected for deviations from average conditions.

In setting up a calibration for a series of compounds, it is usually convenient to take the compounds in groups of three, using two or three known mixtures. To extend the calibration to include other compounds which might be found in samples for analysis together with those of a certain calibrated group, it is necessary to use known mixtures containing at least one compound of that group to ensure that corrections are made to the same average condition.

Once the corrected intensities have been obtained, a quantitative analysis is carried out (as shown in Table II for a four-component mixture) by dividing the effective intensity of each analysis line, I_e, by the corresponding corrected intensity, I_c, and averaging the results from the different lines of each compound, $P_{av.}$ These values are proportionally corrected to a total of 100% if all the compounds in the mixture are included in the analysis, P_c.

If the analysis does not include all the compounds in a mixture, it is necessary to determine the total percentage of all those which are included by some independent method. For example, the aromatic portion of an aromatic mixture containing some paraffinic material can be analyzed because the scattering of paraffins is weak compared to that of aromatics, particularly if the paraffinic material contains a number of compounds. In this case, the total aromatic content must be obtained by one of the quantitative methods for determining total aromatics such as acid absorption or silica gel adsorption.

Strictly speaking, the results of an analysis by means of Raman spectra should be expressed in terms of mole per cent. However, the mixtures usually analyzed are made up of closely related or isomeric compounds whose molecular weight and density are nearly constant. When this is true, no significant error is made in expressing the analytical data in terms of volume per cent.

RESULTS

As illustrations of the results obtainable by means of Raman spectra, representative analytical data for several typical mixtures are presented in Tables III, IV, and V. Table III contains results on a number of C_8 aromatic mixtures. In Table IV data on several four-component C_9 aromatic mixtures are given, while Table V exhibits data on ternary mixtures of trimethylpentanes. The average deviation for paraffinic samples is significantly higher than that for aromatic samples. This is a consequence of the fact that the Raman lines of paraffins are weaker and more diffuse than those of aromatics and hence are more difficult to treat quantitatively.

Table V. Analysis of Trimethylpentane Mixtures

Sample No.	2,2,4-Trimethylpentane Raman analysis	2,2,4-Trimethylpentane Deviation from known composition	2,3,4-Trimethylpentane Raman analysis	2,3,4-Trimethylpentane Deviation from known composition	2,3,3-Trimethylpentane Raman analysis	2,3,3-Trimethylpentane Deviation from known composition
R 497	19	−1	31	1	50	0
R 498	30	0	57.5	−2.5	12.5	2.5
R 870A	78.5	3.5	10.5	0.5	11	−4
R 1046C	59	−1	18	−2	23	3
R 1046D	10.5	0.5	15.5	0.5	74	−1
R 1056A	10	0	45.5	0.5	44.5	−0.5
Maximum deviation		3.5		−2.5		−4
Av. deviation		1		1		2

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PUBLICATION delayed for security reasons.

Operating Characteristics of the Sargent Model XX Visible Recording Polarograph

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The general characteristics of the Sargent-Heyrovský visible recording polarograph are described. Information is presented on its performance in the measurement of half-wave potentials and diffusion currents, and on the operation of the compensator circuit. The performance of the instrument is compared to that of other commercially available recording polarographs.

THE accuracy and reliability of a polarographic analysis depend primarily on the proper control of the various factors that govern the diffusion current, the choice of supporting electrolyte, elimination of interfering substances, and, above all, on an appreciation of the limitations of the method, rather than on the elegance of the electrical instrumentation. An elaborate recording polarograph is not essential to successful applications of polarography; indeed, none of the recording instruments commercially available today is capable of yielding polarographic data of greater accuracy than one can obtain with relatively simple manual apparatus (*3*, *7*, *8*), and some of them are distinctly inferior to the manual equipment in this respect. The sole advantage of a recording polarograph over manual instrumentation is its greater convenience.

There are two types of recording polarographs on the market: (*a*) those that employ galvanometric photographic recording, as in the original Heyrovský-Shikata polarograph (*1*, *3*), and (*b*) those that record the polarogram directly by a pen (or equivalent device) on a moving chart. This paper attempts to present objective information on some of the operating characteristics of the newest instrument of the latter type, the Model XX visible recording polarograph manufactured by E. H. Sargent and Co., Chicago, Ill.

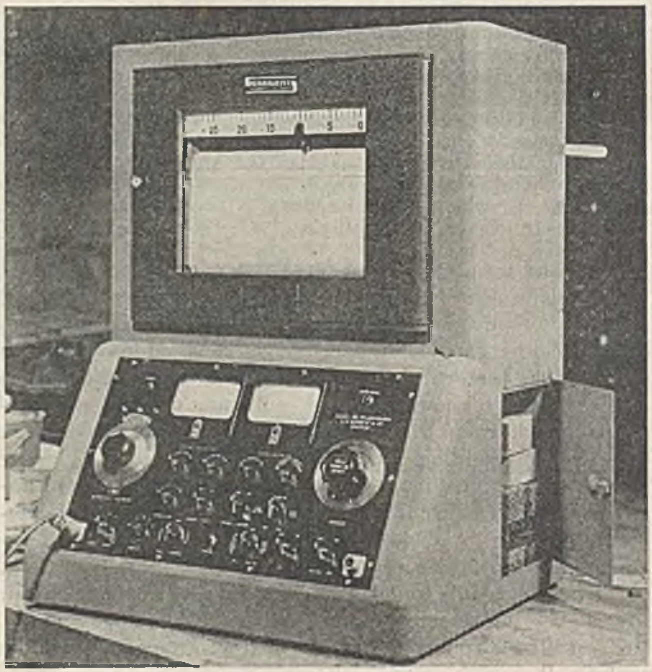
GENERAL

A photograph of the instrument is shown in Figure 1. It is completely self-contained, and to put it in operation it is only necessary to connect a line cord to a 95- to 135-volt, 60-cycle source of alternating current, and to connect another cord to ground. The instrument is robust, with few delicate parts, and is not affected by vibrations. The design of the cabinet leaves nothing to be desired, the numerous controls being mounted on a convenient sloping panel in front of, and below, the recording unit. The recording unit, motors, and chart lights are powered from the alternating current line; self-contained dry batteries are used for the polarographic circuit.

An increasing e.m.f. is applied to the polarographic cell by a motor-driven potentiometer (marked "bridge" on the panel). The resulting current is measured by passing it through a resistance and recording the potential drop, iR, across this resistance with the recording unit. This principle of current measurement has been used very satisfactorily for a number of years in manual equipment (*3*, *7*, *8*). The range of the recording potentiometer is fixed (0 to 5 millivolts) and the current sensitivity is varied by changing the magnitude of the standard resistance.

The continuous chart is 28 cm. wide and it moves at the rate of 3.78 cm. per minute (90 inches per hour). Full rotation of the bridge corresponds to 41 cm. on the chart, and requires 10 minutes 45 seconds. The bridge and chart are driven individually by two synchronous motors, and either can be activated independently of the other or both can be operated synchronously. This good feature, which was also present in earlier models of the Heyrovský-type polarograph, permits the recording of changes in current with time at a constant value of the applied e.m.f.; it is useful in determining rates of reactions involving polarographically active substances—e.g., oxygen.

The bridge is provided with a friction clutch to permit manual adjustment. The attached circular scale is graduated in 100 units, but cannot be read precisely because the index pointer is so far removed from the scale that the parallactic uncertainty is relatively large. The total voltage across the bridge is adjustable from 0 to 3 volts by a variable resistor, and it is indicated on a voltmeter (span potential meter). A potentiometer circuit is also provided for introducing an e.m.f. to the cell independently of the bridge (initial potential control). This enables the starting of a polarogram at any applied e.m.f. from 0 to 3 volts and with any desired voltage (up to 3 volts) across the bridge, and it extends the total range of applied e.m.f. to 6 volts. This is particularly useful when it is desired to make an extended recording of the wave form of a substance with a fairly negative half-wave potential, such as zinc. A switch is provided for changing the zero point of the bridge from its normal end position to the exact center, so that a continuous change from "anodic" to "cathodic polarization" may be obtained. A switch is also present for changing the polarity of the leads to the polarographic cell.



COURTESY E. H. SARGENT AND CO.

Figure 1. Sargent Model XX Visible Recording Polarograph

A "compensator" incorporated in the instrument may be used to send a countercurrent of variable magnitude through the current-measuring resistance to balance out interfering diffusion currents (*2*, *3*, *6*, *9*). The operation of the compensator is discussed in a following section.

The recording unit is a Brown Electronik potentiometer recorder (manufactured by Brown Instrument Co., Philadelphia, Pa.) with a range of 0 to 5 millivolts. The fact that the potentiometer in this recorder is continuously, rather than periodically, balanced causes the instrument to function like a critically

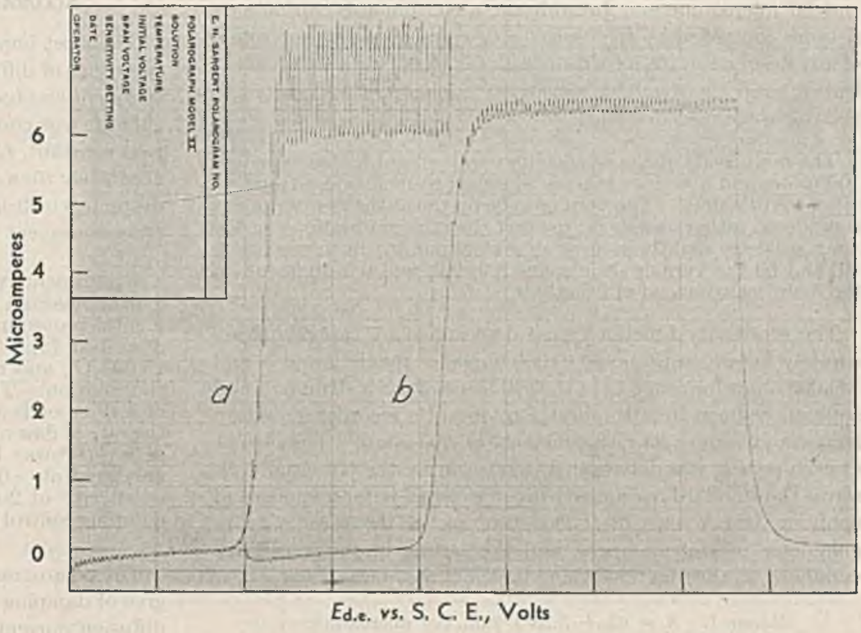


Figure 2. Typical Polarograms of 1 Millimolar Lead Ion in 1 M Potassium Chloride with Different Degrees of Damping

a, damping control in position 1. *b*, damping control in position 5.

damped galvanometer without overshooting or hunting, and thus it is well suited to recording the oscillatory current obtained with the dropping mercury electrode. The recorder has a rapid response, and, provided no external electrical damping is employed, full-scale traverse of the pointer and pen requires only about 5 seconds. Since the e.m.f. indicated by the recorder is the ohmic potential drop across the current-measuring resistance, it is included in the observed values of half-wave potentials, but because the range of the recording potentiometer is only 0 to 5 millivolts the correction will not exceed one half the latter value and is small enough to be neglected in most cases.

The instrument contains an auxiliary circuit, controlled by the zero set rheostat, by means of which the zero position of the recording pen may be adjusted to any position on the scale; like the compensator, this circuit sends a countercurrent through the current-measuring resistors. This adjustment functions satisfactorily, and it is particularly useful when recording polarograms that comprise both anodic and cathodic waves.

Because the accuracy with which half-wave potentials can be measured depends on the accuracy of the span potential and initial potential meters, the latter were checked as follows: The bridge was set to 100 with the outlet leads connected to a potentiometer, and various voltages were set on the meters (by adjustment of the span potential control and initial potential control rheostats) and measured with a potentiometer. The span potential voltmeter was found to be correct within the accuracy with which it could be read (*ca.* ±0.01 volt), but the initial potential voltmeter showed a positive error of 3% over the range from 0.5 to 2 volts. The fact that the applied e.m.f. cannot be measured more precisely limits the usefulness of the instrument for certain research purposes.

The strip chart furnished with the instrument is divided into separate sections, with blank spaces between, the length of each section on the time or voltage axis corresponding to full rotation of the bridge. The voltage axis is provided with ten lines per section, each line corresponding to one tenth of the bridge. The current axis is graduated with millimeter lines. The division into sections is wasteful and inconvenient because care must be taken to start a polarogram well in advance of the end of a section to avoid running into the blank spaces. A chart with continuous markings along the voltage axis would be much more useful. Each section carries in one corner a 7.5 × 14 cm. blocked-in form captioned "E. H. Sargent Polarogram No.", and containing various spaces for noting pertinent data (see Figures 1, 2, and 4). This form has little practical utility and it wastes space. It would also be advantageous for photographic reproduction if the chart were printed in blue lines rather than in green as furnished, and if black ink were used in the pen rather than red.

It is advantageous in recording a series of polarograms to "nest" them together on the chart, especially in preparing illustrations for reproduction. It is awkward to do this with the present instrument, because when the chart is turned back by hand the paper is not taken up on the original roll but accumulates in the back of the chart carriage. If the original roll were provided with a knob, so that it could be turned to take up the slack, this operation would be greatly facilitated. It would also be convenient if some device were provided to support the pen out of contact with the chart to avoid recording during preliminary adjustments of the controls.

It was observed that the instrument, even though grounded, is somewhat sensitive to disturbances by other electrical apparatus in its neighborhood. For example, even with the applied potential switch in the "off" position, a displacement of the recorder zero was obtained when the stirring motor of an adjacent water thermostat was turned on, and also when the thermostat relay operated. (The thermostat and relay also were grounded.) Because of this effect the thermostat was always turned off during the recording of polarograms. It was noted that the "pick-up" effect disappeared when the cell leads were disconnected completely from the instrument, which leads the writer to believe that the effect is due to defective design of the applied potential switch rather than the recording unit.

CELLS

Two types of cells were furnished with the instrument, and in the writer's opinion neither is satisfactory. One cell is of the Erlenmeyer flask type, much used in the early days of polarography but long since obsolete, which requires the use of mercury as anode and cannot be thermostated conveniently. The other cell, which is in the shape of a cylinder with an elaborate ground-glass top, also uses a mercury pool anode and is even less satisfactory than the first, because the anode connection terminates in a radio grid cap sealed on the bottom of the vessel, which makes it impossible to place the cell in a water thermostat. The undesirability of a mercury pool anode, as well as the importance of temperature control, has been discussed elsewhere (*3*). Satisfactory cells and dropping electrode assemblies are not available commercially, despite the fact that these are at least as important units of polarographic instrumentation as the electrical circuit.

The dropping electrode assembly furnished with the instrument, consisting merely of a capillary connected directly to a mercury leveling bulb by rubber tubing, is inadequate for serious work because no provision is made for measuring or reproducing the head of mercury. A stand-tube assembly, preferably with a stop-clock circuit for automatically measuring the rate of flow of mercury (*5*), is most useful for rapid, routine analyses by means of standardized diffusion current constants (*4*). The time is past when polarographic analyses had to be based on frequent, time-wasting "comparison calibrations".

CURRENT SENSITIVITY FUNCTIONS

The sensitivity is varied by adjusting the resistance across which the recorder is connected to record iR drop. Three ranges are selectable by the selector switch marked "Range", with full-scale (28-cm.) deflections corresponding approximately to 0.5, 5, and 50 microamperes. In addition, a continuously variable resistance controlled by the "sensitivity vernier" permits selection of any desired sensitivity within each range. This is an excellent feature, and the available sensitivity ranges are well suited to polarographic measurements.

The main scale of the sensitivity vernier is graduated from 0 to 100 units, and a vernier scale is attached to facilitate estimation of tenths of a unit. The vernier scale on the author's instrument is rendered rather useless by the fact that the graduations on the main scale are slightly in error at several points; at divisions 10, 40, and 90 the vernier scale spans 8.9, 9.2, and 9.2 divisions on the main scale instead of exactly 9.

The sensitivity functions were determined by connecting accurately known resistances (10,000 ohms for ranges 2 and 3, and 100,000 ohms for range 1) to the cell leads of the instrument, and applying voltage from the bridge to obtain a recorder deflection large enough for exact measurement (*ca.* 200 mm.). The current at each setting was determined by measuring the potential drop across the standard resistance with an external potentiometer and applying Ohm's law (*3*). Denoting by S the sensitivity in millimeter per microampere, and the setting of the sensitivity vernier by V, the functions found for the three ranges were

Range 1. $S = 65 + 5.28\ V$ mm. per microampere
Range 2. $S = 6.0 + 0.538\ V$
Range 3. $S = 0.06 + 0.0533\ V$

With different instruments the constants may be slightly different, but the equations will probably be of the same form. Note that the slopes of the sensitivity lines change by a factor of 10 between each range; the intercepts also change by a factor of 10 between ranges 1 and 2, but by a factor of 100 between ranges 2 and 3.

The sensitivity is conveniently denoted by a symbol like 2-60, signifying sensitivity range 2 and the sensitivity vernier at 60.

An advantage of an instrument of this type over a recording galvanometer is that the sensitivity functions need to be determined only once, whereas a galvanometer requires more or less frequent checking.

DAMPING CONTROL

A damping control is provided to decrease the oscillations resulting from the growth and fall of the mercury drops at the dropping electrode. It functions by introducing capacitors of various magnitudes in parallel with the current-measuring resistors. The fundamental principles of condenser damping in polarographic measurements have been discussed in detail elsewhere (*3*, *6*). Five different degrees of damping, corresponding to five different values of the capacitance, are available.

It is essential that the capacitors used in this type of damping have no appreciable direct current conductance, as otherwise the sensitivity will be altered when they are used. To test this point the sensitivity should be determined with steady direct current with the damping control in its several positions. Using steady direct current, and with the sensitivity control in either range 2 or range 3, the sensitivity functions of the author's instrument showed no change when the position of the damping control was varied, indicating that the capacitors were satisfactory.

With the sensitivity control in range 1 it is not feasible to use more damping than that provided by position 1 of the damping control. Even with the damping control in position 1 the recorder is slow in sensitivity range 1, and when the damping is increased the response becomes too sluggish for practical measurement.

Although the sensitivity with steady direct current is not influenced by the position of the damping control, the sensitivity for oscillatory currents is affected. As demonstrated below, diffusion currents recorded by the instrument with the dropping electrode vary with the degree of damping employed (see Figure 3).

ACCURACY OF DIFFUSION CURRENT MEASUREMENT

The most important function of a polarograph is the accurate recording of diffusion currents; therefore, this quality of the instrument was tested with some care. Lead ion in 1 *M* potassium chloride was chosen as a test substance because its diffusion current constant, $i_d/(Cm^{2/3}t^{1/6})$, has recently been established more accurately than that of any other substance over a wide range of dropping electrode characteristics and by three different methods of measurement (*8*).

Experiments were performed with 1.000 millimolar lead ion in 1 *M* potassium chloride containing 0.01% gelatin, the experimental procedure being virtually identical with that previously described (*8*). The cell was placed in a water thermostat at 25.00° C., and nitrogen was used to remove dissolved air from the solution. The dropping mercury electrode had a drop time of 3.49 seconds at −0.7 volt *vs.* the saturated calomel electrode, the rate of flow of mercury was 1.50 mg. per second, and the value of $m^{2/3}t^{1/6}$ was 1.615 mg.$^{2/3}$/sec.$^{1/2}$. The diffusion current was measured at −0.7 volt *vs.* the saturated calomel electrode, at a sensitivity of 2-50 (32.9 mm. per microampere), and with the damping control in its various positions from 1 to 5, inclusive.

The polarograms in Figure 2 demonstrate the effect of the degree of damping on the magnitude of the oscillations and on the diffusion current. Taking the average of the oscillations as a measure of the diffusion current, which is the generally accepted practice (*3*, *8*), the diffusion current with the damping control in position 5 is 6.5% smaller than with the damping control in position 1.

The gradual decrease in the observed diffusion current constant with increasing degrees of damping is shown graphically in Figure 3; the lengths of the vertical lines represent the magnitudes of

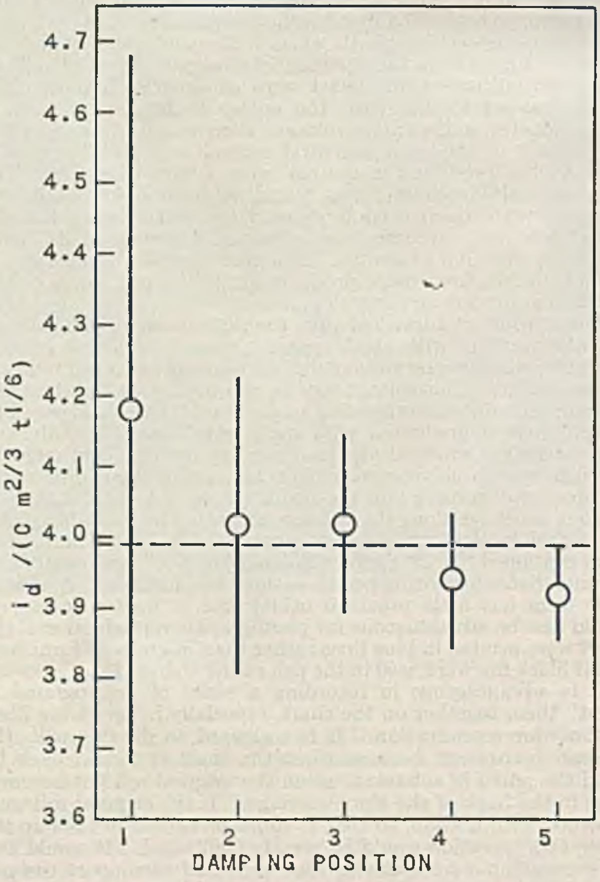


Figure 3. Influence of Degree of Damping on Observed Diffusion Current of Lead Ion in 1 *M* Potassium Chloride

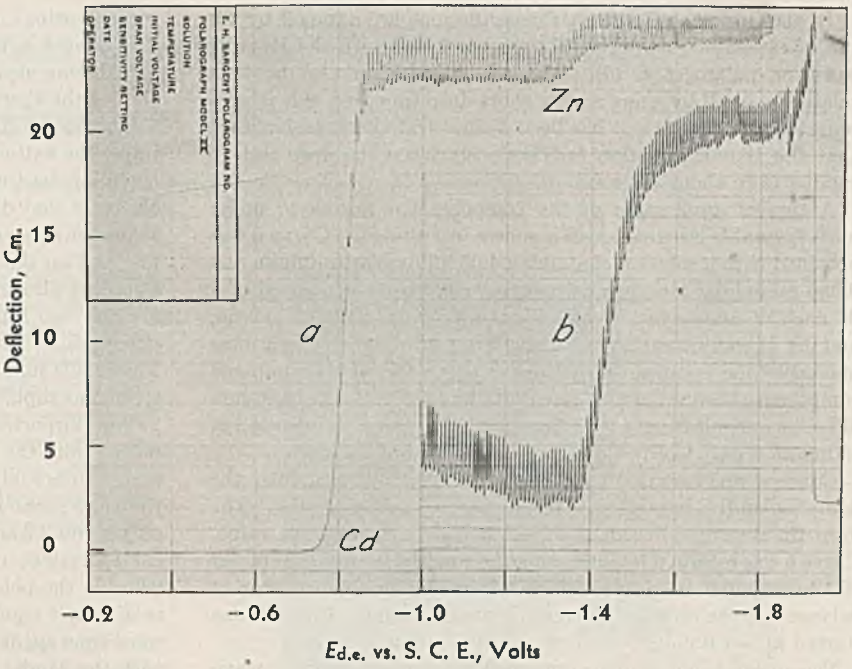


Figure 4. Operation of Compensator in Determination of 0.386 Millimolar Zinc

In presence of 4.65 millimolar cadmium in 1 *M* ammonia-1 *M* ammonium chloride-0.005% gelatin. *a*, recorded at sensitivity of 8.7 and, *b*, at 102 mm. per microampere

the recorder oscillations, and the average of the oscillations is indicated by circles in each case. The horizontal dashed line represents the diffusion current constant found by Lingane and Loveridge (*8*) at the same value of $m^{2/3}t^{1/6}$ used in the present experiments. This value (3.99 ± 0.02) is the average obtained by three different methods of measurement, including manual measurement by the resistance-potentiometer technique, manual measurement with a Leeds & Northrup Type HS galvanometer, and measurement with a Sargent-Heyrovský Model XI photographically recording polarograph. It has been established that these three methods yield results that agree to about 0.5% (*8*). The diffusion current constant measured by the present instrument is considerably too large with the damping control in position 1, but with greater degrees of damping the values agree fairly well (*ca.* ±1%) with the accepted value.

Results exactly similar to those above were obtained with lead in sodium hydroxide solution, and with zinc in ammoniacal medium. It may be concluded that the present instrument records different currents with reasonably satisfactory accuracy, providing that the damping is adjusted so that the magnitude of the recorder oscillations does not exceed about 10% of the average current.

ACCURACY OF HALF-WAVE POTENTIAL MEASUREMENTS

According to the author's experience the half-wave potentials recorded by this instrument tend to be somewhat too large, and the error depends on the degree of damping used in recording the polarogram. For example, the observed half-wave potential of 1 millimolar lead ion in 1 *N* potassium chloride at 25° C. was −0.444 volt *vs.* the saturated calomel electrode when the polarogram was recorded at a sensitivity of 2-50 with the damping control in position 1, and −0.460 volt with the damping control in position 5. The accepted value is −0.435 volt (*3*).

The H-cell used had a resistance of less than 500 ohms, and the half-wave current was 3 microamperes, so the *iR* drop in the cell did not exceed about 1.5 millivolts. Since the total range of the recorder is only 5 millivolts, the total *iR* drop across both the cell and current-measuring resistance could not have been greater than about 4 millivolts at the half-wave point on the polarograms. When this correction is applied to the observed values they become −0.440 and −0.456 volt, respectively.

With the damping control in position 1 the observed half-wave potential is in reasonably satisfactory agreement with the accepted value, but in damping position 5 the observed value is about 20 millivolts too large. In sensitivity range 1 the error is considerably larger for a given degree of damping (see Figure 4). It is inevitable that any type of recording polarograph will show some error in half-wave potentials because of unavoidable lag in the galvanometer or recording unit, and when maximal accuracy is desired, as, for example, in analyzing wave slopes or in obtaining data from which thermodynamic conclusions are to be drawn, the measurements are best made with manual apparatus, or by manual scanning with a recording instrument. The error due to recorder lag with a high degree of damping can be minimized by employing a relatively small bridge voltage in conjunction with a suitable setting of the initial potential, but since the initial potential cannot be set more precisely than about ±0.01 volt at best, this is about the limit of accuracy of the instrument. The accuracy of the instrument is probably sufficient for routine work.

OPERATION OF THE COMPENSATOR

Suppose that a solution to be analyzed contains two reducible substances, *A* and *B*, that the half-wave potentials differ by at least 0.2 volt, so that the two waves are well separated, and that the half-wave potential of *A* is more positive than that of *B*. Since the wave of *A* precedes that of *B*, the sensitivity can be adjusted to the optimum value for determining *A*, regardless of the relative concentrations of *A* and *B*. However, if the concentration of *B* is much smaller than that of *A*, and since the sensitivity must necessarily be adjusted to record the total double wave, the wave of *B* may be so small that it cannot be measured precisely.

In order to determine the minor constituent *B* without a preliminary separation from *A*, Hohn (*2*), Thanheiser and Willems (*9*), and Lingane and Kerlinger (*6*) recommended that the interfering diffusion current of *A* be balanced out ("compensated") by sending an opposing current of equal magnitude through the current-measuring device from an outside source. The sensitivity of the recording unit may then be increased until the wave of *B* is large enough for convenient measurement. This is the function of the compensator in the present instrument.

The chief limitations of the compensation method are that (1) only the average current is compensated, and not the oscillations, so some means of damping must be employed to prevent the oscillations from becoming enormous when the sensitivity is increased, and (2) imperfections in the diffusion current of *A* are also magnified and tend to distort the magnified wave of *B* (*3*, *6*). Hence, the compensation method can only be applied to very well developed waves, and with not too disproportionate concentrations of *A* and *B*.

In the present instrument the oscillations are damped by the use of capacitors, as previously recommended with the Heyrovský-type polarograph (*6*). The oscillations can also be kept relatively small by using a very short drop time, but this is very objectionable, because it has been demonstrated conclusively (*8*) that the Ilkovič equation fails seriously when the drop time is smaller than about 1 second.

A typical application of the compensation technique under most favorable circumstances is shown in Figure 4. Curve *a* was obtained with a solution containing 4.65 millimolar cadmium and 0.386 millimolar zinc in a supporting electrolyte composed of 1 *M* each of ammonium chloride and ammonia, 0.005% gelatin, and 0.1 *M* sodium sulfite to remove oxygen. This case is a most favorable one because the half-wave potentials of the ammonia complexes of cadmium and zinc differ by 0.55 volt, the cadmium diffusion current is very well developed, and the concentration of cadmium is only twelve times larger than that of the zinc.

Curve *a* was recorded with a sensitivity of 2-5, and with the damping control in position 5 to provide maximal damping. The drop time was 2.80 seconds at −1.2 volts, an optimum value. Curve *b* was recorded by increasing the sensitivity to 1-7 (a factor of 12 compared to curve *a*), and adjusting the compensator to balance out the diffusion current of the cadmium. Curve *b* was started at −1.0 volt.

The author is not at all convinced that the magnified zinc wave (curve *b*) can be measured with any greater real accuracy than the original zinc wave in curve *a*, which, although small, is very clearly developed. Accurate measurement of a diffusion current is more dependent on the quality of a wave than on its mere magnitude. The measurement of the magnified zinc wave is complicated by the magnification of the normal decrease of the cadmium diffusion current with increasing potential, by the magnification of imperfections in the cadmium diffusion current, which render extrapolation uncertain, and also by the fact that with sensitivity range 1 and the damping control in position 5 the recorder is so sluggish that it lags very considerably and the diffusion current of the zinc is hardly reached before the final current rise. This lag also causes a spurious shift of nearly 0.1 volt in the half-wave potential of the zinc. Curve *b* could not be recorded with less damping because the oscillations were inconveniently large.

According to the writer's experience, claims that the compensation technique largely eliminates the need for chemical separations are much too optimistic.

SUMMARY

The writer would list the following as significantly good qualities of the Model XX polarograph in order of relative importance: (*a*) the instrument is robust and immune to vibrations, (*b*) the current sensitivity functions need be determined only once, eliminating periodic calibration, (*c*) the sensitivity is continuously variable, (*d*) diffusion currents may be recorded as a function of time at a constant applied e.m.f., and (*e*) the polarogram is recorded visibly.

On the debit side may be listed: (*a*) observed diffusion currents vary with the degree of damping employed, (*b*) half-wave potentials vary with the degree of damping and may be significantly in error under certain operating conditions, (*c*) the compensator appears to be of little practical value, and (*d*) the cells and dropping electrode assembly supplied are inadequate.

A detailed discussion of the comparative characteristics of various commercially available polarographs would be beyond the intended scope of this paper, but some general points might be mentioned. There are only two other recording polarographs on the market in this country, the Model XII Heyrovský polarograph manufactured by the E. H. Sargent Co., which employs photographic recording, and the Electrochemograph of the Leeds & Northrup Co. which is a visible recording instrument incorporating a modified Micromax potentiometer recorder. The Model XX is the most expensive of the group, its price of $1500 being nearly three times that of the Model XII and twice that of the Electrochemograph.

The Model XII is by far the simplest to operate and, according to the writer's experience, it is the most reliable and generally useful of the three instruments. It has been demonstrated conclusively that diffusion current constants obtained with this instrument agree exactly with those measured by manual methods (*9*), and on the basis of numerous data it is known that the instrument also measures half-wave potentials accurately. These are the two fundamentally important functions of a recording polarograph, and they are discharged more satisfactorily by the Model XII instrument than by either the Model XX or the Electrochemograph.

The purported inconvenience of developing the photographic record from the Model XII polarograph is more illusionary than real. In actual practice, as in most other methods of analysis, the time spent in the final instrumental measurement is usually only a small fraction of that consumed in the preliminary chemical operations required to prepare the solution, and therefore whether the polarogram is recorded photographically or visually is of minor significance. The writer is not convinced that the total time spent in analyzing a series of a dozen similar samples with the Model XX instrument would be significantly less than with the Model XII, if one includes all operations from the weighing of the sample to the recording of the final result.

A real disadvantage of the Model XII, which is shared to some extent by the Electrochemograph, is sensitivity to vibration, and in certain locations in industrial laboratories special vibration-free mounting may be necessary. Under such conditions the Model XX, which appears to be completely indifferent to even severe vibration, becomes the logical choice.

In both the Model XX and the Electrochemograph the visible recording feature has been achieved by sacrificing a great deal of simplicity, and both instruments have more complex personalities than the Model XII. From the viewpoint of the academician interested in the instruments for their own sake this makes them more interesting, but one who planned to put the instruments into the hands of sketchily trained technicians might well have a different opinion. The Electrochemograph is the more complicated of the two instruments, and the writer's experience with it has been less satisfactory than with the Model XX. The periodically balancing recorder in the Electrochemograph possesses more lag, and seems to be less adaptable to polarographic measurements, than the continuously balanced recorder in the Model XX.

A unique advantage of both the Model XX and the Electrochemograph is that they can be used for recording changes in diffusion current over an extended period of time at a constant applied potential. Hence these instruments may be valuable in kinetic studies for following slow reactions involving polarographically active substances. They should also be useful for certain control purposes, such as recording changes in oxygen concentration of solutions over long periods of time.

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Automatic Determination of Aniline Point of Petroleum Products

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An apparatus is described for the automatic determination of aniline point of petroleum products. The basic principle involved comprises the use of the electric eye as a substitute for visual observation. The test sample is internally heated or cooled, the temperature is maintained uniform by stirring, and temperature equilibrium is automatically accomplished by a relay system. The relay system which controls the heating or cooling is activated by directing a light beam through the sample on a photocell; the light beam being interrupted periodically as the sample clears or clouds with slight temperature change. The flashing of a lamp bulb indicates when equilibrium temperature is reached.

THE A.S.T.M. defines aniline point (*1*) as "the minimum equilibrium solution temperature for equal volumes of aniline and petroleum product".

Many attempts have been made to adapt the test to dark-colored products. Donn (*3*) proposed determining the temperature at which a break occurred in the viscosity-temperature curve. Van Wijk and Boelhouwer (*8*) proposed the detection of a change in transparency to infrared radiation by the use of a thermopile, while Matteson, Zeitfuchs, and Eldredge (*6*) described an apparatus also employing infrared radiation but using a photocell and microammeter. Williams and Dean (*9*) suggested a "circulating test tube" with visual observation through a 2.0-mm. layer. Carr and Agruss (*2*) and Madsen (*5*) recommended an apparatus for determining equilibrium temperature visually through a film of the sample.

Geddes (*4*) in order to overcome the difficulty and hazard involved in determining high aniline points of highly paraffinic lubricating oils proposed substituting *N*-methylaniline for aniline. Data indicate that *N*-methylaniline points are approximately 77° C. lower than aniline points.

The purpose of this paper is to describe an apparatus that determines aniline points automatically and has the definite advantage that at equilibrium temperature the thermometer mercury column remains practically constant, varying usually not more than 0.2° C.

APPARATUS

1. Air-drying tubes, 12.0 cm. × 17 mm. in outside diameter, filled with 8-mesh Drierite.
2. Bunsen valve 2.5-inch piece of gum tubing, 9 mm. in outside diameter, 5-mm. in inside diameter.
3. Indicating lamp bulb, ordinary, frosted.
4. Knife-switch, double-pole, single-blade.

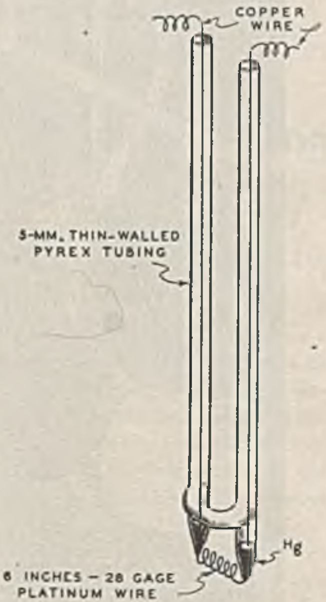
COPPER WIRE
5-MM. THIN-WALLED PYREX TUBING
Hg
6 INCHES – 28 GAGE PLATINUM WIRE

Figure 1. U-Tube for Conducting Cold Carbon Dioxide–Air Mixture

Contains heating unit

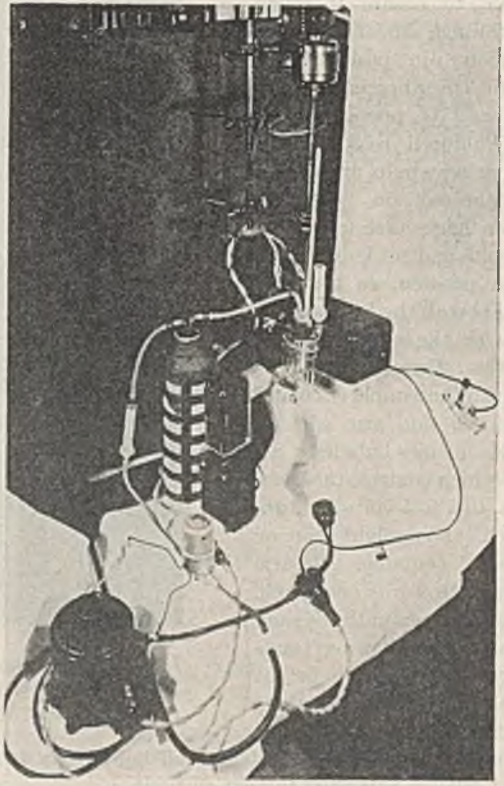

Figure 2. General View of Apparatus

5. Light source, General Electric Catalog 98 × 264 Mazda 1133, 32 C, 6- to 8-volt. 3.8-cm. condensing lens. General Electric transformer, Catalog 71G620 KVA 0157, 50/60-cycle 115-volt to 4.8-volt.
6. Photocell and relay Photoelectric relay CR7505 K100-GZ, 115-volt 50/60-cycle. Connections K-6919764, phototube 923 (2nd tube ZG-479).
7. Platinum heating unit, 15.0 cm. of No. 28 gage (see Figure 1).
8. Plexiglas air-jacket, made from 0.15-cm. sheet.
9. Sample container, modified Thiele melting point tube. Over-all length, 17.8 cm. Main body: length 8.25 cm. diameter 2.54 cm. Top opening, 3.5 cm. Charging opening, approximately 12 mm.

Circulating side arm, 12-mm. outside diameter. Pyrex tubing, approximately 7.6 cm. over-all length, with flattened area of approximately 2.0-mm. inside diameter and with a centered bulls-eye of about 0.6-cm. diameter, the sides of which are just close enough together to allow a thin layer of sample to circulate between.

Interchangeable ground-glass joints have been tried, but cork has proved satisfactory.

10. Solenoid valve, General Electric CR9503, 115-volt.
11. Stirrer, steel, 0.3-cm. diameter, 41.6-cm. shaft, equipped with 1.3-cm. vertical blades.
12. Stirrer-motor equipped with rheostat.
13. Thermos bottle. Quart size filled with pieces of dry ice stoppered with a rubber equipped with 5- to 6-mm. Pyrex tubes, outlet tube extending to bottom. Wrapped for protection against breakage.
14. Thermometer, A.S.T.M. aniline point. It is believed that one thermometer of suitable range can be used in view of constancy of the temperature at equilibrium point.
15. U-tube. 5.0-mm. Pyrex tubing for circulating cold air and

containing heating unit (Figure 1). Thin-walled tubing is necessary for efficient cooling.

PROCEDURE

For Aniline Points above Room Temperature. Measure sufficient sample aniline through the charge inlet into the sample container to ensure thorough mixing through side arm. Place thermometer in position and attach to stirrer bearing with an elastic band to prevent vibration. (Photocell relay circuit, indicating lamp bulb, and Variac are connected in parallel.) Switch on light source and photocell circuits and set knife switch blade in position, so that the relay will break the heating unit circuit when the solution is clear. Start the stirrer and adjust speed until the sample circulates through the side arm without drawing in air bubbles. Set Variac, which controls the heating unit, to 3 to 5 volts and turn on switch. Focus light beam on flat area of container side arm and direct towards photocell. Heating continues until the sample clears, thus allowing transmittance of light beam to the photocell and thereby breaking the heating circuit. The sample cools immediately, clouds, and shuts off light beam to photocell, and relay is activated to heat-on position. These clearing and clouding cycles are uniform and of very short duration and are indicated by the flashing lamp bulb.

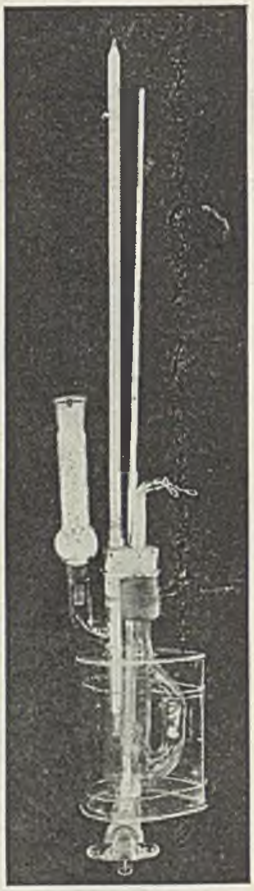

Figure 3. Close-Up of Container

Table I. Aniline Point Determinations

Sample No.	Description	Results Proposed automatic ° C.	A.S.T.M. ° C.
1	65 ml. of benzene diluted to 100 ml. with *n*-heptane	−11.15, −11.4	−11.4
2	60 ml. of benzene diluted to 100 ml. with *n*-heptane	−3.4, −3.6	−3.7
3	50 ml. of benzene diluted to 100 ml. with *n*-heptane	10.05, 10.2	10.1, 10.1
4	43 ml. of benzene diluted to 100 ml. with *n*-heptane	20.3	20.2
5	Gasoline cut from still	30.8	31.0
6	34 ml. benzene diluted to 100 ml. with *n*-heptane	31.2	31.3
7	Light-colored naphtha	35.7, 35.7	35.9
8	Gasoline cut from still	39.1	39.2
9	Gasoline cut from still	40.8	40.8
10	Light-colored naphtha	49.6, 49.7, 49.6	49.7
11	Diesel fuel	62.0	62.0
12	*n*-Heptane	68.9, 68.9, 69.0	69.1, 69.2
13	Light-colored naphtha	77.6, 78.0, 77.7	77.8
14	Lubricating oil, NPA color 3	111.0	111.2

Table II. Mixed Aniline Point Determinations

Sample No.	Description	Results Proposed automatic ° C.	A.S.T.M. ° C.
7	Light-colored naphtha	53.2	53.4
10	Light-colored naphtha	59.8	60.0
13	Light-colored naphtha	73.0	73.2

Temperature is maintained practically constant, holding usually within 0.2° C. Adjust Variac, if necessary, according to the difference between test and room temperatures.

Shut off electric circuits upon completion of test. Drain sample by opening stopcock. Rinse sample container thoroughly with suitable solvent (acetone, benzene, or mixture of both) through charge opening and then apply vacuum through stopcock to dry container.

For Aniline Points below Room Temperature. The presence of water seriously interferes with the accuracy of aniline point determinations (7). In determining aniline points occurring below room temperature, air will be drawn into the sample container as cooling takes place. This might be serious in locations where excessive humidity is common. Therefore, the following precautions should be observed.

Make certain that the stopper and fittings are tight. Fit a drying tube into the charge opening by means of a rubber stopper, after sample and aniline are in the container, to act as dry-air breather opening. Insert the thermometer into position through a snug-fitting rubber sleeve.

Replace heating unit circuit with solenoid-activated cooling circuit and set Variac to 115 volts. (Solenoid, photocell relay circuit, and indicating lamp bulb are in parallel.) Insert Bunsen valve in air line between laboratory air supply and solenoid valve. connect the outlet of the solenoid valve to a drying tube, which in turn is connected to the thermos bottle containing the dry ice; make final connection to U-tube in sample container. Turn on the air until an excess blows through the Bunsen valve. Switch on light source, photocell circuit, and stirrer, and reverse knife switch blade in position so that relay breaks circuit to solenoid when the sample clouds. Cooling continues until clouding occurs, thus interrupting the light beam to the photocell which breaks circuit to solenoid, closes valve instantly, and diverts the air through the Bunsen valve. The sample warms immediately and clears, again allowing transmittance of the light beam to the photocell, which activates relay to close solenoid circuit and thereby opens air valve. These clearing and clouding cycles are indicated by the flashing of the lamp bulb and produce a practically constant equilibrium temperature.

Shut off electric circuits and clean container as directed above:

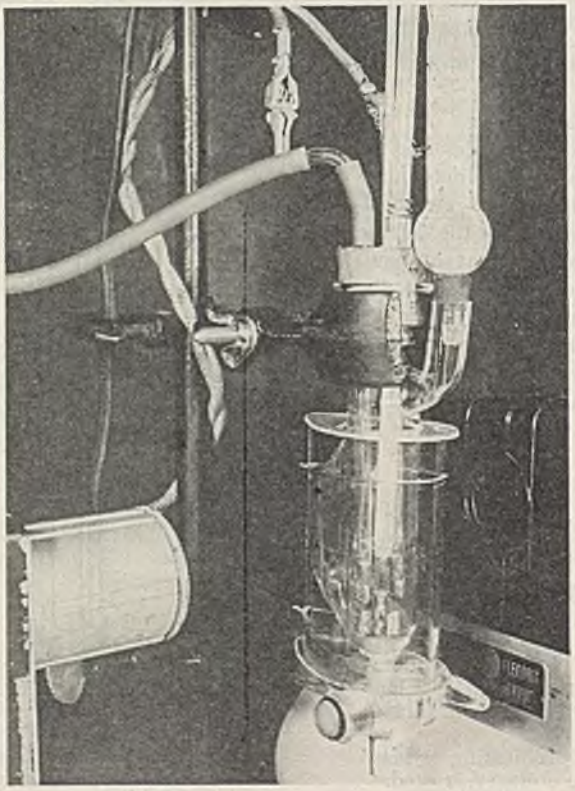

Figure 4. Light Source and Photocell

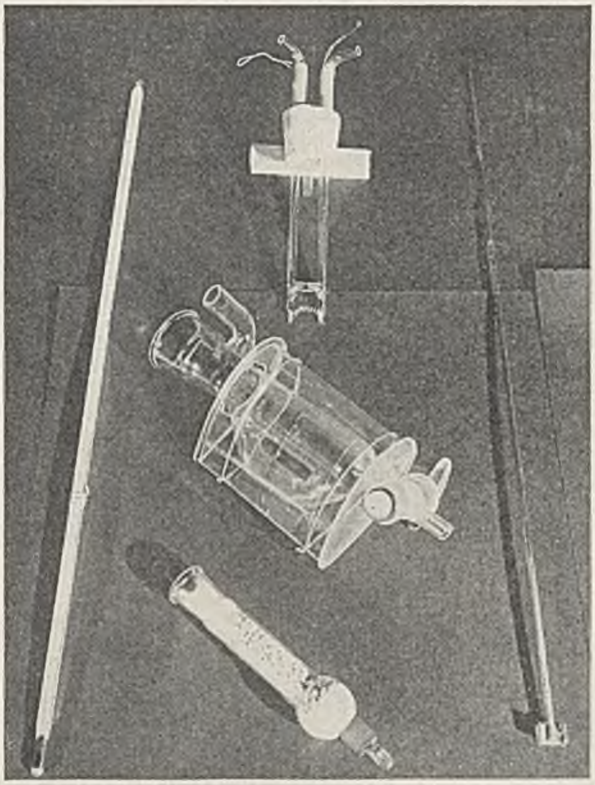

Figure 5. Sample Container Disassembled

Tables I and II show the reproducibility with the apparatus and the close agreement with results obtained by the A.S.T.M. procedure.

Table III covers a few tests which indicate the adaptability of this apparatus to dark petroleum products. The samples cover the A.S.T.M. color range from −7 to very much darker than 8. Incidentally, while there is no doubt a limit of sample color beyond which this apparatus may not function, changes in sample container design and a more sensitive light source (possibly infrared) and photocell combination may permit the testing of practically all dark products.

Table III. Aniline Point of Dark-Colored Petroleum Products

No.	Sample Color, Lovibond (500 Amber Series), 0.25-Inch Cell: As is	Diluted with kerosene 9 to 1	A.S.T.M.	Results Proposed Automatic, ° C.
A	350	...	7−	82.2
B	450	...	8−	116.8
C	700	...	8+	95.5
D	>750	95	8+	104.4
E	>750	>750	8+	81.3

Figure 2 shows the general setup.

Figure 3 pictures the sample container plus jacket, etc., and Figure 4 pictures container in position between light source and photocell. The clip which prevents the thermometer from slipping through the glass sleeve in the stopper is replaced by a tight-fitting rubber sleeve when testing samples whose aniline points are below room temperature.

Figure 5 pictures sample container, U-tube, stirrer, and thermometer disassembled.

Tentative steps are under way for the manufacture of this apparatus by the Precision Scientific Company, Chicago, Ill.

ACKNOWLEDGMENT

The author wishes to extend his appreciation to J. L. Koehler and A. Herzog for determining the A.S.T.M. aniline points, to J. H. Lange for obtaining the electric-eye apparatus, and to R. Work for making the glass apparatus.

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An Automatic-Recording Ultraviolet Photometer for Laboratory and Field Use

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The rates of adsorption processes or chemical reactions involving a gas which absorbs ultraviolet light can be followed readily with an ultraviolet photometer. An automatic-recording instrument is described capable of detecting concentrations of the order of a part per million. This apparatus has been applied to the evaluation of the efficiency of adsorbents against toxic gases, to field studies of the travel of gas clouds, and to fundamental investigations in the kinetics of gaseous reactions.

IN TESTS of the protection of absorbents against toxic gases and in field studies of the travel of gas clouds, it is highly desirable to have an instrument which will follow rapid changes in concentration and will detect minute quantities of certain test gases. In laboratory tests of the efficiency of adsorbents, a knowledge of the variation of effluent concentration with time is necessary for both practical and theoretical assessment, and since this concentration-time curve (Figure 1) is frequently very steep, a rapid, recording analyzer is most desirable. In field tests a cloud of toxic gas may pass a station in less than a minute and may exhibit large variations in concentration within that short period (Figure 2), so that a rapid-recording device becomes essential.

A number of the important war gases—for example, phosgene (*2*) and chloropicrin (*4*)—exhibit strong absorption of ultraviolet radiation. This property may be used to advantage as an analytical tool and has been so applied by Woodson (*9*) and others (*1*, *3*, *6*). The instrument described in this paper has a number of advantages over those previously described. For increased precision in analysis, a null-point measuring circuit has been introduced similar to one already described (*3*). To avoid the necessity of frequent recalibration as the intensity of the light declines or when the source must be replaced, an arrangement has been inserted whereby the absolute intensity of the radiation may be measured. Finally, provision has been made for the use of an automatic-recording microammeter which may be introduced or removed from the circuit by the flip of a single switch.

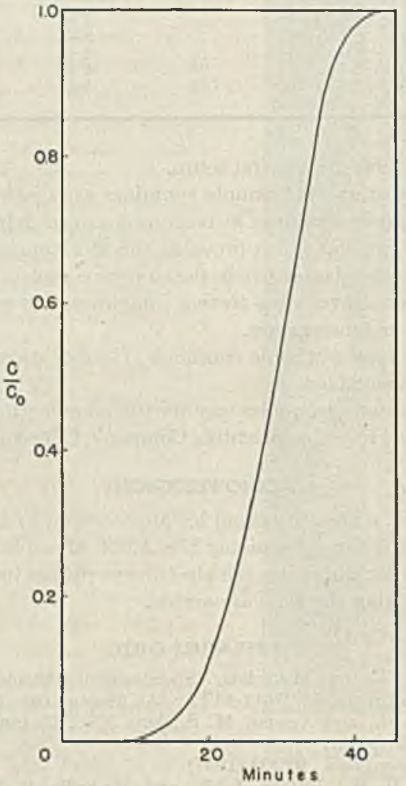

Figure 1. Effluent Concentration from a Column of Charcoal

PRINCIPLE OF THE PHOTOMETER

In quantitative photometric work it is customary to treat the data in terms of Beer's law

$$\log(I_0/I) = e\,c\,d \qquad (1)$$

where I_0 is the intensity of the light passing through an absorption cell of d cm. length, containing none of the light-absorbing material, I is the intensity of the light traversing the same cell containing the light-absorbing substance at a concentration of c moles per liter, and e, the molecular extinction coefficient, is a quantity which depends on the compound, on the wave length, and occasionally on the concentration. In the present instrument, the light intensity is translated into a voltage. Since the number of electrons emitted by the photocell is proportional to the intensity of the incident light and since the voltage, V, is created by the flow of electrons through a constant resistance, R_1, it follows that

$$V = kIR_1 \qquad (2)$$

where k is a constant.

Consequently Beer's law assumes the form

$$\log\frac{V_0}{V} = e\,c\,d \qquad (3)$$

To obtain increased sensitivity in detection, balanced-photocell, electrical circuits have been devised to read the change from V_0 when a light-absorbing substance is present. This change, v, is related to V by the equation

$$v = V_0 - V \qquad (4)$$

Consequently, Beer's law assumes the form

$$\log\frac{V_0}{V_0 - v} = e\,c\,d \qquad (5)$$

A schematic diagram of the optical and electrical system is illustrated in Figure 3. The principle of its operation is simple.

If light is allowed to fall on the photocell, P_1, a stream of electrons will flow toward and through the grid leak, R_1, and will create a potential drop across this high resistance. If S_1 is switched to the left-hand circuit, but S_6, S_7, and *POT.* are all adjusted to zero e.m.f., then the potential drop across the grid leak will be impressed on the amplifier and cause a deflection in the plate-current galvanometer, *GALV.*, or on the recorder. The magnitude of this potential drop can be measured accurately by imposing a counterpotential through the batteries, B_2 and B_3, and the potentiometer, *POT.*, until the galvanometer, or recorder, returns to its initial reading. In this manner the value of V_0 may be determined.

If now two beams of light of equal intensity are allowed to fall on the two photocells, P_1 and P_2, respectively, and if these photo-

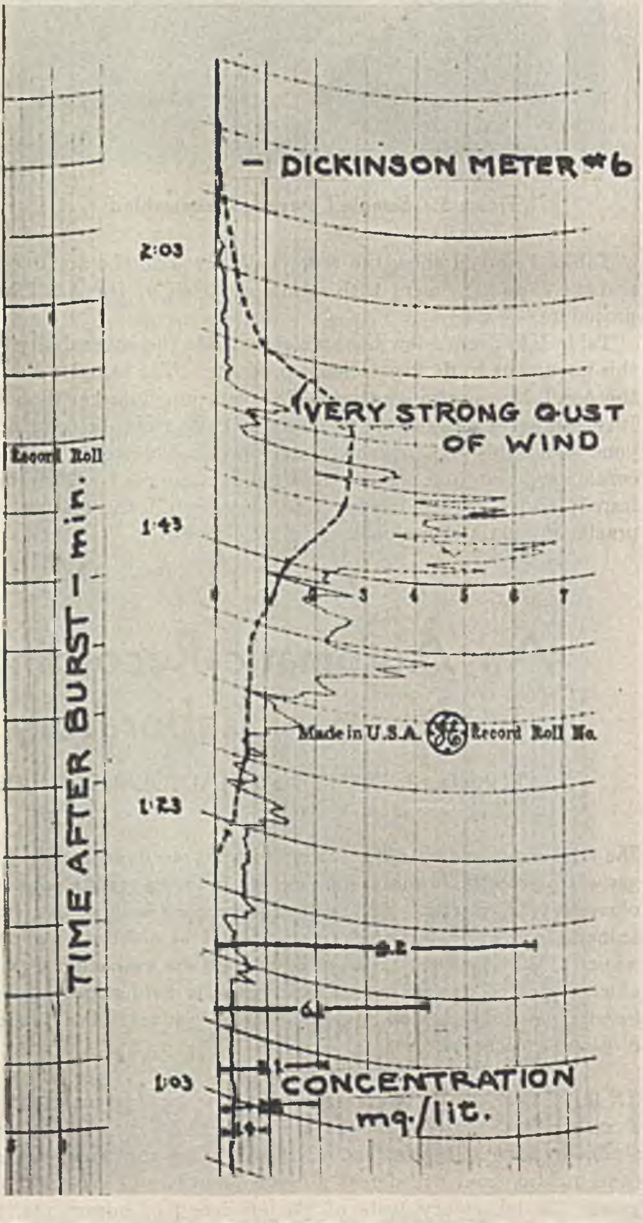

Figure 2. Automatic Record of Gas Concentration in a Field Test

cells are identical in response, no net flow of electrons through R_1, and consequently no potential drop, is observed. (In practice, of course, the photocells are not identical, and it is necessary to use a set of diaphragms to balance the outputs, as is described in the section on operation.) If a light-absorbing substance is interposed between the light source and one of the photocells, the electrical balance is disturbed and a potential drop will be impressed across R_1. This potential may be balanced, with S_1 switched to the left, by potentiometer, *POT.*, and batteries B_2 and B_3 if necessary, to obtain the value of v. To detect very small changes in v, S_1 is switched to the right and a Leeds & Northrup student-type potentiometer introduced into the circuit. A difference of about 0.001% in light intensity can be detected thereby.

When the automatic recorder is to be used, S_3 is switched to the right, and the changes in intensity of light, due to changes in concentration of absorbing material, are continuously recorded on a chart. The deflections are then calibrated by imposing a counter-potential on the grid leak by means of the potentiometer and batteries B_2 and B_3.

CONSTRUCTION OF PHOTOMETER

Light Source. The most recent model of the photometer has been constructed to enable the use of either a General Electric T-10 germicidal lamp or a Westinghouse WL-793 sterilamp as the source of ultraviolet light. The GE lamp has proved more satisfactory but for a time was not manufactured. Whereas 95% of the radiation of the GE lamp is at 2537 Å. (*5*), 84% of the radiation of the Westinghouse lamp is concentrated at this wave length (*8*).

The current going through the GE lamp was stabilized by a constant-current circuit whose theory has been discussed by Steinmetz (*7*) and which has been used for the same purpose by Hanson (*1*). Constant voltage is obtained with the aid of a Sola transformer or a Raytheon voltage stabilizer. With the WL-793 lamp it is also necessary to use a special 220-volt transformer.

Provision has been made also for operating the GE lamp from a direct current source. For this purpose three 45-volt B batteries (Burgess No. 21308) are connected in series with a 2500-ohm, 50-watt rheostat (Ohmite No. 0328), and inserted into the light-source circuit in place of the 110-volt alternating current. To start the lamp, the rheostat is turned to zero resistance, for only with the full 135 volts across the electrodes will the mercury arc strike. Once the lamp is in operation, however, the rheostat is adjusted to decrease the intensity of the ultraviolet radiation to a suitable value. Under normal operating conditions, the direct current flowing through the lamp is about 20 milliamperes.

Absorption Cell. Side arms were blown on to a Pyrex tube, which was then cut with the aid of a glass saw to a length of 20 cm. Windows of Corning ultraviolet-transmitting glass No. 791 were

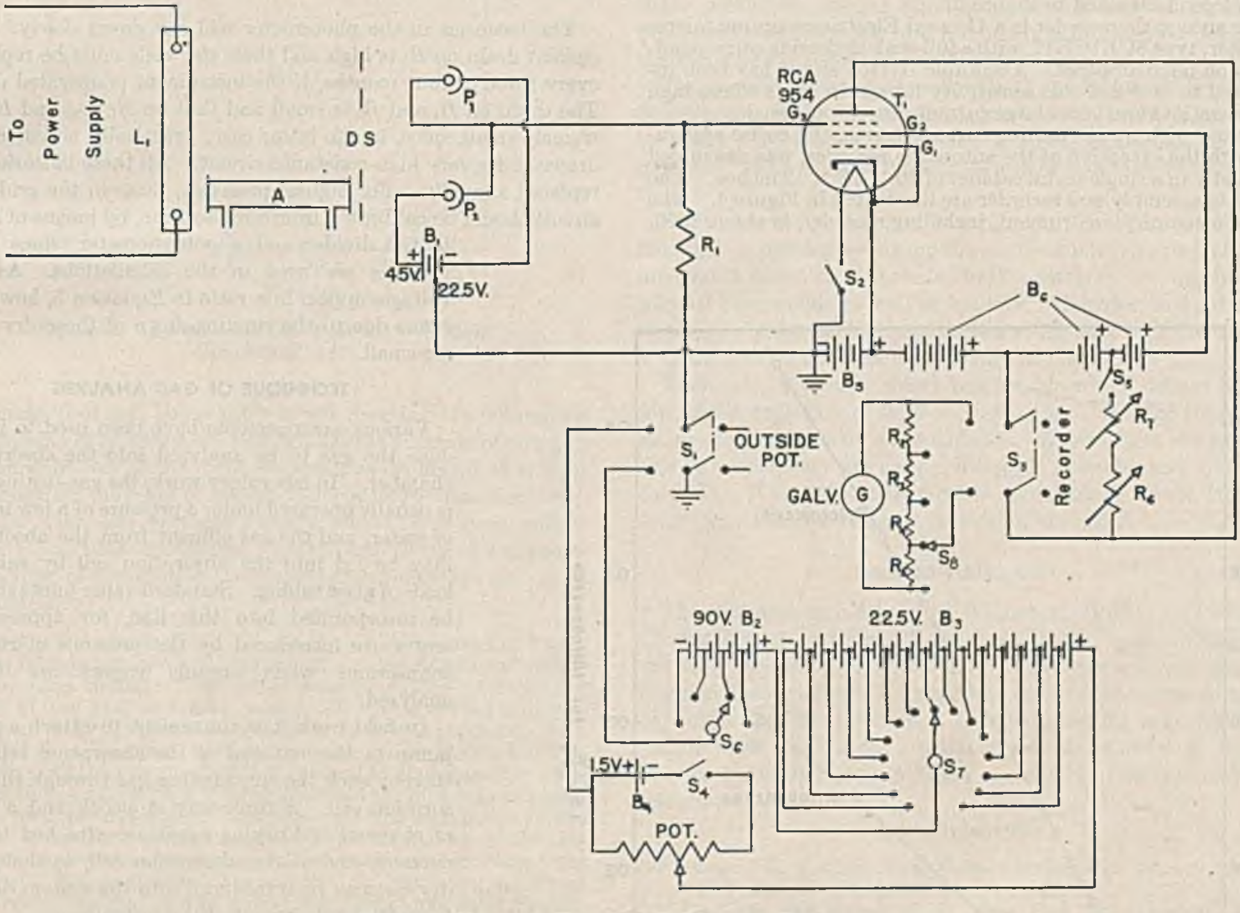

Figure 3. Schematic Diagram of Ultraviolet Photometer

Galv.	GE galvanometer 32 C 205 G 1
P_1, P_2.	R.C.A. 935 phototubes
R_1.	I.R.C. type H 1 2000 megohms
R_2.	10 ohms
R_3.	200 ohms
R_4.	1000 ohms
R_5.	10,000 ohms
R_6.	General Radio Co. potentiometer type 371-A, 25 watts, 1000 ohms
R_7.	General Radio Co. potentiometer type 371-A, 25 watts 50,000 ohms
Pot.	General Radio Co. potentiometer type 314-A, 6 watts, 20,000 ohms
T_1.	RCA 954
S_1.	Double-pole double-throw toggle switch
S_2, S_4, S_5.	Single-pole single-throw toggle switch
S_3.	Double-pole double-throw jack switch, Mallory 762
S_6, S_8.	Single-pole 5 place Mallory selector switch 3215-J
S_7.	Single-pole 17 place Mallory selector switch 32117-J
B_1.	Burgess W30 BP
B_2.	2 Burgess 5308 in series
B_3.	3 Burgess 5540 in series
B_4.	Burgess 4 F H
B_5.	3 Burgess 4 F H in series
B_6.	Burgess 5156 with Fahnstock clips
L_1.	G E T-10 germicidal lamp or Westinghouse WL-793 sterilamp
DS.	Diaphragm and shutter
A.	Absorption cell

110-volt A.C. obtained from constant voltage source connected to building mains

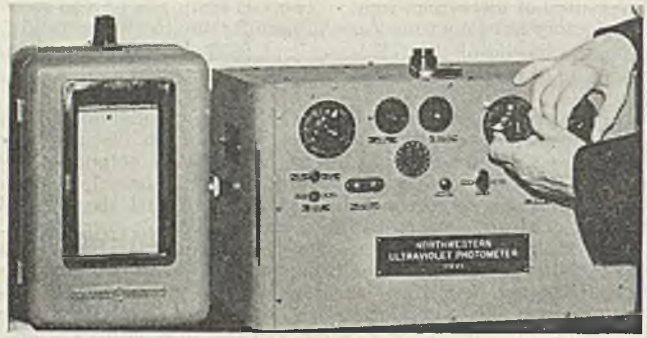

Figure 4. Ultraviolet Photometer and Recorder

sealed to the tubes with Cenco Sealstix cement. Glass tubes were then sealed to the side arms and led outside the photometer cabinet, so that they served as an inlet and outlet for the gas to be analyzed.

Detecting and Recording Circuits. RCA 935 phototubes serve as the light-sensitive elements. The photocurrents are amplified in an electrometer circuit using an RCA 954 acorn pentode tube as previously described (*3*). The details are specified adequately in the legend attached to Figure 3.

The automatic recorder is a General Electric recording microammeter, type 8CE1CK12, with a full-scale deflection corresponding to 56 microamperes. A suitable Ayrton shunt has been introduced to decrease this sensitivity for use in cases where high concentrations and hence large currents are encountered.

For use with an alternating current source, the entire apparatus, with the exception of the automatic recorder, was assembled compactly in a single metal cabinet of 20 × 12 × 12 inches. The complete assembly and recorder are illustrated in Figure 4. The cost of a complete instrument, including recorder, is about $800.

OPERATION OF PHOTOMETER

The first step in operating the photometer is to start the electrical current flowing through the ultraviolet lamp and through the amplifying circuit. There is always a drift while the electrometer tube, ultraviolet lamp, and constant-voltage transformer are warming up. A preliminary period of about half an hour is necessary before the galvanometer deflection, a measure of overall stability, becomes sufficiently steady for measurements to be made. During this period the shutters are kept closed.

The electrical circuits having been stabilized, one proceeds to measure V_0. The shutter in front of P_1 is opened and the diaphragm and counterpotential are adjusted to a suitable balance. The balance may be obtained with the galvanometer, *GALV.*, or the recorder as the null-indicating device. The exact value of the counterpotential is then recorded.

The counterpotential is then decreased to zero and the shutter in front of P_2 is opened. The diaphragm of this compartment is adjusted so that the light intensities impinging on the photocells are equalized, as indicated by a null reading in the plate-current galvanometer, the sensitivity of the shunt being adjusted progressively to its highest value.

During the preceding operations pure dry air is maintained in the absorption cell. Once the instrument has been balanced, one may introduce the absorbing gas. Its presence decreases the intensity of the light reaching one of the photocells, and creates an unbalance which may be counteracted by applying a potential with *POT.*, B_2 and B_3. The magnitude of this potential is v. With the aid of Equation 5 and a calibration curve the concentration may be determined readily.

The batteries in the photometer will run down slowly. The current drain on B_5 is high and these dry cells must be replaced every three or four months, if the instrument is operated daily. The drain on B_4 and B_6 is small and that on B_1, B_2, and B_3 extremely small, since, in the latter case, practically no current is drawn in its very high-resistance circuit. All these batteries are replaced annually. For highest precision, those in the grid-leak circuit should be calibrated from time to time, by means of a potential divider and a potentiometer, since their voltages are used in the calculations. As the voltages appear in a ratio in Equation 5, however, errors due to the running-down of these dry cells are small.

TECHNIQUE OF GAS ANALYSIS

Various arrangements have been used to introduce the gas to be analyzed into the absorption chamber. In laboratory work, the gas-testing line is usually operated under a pressure of a few inches of water, and the gas effluent from the absorbent may be led into the absorption cell by suitable leads of glass tubing. Standard-taper joints should be incorporated into this line, for appreciable erorrs are introduced by the presence of rubber connections when organic vapors are being analyzed.

In field work it is convenient to attach a small pump to the exit end of the absorption cell and thereby suck the surrounding gas through the absorption cell. A three-way stopcock and a tube of charcoal and drying agent are attached to the entrance end of the absorption cell, so that pure dry air may be introduced into the system during the initial adjustment of the instrument.

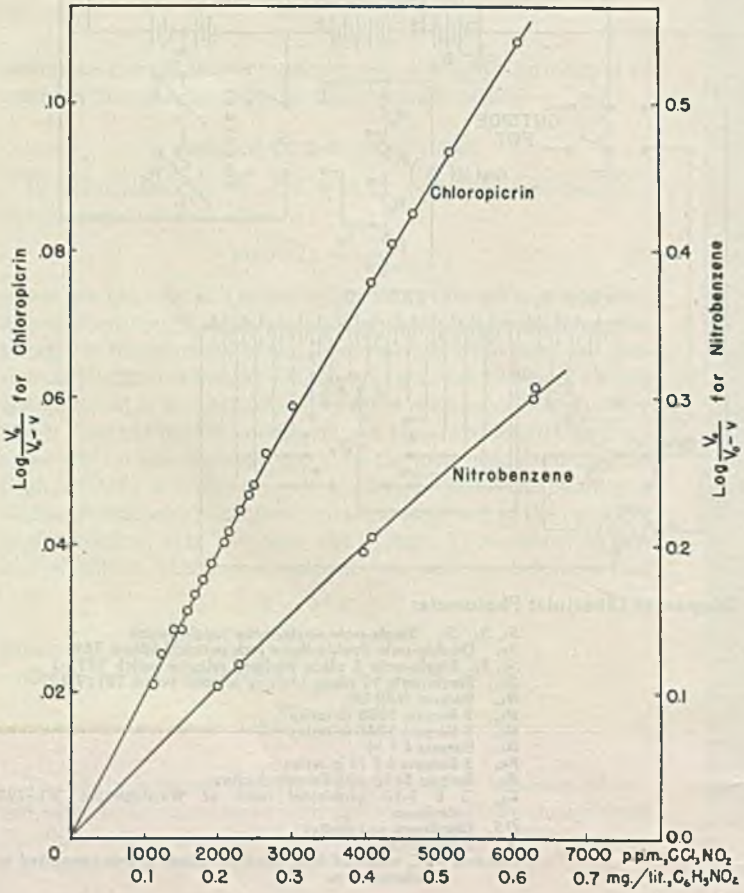

Figure 5. Calibration Curves for Chloropicrin and Nitrobenzene

Table I. Sensitivity of Detection

Gas	Sensitivity *P.p.m. (by volume)*
Chloropicrin	1
Phosgene	1
Mustard gas	3
Chlorine	3
Nickel carbonyl	0.5
Iodine	0.5
Toluene	0.2
Chloroacetophenone	0.03
Mercury	0.0001

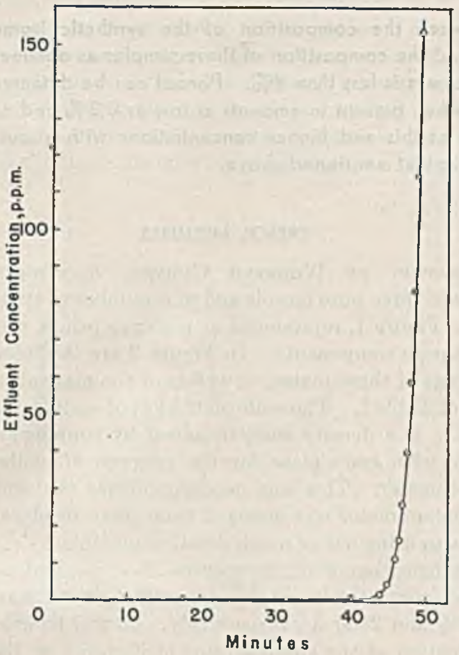

Figure 6. Penetration Curve at Low Effluent Concentrations

In many field and house trials it was necessary to maintain a large number of sampling stations, so that the duration of presence and concentration of the toxic gas could be evaluated at various distances from the point of release. The construction of photometers for each one of these stations would have been unduly expensive and time-consuming. Therefore, instead of a photometer, a rack of a dozen or more sampling bulbs was set up at each station.

These bulbs consisted of a long body of about 50-mm. Pyrex tubing, rounded at one end and sealed at the other to standard 10-mm. glass tubing. The bulbs were evacuated prior to the release of the gas, and then sealed off. At specified intervals during a "shoot", the tapered tip of a bulb was scratched with a file and then broken. Air containing the toxic gas rushed into the bulb until the pressure inside was equal to that outside. The tip was then sealed with a suitable wax and the bulb was returned to the rack for subsequent analysis. At the conclusion of the "shoot" the bulbs were all assembled at a central station containing one or two photometers and the contents of each were analyzed. For analyses in these cases, the sampling bulb was attached to one end of the inlet three-way stopcock of the absorption cell, which was then evacuated up to the stopcock, and the latter was then opened, so that the contents of the bulb could diffuse into the absorption cell.

APPLICATIONS

In all analyses a calibration curve must be obtained first. Typical curves, for chloropicrin and nitrobenzene, are shown in Figure 5. These were obtained by passing each gas at a series of known concentrations through the photometer and recording the voltages, v, that were observed. The function indicated by Equation 5 was then plotted, as is illustrated in Figure 5. The curves obtained are not linear, probably because of the stray light in the radiation source. The nonlinearity introduces no difficulty however, for in any test run concentrations may be determined readily by reference to a large-scale reproduction of Figure 5.

In a theoretical analysis of the nature of the removal process in a flowing system, it is necessary to have a detailed time-history of the concentration effluent from the absorbent. A typical curve of this type is shown in Figure 1. With manual control it is possible to obtain a reading every 30 seconds. With the recorder one obtains, of course, a continuous record. In either event the concentrations are essentially instantaneous values, the lag in the electrical circuits being completely negligible.

The extreme sensitivity of detection is illustrated in Figure 6, which shows a penetration curve for chloropicrin passing through charcoal. Individual readings, collected by manual control, are shown in this figure. This curve makes it possible to study the nature of the penetration at very low effluent concentrations.

A typical field test, as well as an example of the use of the recorder, is illustrated in Figure 2. For purposes of comparison the readings of an automatic-recording conductivity meter are shown on the same graph (scale different). It is obvious that the photometer retains the "fine-structure" of the variation in gas concentration, whereas the conductivity meter smooths out relatively large variations. As is also illustrated in Figure 2, the dense portion of the gas cloud passed the station at which the photometer was situated in a fraction of a minute, yet details of the variations in concentration have been recorded clearly.

The instrument is also applicable to many kinetic problems. It has been used by Blacet, Blaedel, and Lewis, in this laboratory, to study the rates of conversion of nitric oxide into nitrogen dioxide. Their work will be described in a subsequent publication.

In general the photometer is applicable to any kinetic or thermodynamic problem requiring the analysis of a gas which absorbs ultraviolet radiation. Included in this category are organic conjugated compounds as well as ketones, aldehydes, and nitro derivatives. A few typical sensitivities which have been determined with the present instrument are shown in Table I.

There are, of course, many compounds which do not absorb ultraviolet radiation of 2537 Å wave length and for these substances the instrument is not suitable. A few of the war gases in this latter category are arsine, hydrogen cyanide, and cyanogen chloride. Where the instrument is applicable, however, it offers a very rapid and convenient method of analysis.

ACKNOWLEDGMENT

The authors are indebted to William E. Roake, L. P. Saxer, Charles Eckert, and Frank Lamb for their aid in assembling and testing a number of photometers. The advice and assistance of Norman Nachtrieb in the design and construction of some of the critical parts of the instrument are also gratefully acknowledged.

This work was carried out under a contract between Northwestern University and the Office of Scientific Research and Development.

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Quantitative Analysis of Isomeric Cresols and Cresol-Phenol Mixtures

By Ultraviolet Absorption Spectra of Vapors

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A procedure for the quantitative analysis of isomeric cresols and cresol-phenol mixtures is described. Spectrograms of the vapor in equilibrium with liquid mixtures are taken under fixed conditions for a number of synthetic samples. Working curves are prepared from the measured densities of select bands in the absorption spectra and the known concentrations in the samples. The mean deviation between the composition of the synthetic isomeric cresol samples and the composition of these samples as obtained from the working curves is less than 2%. Phenol can be detected in cresol mixtures when present in amounts as low as 0.3% and can be analyzed for at this and higher concentrations with about the same precision as that mentioned above.

THE ultraviolet absorption spectra of aromatic molecules in the vapor state have a number of features which suggest their use in analytical chemistry. All aromatic compounds absorb light in the region of 2500 to 3000 Å., owing to an electronic transition involving the excitation of the pi electrons in the ring, corresponding to the A_{1g}–B_{2u} transition in benzene (*4*, *5*).

The electronic transition is very structure-sensitive and the ultraviolet absorption spectra should be effective in bringing out peculiarities in compounds of similar structure.

The ultraviolet absorption of aromatics in the liquid state has been widely used in analyses. The use of the liquid state has the important disadvantage that the fine structure so characteristic of the vapor spectrum is largely wiped out and with it much of the individuality of the spectra of the various aromatic compounds. Cole (*2*) has analyzed air for toluene and benzene, using ultraviolet absorption. In 1944 Berton (*1*) discussed the analysis of aromatic compound mixtures by means of vapor ultraviolet spectrography. He reproduced spectrograms of mixtures of aromatic compounds but gave no quantitative data except the results of analyses for toluene and benzene in air. In this he had been completely anticipated by Cole who, three years earlier, published complete analytical data, including the working curves for both toluene and benzene. Berton probably did not have access to the American journals during the war.

EXPERIMENTAL

The spectrograph used in this work and described in earlier investigations (*3*) was a 3-meter grating instrument with modified Eagle mounting. The absorption cell was quartz, 70 cm. long, with two outlets, one to a reservoir holding the sample, the other to a Hyvac pump through a stopcock and trap. Ground-glass joints lubricated with Apiezon L were used. A 2.5-kv.-amp. hydrogen discharge tube provided the illumination.

Synthetic samples were prepared and introduced into the reservoir and were maintained at 25° C. The cell, cleaned by rinsing with acetone and ether and with the ground-glass joints completely relubricated after the preceding run, was exhausted for 10 minutes and a time interval of 10 minutes was allowed for attaining equilibrium after the system was isolated from the pump. All the exposures were taken in the first order of the spectrograph (slit width, 0.05 mm.) and were of 10 minutes' duration. Eastman 103-0 spectrographic plates were used and given a tray development of 8 minutes with D76c at 19° C. with manual agitation, this development being estimated to give a gamma of about 1 (a degree of contrast such that the slope of the curve of density versus the logarithm of the exposure would be about 1). The developer used had to be mixed very carefully if consistent results were to be obtained from different batches of developer. The plates were scanned with a Leeds & Northrup microphotometer.

CRESOL MIXTURES

PREPARATION OF WORKING CURVES. Spectrograms were taken of the three pure cresols and of a number of synthetic mixtures. In Figure 1, reproduced as negative prints, are the spectra of the pure components. In Figure 2 are the microphotometer tracings of these plates, as well as of the plate obtained from sample 5 of Table I. The scale on the left of each microphotometer tracing is a density scale obtained by running an Eastman stepwedge with each plate for the purpose of calibrating the microphotometer. This was necessary, since the sensitivity of the microphotometer was changed from plate to plate in such a manner as to bring out as much detail as possible.

The strongest bands of the spectra of *o*-, *m*-, and *p*-cresol are designated, respectively, as A_0, A_m, and A_p with wave lengths 2744, 2779, and 2830 Å., respectively. It will be evident from an examination of the spectrograms of Figure 1 or the tracings of Figure 2 that the A_0 band and the A_p band are relatively independent. Thus the density of the center of each band will serve as an independent measure of the concentration of the corresponding cresol in the sample. In Figures 3 and 4 are given the working curves for *o*-cresol and *p*-cresol as they were obtained from the various synthetic mixtures. The "density Δ" is the den-

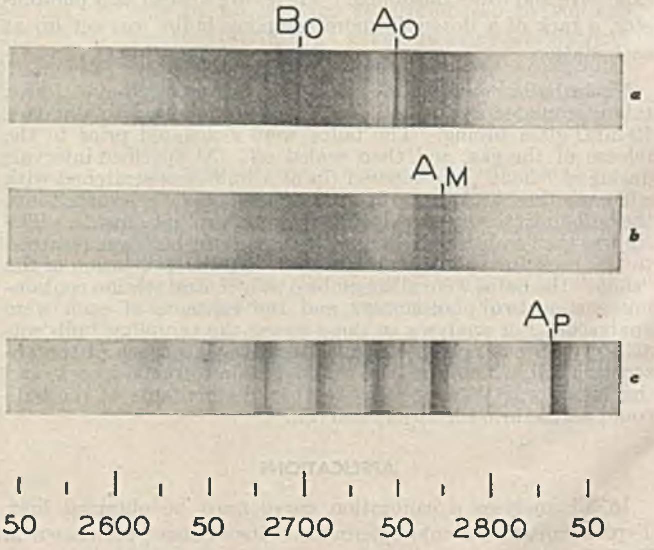

Figure 1. Near Ultraviolet Absorption Spectrograms of Cresol Vapors

a. *o*-Cresol. *b.* *m*-Cresol. *c.* *p*-Cresol.

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sity difference between the background of the band and the center of the band. This roughly cancels the variations in the intensity of the light source and in development.

The meta band, A_m, has a relatively low extinction coefficient and is overlapped by an ortho band of almost equal intensity. Therefore it was not possible to determine the meta concentration by the direct method which was used for the ortho and para isomers. The difference in density between bands from two different compounds in a single mixture is a more sensitive function of concentration than the density of either band alone. The density difference, called Δ', was taken between band A_m and the second strongest ortho band, labeled B_0 (λ = 2694 Å.) on the spectrograms of Figure 1. B_0 was used instead of A_0 to avoid the effect of strong absorption mentioned below. Since the para isomer also absorbs slightly in this region, a working curve of Δ' versus per cent meta was first prepared from meta-ortho mixtures. The three-component synthetic mixtures were then analyzed and a correction curve was determined (see Figure 5) that would eliminate the effect of the p-cresol on the two-component density Δ'-% meta curve mentioned previously. The procedure is as follows:

> The amounts of ortho and para are first determined. Then the para density correction is determined from Figure 5 and added to the Δ', determined from the microphotometer record. The composition of meta in terms of ortho is then read off Figure 6, using the corrected density, Δ'. Then meta is known in terms of ortho and the per cent meta in the complete sample may be calculated.

Each working curve that is drawn represents an average of the results in terms of the density Δ as a function of concentration.

Discussion of Results. The Beer-Lambert law is fairly well obeyed for low concentrations of the components but not for the higher concentrations, particularly in the case of the ortho isomer. This is because the absorption of these bands is so strong that the exposure in the center of the bands falls below the linear portions of the density-exposure curve given in Figure 6. (This curve is the experimentally determined characteristic

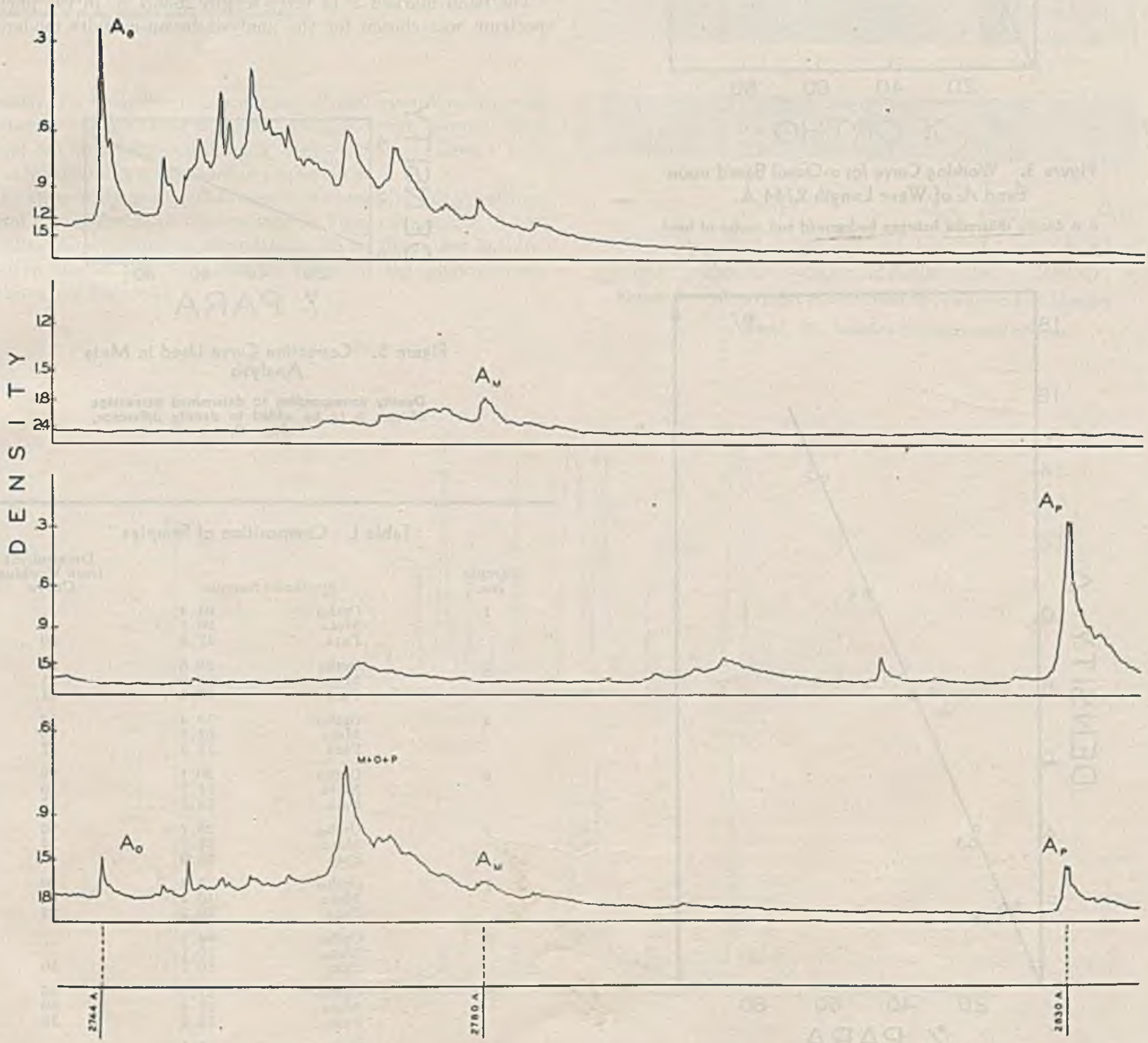

Figure 2. Microphotometer Tracings of Spectrograms of Figure 1

a. o-Cresol. *b.* m-Cresol. *c.* p-Cresol. *d.* Sample of 30.1% ortho, 31.7% meta, and 38.2% para curve of Eastman 103-0 spectrographic plates when processed as described above.) Consequently, samples of 50% or higher ortho or 70% or higher para cannot be analyzed directly. However, a known amount of para or ortho, respectively, or of meta may be added to bring the relative concentrations down. Another possible method of analyzing for high percentages of ortho or para involves the use of an additional short cell, whose length relative to the length of the original cell is known.

The straight-line portion of the curve indicates also that Raoult's law is obeyed, at least over that region.

In Table I are given the concentrations of the three cresol isomers in various synthetic samples as determined from the working curves and the experimental data, except for the samples with very high ortho or para concentrations. The compositions of the corresponding synthetic samples are given in the same table. The mean deviation between the two is less than 2%.

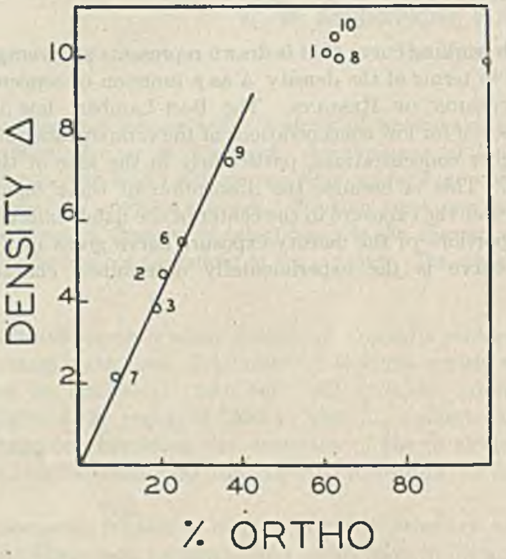

Figure 3. Working Curve for o-Cresol Based upon Band A_0 of Wave Length 2744 Å.

Δ is density difference between background and center of band

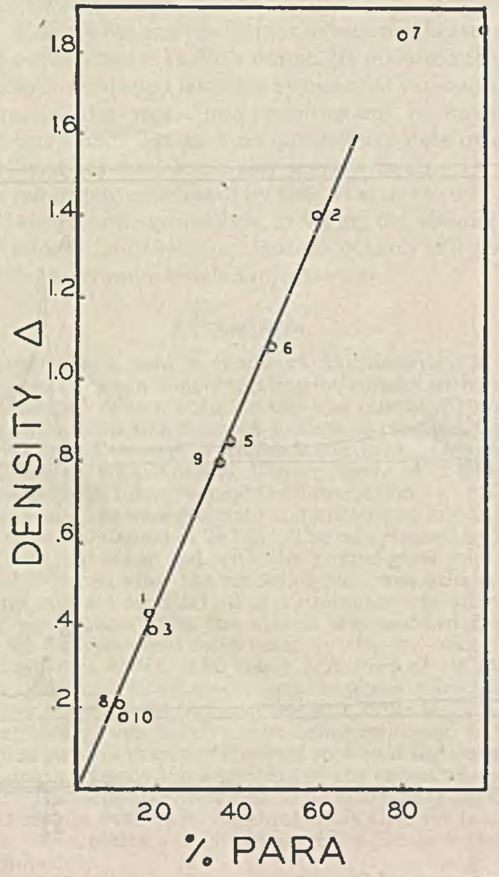

Figure 4. Working Curve for p-Cresol Based upon Band A_p of Wave Length 2830 Å.

CRESOL-PHENOL MIXTURES

Preparation of Working Curves. In Figure 8 are reproductions of spectrograms of pure phenol and of a phenol-cresol mixture of 16.4% phenol. Figure 9 shows microphotometer tracings of the above spectrograms. It will be noticed from 9, *b*, that the spectrum of phenol is much more strongly developed than that of the *o*-, *m*-, or *p*-cresols. The strong bands (A_0 and A_p) of the *o*-cresol and *p*-cresol spectra are, however, completely independent of the phenol spectrum, whereas the relatively weak spectrum of *m*-cresol is completely lost in that of phenol.

The band marked *P* of wave length 2636.7 Å. in the phenol spectrum was chosen for the analysis because of its moderate

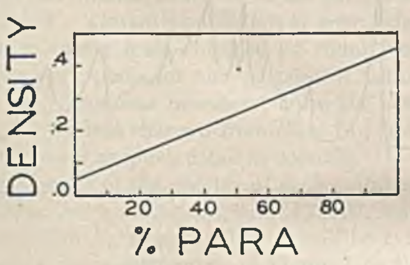

Figure 5. Correction Curve Used in Meta Analysis

Density corresponding to determined percentage of para is to be added to density difference, $A_m - B_0$

Table I. Composition of Samples

Sample No.	Synthetic Sample		Determined from Working Curve
1	Ortho	61.4	..
	Meta	20.7	..
	Para	17.8	20
2	Ortho	20.6	22
	Meta	20.0	21
	Para	59.4	61
3	Ortho	19.4	18
	Meta	61.8	59
	Para	18.8	17
5	Ortho	30.1	29
	Meta	31.7	30
	Para	38.2	37
6	Ortho	25.7	26
	Meta	26.3	26
	Para	48.0	47
7	Ortho	9.4	10
	Meta	10.4	12
	Para	80.2	80
8	Ortho	64.2	..
	Meta	25.1	..
	Para	10.7	10
9	Ortho	37.3	35
	Meta	27.4	30
	Para	35.3	35
10	Ortho	63.1	..
	Meta	26.2	..
	Para	10.6	9

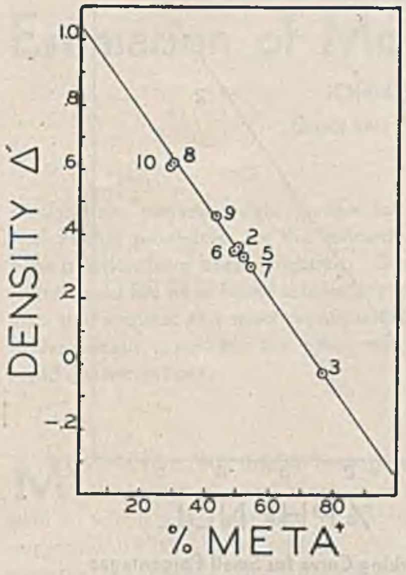

Figure 6. Working Curve for *m*-Cresol

Corrected density difference between A_m of λ = 2779 Å. and B_0 of λ = 2694 Å. is plotted against percentage of meta, where meta + ortho content is taken as 100%

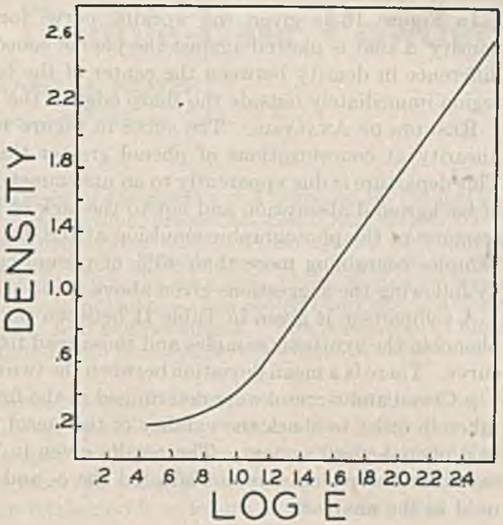

Figure 7. Characteristic Curve of Eastman 103-0 Spectrographic Plate, Developed as Described in Text

intensity, its complete independence of the cresol spectra, and its sharpness. In these mixtures, then, *o*-cresol, *p*-cresol, and phenol can be determined directly, and *m*-cresol is known if it is the only remaining component of the mixture.

The apparently small differences in the intensities of the strong phenol bands shown in the tracings in Figure 9 are due to the fact that the exposures in these bands fall on the rather flat, insensitive toe of the characteristic curve of the photographic emulsion (see Figure 7).

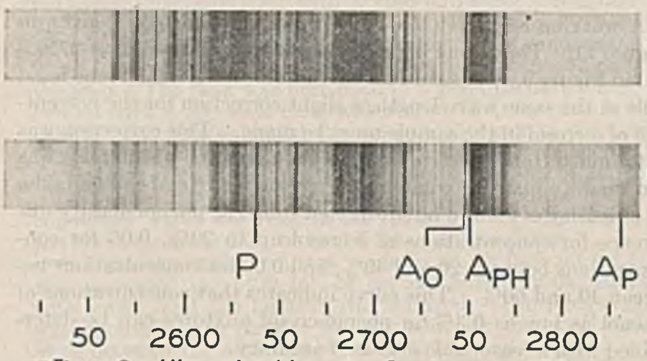

Figure 8. Ultraviolet Absorption Spectrograms of Vapors

a. Pure phenol. *b.* Sample 4 of phenol-cresol mixtures

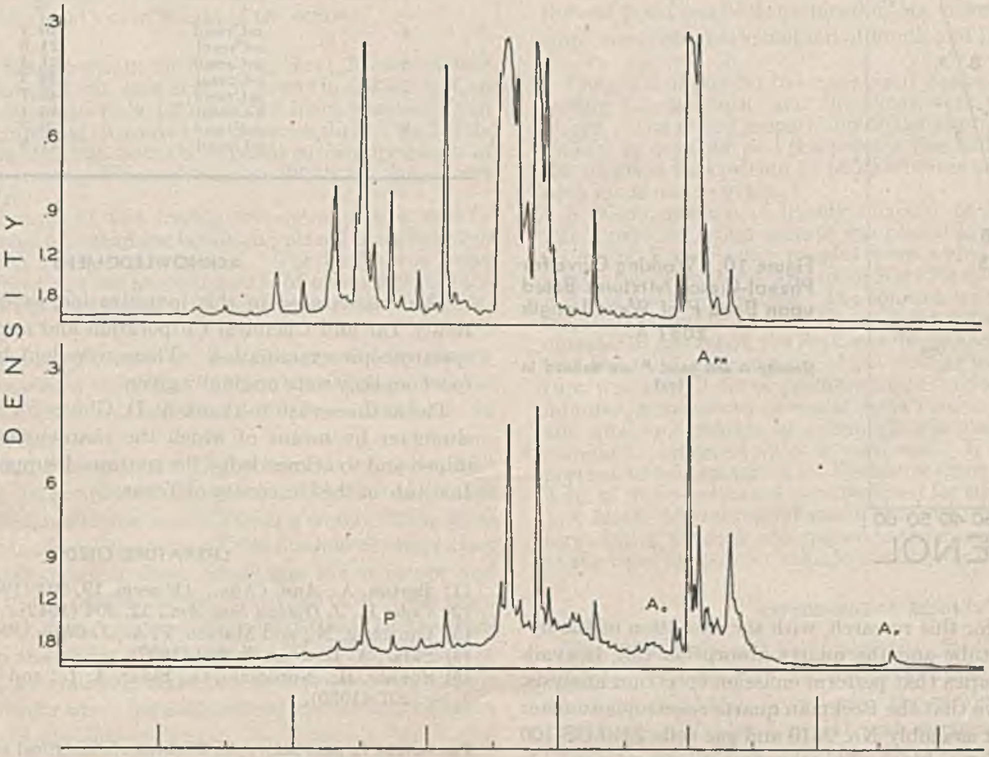

Figure 9. Microphotometer Tracings of Spectrograms of Figure 8

In Figure 10 is given the working curve for phenol. The density Δ that is plotted against the phenol concentration is the difference in density between the center of the band *P* and the region immediately outside the sharp edge of the band.

Results of Analysis. The curve in Figure 10 departs from linearity at concentrations of phenol greater than about 40%. This departure is due apparently to an unsymmetric development of background absorption and not to the lack of linearity in the response of the photographic emulsion at the densities involved. Samples containing more than 40% of phenol can be analyzed by following the suggestions given above.

A comparison is given in Table II between the percentages of phenol in the synthetic samples and those read from the working curve. There is a mean deviation between the two of less than 3%.

p-Cresol and *o*-cresol were determined in the first four samples taken in order to check the validity of the cresol working curves in a phenol-cresol system. The results given in Table III indicate that the phenol has not affected the *o*- and *p*-cresol bands used in the analyses.

ANALYSIS OF SAMPLES OF LOW PHENOL CONCENTRATION

A working curve for low concentrations of phenol is given in Figure 11. The strong band of phenol marked A_{PH} (λ = 2750.3 Å.) in Figure 9, *b*, was used for this curve. As a weak ortho band falls at the same wave length, a slight correction for the percentage of *o*-cresol in the sample must be made. This correction was determined from separate samples containing no phenol, but was too small to justify a complete correction curve and can be taken as a density of 0.03 to be subtracted from the phenol density difference for concentrations of *o*-cresol up to 20%, 0.06 for concentrations between 20 and 40%, and 0.09 for concentrations between 40 and 60%. This curve indicates that concentrations of phenol as low as 0.3% in phenol-cresol mixtures can be determined with a reasonable degree of accuracy.

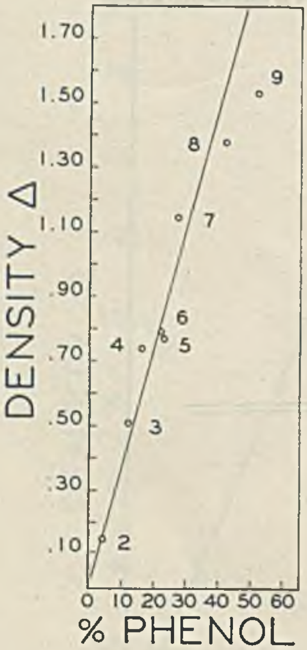

Figure 10. Working Curve for Phenol-Cresol Mixtures Based upon Band *P* of Wave Length 2637 Å.

Density Δ and band *P* are defined in text

The apparatus for this research, with the exception of the hydrogen discharge tube and the quartz absorption cell, is available in all laboratories that perform emission spectrum analysis. The authors believe that the Beckman quartz spectrophotometer with compartment assembly No. 2510 and gas cells 2310-GS-100 can be used for this analysis. This instrument was not available to the authors at the time this work was carried out.

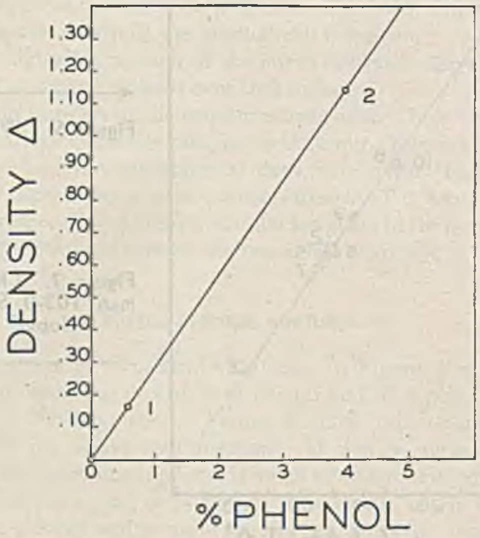

Figure 11. Working Curve for Small Percentages of Phenol in Phenol-Cresol Mixtures

Based upon phenol band A_{PH} of wave length 2750 Å.

Table II. Percentages of Phenol in Synthetic Phenol-Cresol Mixtures and Those Read from Working Curve of Figure 10

Sample	Synthesis %	Analysis %
2	4.0	4
3	12.4	13
4	16.4	19
5	23.1	20
6	21.5	22
7	26.5	31
8	41.5	37

Table III. Analyses of Four Arbitrarily Chosen Samples of Phenol-Cresol Mixtures

Sample		Synthesis %	Analysis %
4	*p*-Cresol	40.1	40
	o-Cresol	21.5	23
6	*p*-Cresol	21.4	20
	o-Cresol	24.3	22
7	*p*-Cresol	43.7	43
	o-Cresol	15.1	17
8	*p*-Cresol	20.7	21
	o-Cresol	21.8	20

ACKNOWLEDGMENT

The cresols used in this investigation were prepared by the Reilly Tar and Chemical Corporation and appeared pure under spectroscopic examination. These were lent by R. J. Williams, to whom they were originally given.

The authors wish to thank A. D. Glover for the use of the sensitometer by means of which the characteristic curve was obtained and to acknowledge the continued support of the Research Institute of the University of Texas.

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Presented in part before the Division of Analytical and Micro Chemistry, at the 109th Meeting of the American Chemical Society, Atlantic City, N. J.

Estimation of Moisture in Solventless Double-Base Powders

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Desiccation, cone-and-dish, carbon tetrachloride distillation, and Karl Fischer procedures for the estimation of moisture in ballistite-type powders have been compared. Desiccation over concentrated sulfuric acid has been found satisfactory with respect to accuracy and also the simplest and most reproducible of these procedures, but under certain conditions the other methods are feasible for more rapid determinations.

MOST solventless double-base powder manufactured at the present time is a mixture of nitrocellulose and nitroglycerin to which a few per cent of stabilizers, plasticizers, and inorganic salts have been added. Powders of this type are not notably hygroscopic, but finished samples in equilibrium with their surroundings contain a few tenths of a per cent of moisture. Precise control of the concentration of this constituent is essential to ensure satisfactory behavior of the finished powder. Several procedures for the estimation of moisture in smokeless powders have been reported (*2*, *3*, *4*), many of which are tedious and involved or are not capable of the necessary accuracy. The authors have selected the four procedures that appear most promising and have compared them carefully with regard to accuracy, reproducibility, and ease of operation, using several samples of ballistite-type powder containing approximately 0.2% moisture. The results of these comparisons are presented below, together with specific recommendations based upon them.

EXPERIMENTAL PROCEDURES

DESICCATION PROCEDURE. The desiccation procedure for the estimation of moisture involves storing the powder sample in a desiccator until the weight is constant; the moisture content is calculated from the total loss in weight of the sample.

If the powder sample was in the form of a sheet, it was cut into pieces approximately 1 cm. on a side; if it was in the form of an extruded grain, approximately 1.25 cm. (0.5 inch) were cut from the end of the grain and discarded; successive slices 1 to 2 mm. in thickness were then cut from the exposed surface by means of a guillotine-type cutter. These slices were finally cut into pieces of convenient size.

A 10-gram sample of the freshly cut powder was rapidly weighed into a large dry weighing bottle and placed in a desiccator over concentrated (96%) sulfuric acid. The bottle was tared during the weighing against another bottle of approximately the same size, which was then stored in the desiccator with the sample.

The sample was reweighed every 2 or 3 days until the change between two successive weighings was less than 1 mg., and the percentage of moisture was calculated from the total loss in weight of the system.

CONE-AND-DISH PROCEDURE. The cone-and-dish procedure involves heating the sample to be analyzed in a shallow aluminum dish of special design which is covered with a snugly fitting glass cone (*6*). The successful operation of this method depends upon the assumption that under these conditions the moisture and volatile solvent in the powder diffuse out at the base of the cone, and that any other constituents which are volatilized by the heating condense on the cooler inner surface. Therefore the loss in weight of the entire system is taken to represent the total volatile content of the powder which for a solventless powder may be taken to be the moisture content.

A 10-gram sample of the powder was prepared by the method used for the desiccation procedure described above. This sample was weighed into a cone-and-dish system of standard design, which was tared against another cone-and-dish. The system was placed for 2 hours on a closed bath heated by steam at atmospheric pressure and was then cooled overnight in a desiccator over sulfuric acid and reweighed. The percentage of moisture was calculated from the total loss in weight of the system.

CARBON TETRACHLORIDE DISTILLATION PROCEDURE. The carbon tetrachloride distillation procedure involves refluxing a large sample of powder with carbon tetrachloride and catching the condensed vapors in a trap which retains the water but permits the carbon tetrachloride to return to the boiling flask (*1*).

A 100-gram sample of powder was weighed into a 1-liter round-bottomed flask equipped with a standard-taper joint, and 400 ml. of carbon tetrachloride saturated with water were added. A moisture trap for retaining the water in the condensate was fitted to the flask, and a reflux condenser was mounted on top of the trap. The flask was immersed in a graphite bath which was heated with a 500-watt electrical heater, and the carbon tetrachloride was refluxed until the amount of water in the tube of the moisture trap did not appear to be changing with time. Two to 4 hours were found to be a satisfactory time of refluxing. At the end of the run the heater was shut off and the volume of condensed water was read as the difference between the top of the lower meniscus and the top of the upper meniscus.

A blank determination was made in which 0.20 ml. of water was measured into 400 ml. of carbon tetrachloride saturated with water, and the mixture was refluxed. The percentage of water found in the powder was corrected for the small discrepancy between the amounts of water taken and detected in this blank determination.

KARL FISCHER PROCEDURE. The Karl Fischer reagent is a solution of iodine and sulfur dioxide in pyridine and methanol. This reagent combines with water stoichiometrically (*7*), and the end point can be determined either visually or by the "dead-stop" conductometric method of Foulk and Bawden (*5*).

The grain of powder to be analyzed was cut into slices approximately 1 mm. thick, and the slices were then cut into small pieces. The entire preparation of the sample was carried out as rapidly as possible, and the powder was added to the solvent in the titration flask within 15 to 20 minutes after the first cut had been made on the grain.

A 60-ml. portion of freshly mixed 1 to 1 ether-methanol or 1 to 1 pyridine-ethyl acetate was placed in a titration flask, and 10 ml. of Karl Fischer reagent were added. The mixture was stirred for one minute, and more Karl Fischer reagent was added if it was not still in excess. The solution was finally titrated conductometrically to the anhydrous point with a standard solution of water in methanol, the flask was disconnected from the apparatus, and the 5-gram sample of cut powder was added. The mixture was stirred for a predetermined period of from 30 to 60 minutes, a measured excess of Karl Fischer reagent was added, and after one minute of stirring it was back-titrated with the standard solution of water in methanol. It was found to be important to add enough Karl Fischer reagent so that no less than 3 ml. of water-methanol were required for the back-titration.

A blank determination was made each day. During this determination the flask was opened to the atmosphere for 10 seconds at the time the powder sample would ordinarily be added.

EXPERIMENTAL RESULTS

Several samples of a sheet ballistite (Radford lot JP 198) were analyzed for moisture by the desiccation, cone-and-dish, and carbon tetrachloride procedures; the results of the analyses are presented in Tables I to III and summarized in Table IV. The data illustrate the precision to be expected from the various procedures and the absolute agreement between them.

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Table I. Estimation of Moisture in JP 198 by Desiccation over Sulfuric Acid

Run No.	Percentage Moisture Detected after Desiccation for 48 hours	132 hours	180 hours
1	0.208	0.217	0.218
2	0.205	0.210	0.212
3	0.207	0.214	0.216
4	0.193	0.201	0.201
5	0.194	0.205	0.204
6	0.185	0.201	0.201
		Av.	0.209

Table II. Estimation of Moisture in JP 198 by Cone-and-Dish Procedure

Run No.	Percentage Moisture Detected after 2-hour heating plus 0.5-hour desiccation	2-hour heating plus overnight desiccation
1	0.147	0.178
2	0.158	0.196
3	0.158	0.205
4	0.164	0.221
5	0.168	0.200
6	0.176	0.197
	Av.	0.200

An extruded grain of ballistite (Radford lot JP 214) was analyzed for moisture by the desiccation and Karl Fischer procedures described above, and the results are compared in Table V.

The analyses presented in Tables I to V illustrate the relative amounts of water detected in representative powders by the various procedures, but they do not provide information as to the absolute accuracy of the procedures. In order to secure this information several samples of powder cut from a grain of ballistite (Radford lot JP 214) were desiccated to constant weight, and some of the desiccated samples were analyzed by various procedures. The other desiccated samples were stored in humidifiers over solutions of glycerol and water until they were again constant in weight. These rehumidified samples were then analyzed for moisture. The results of all these experiments are presented in Table VI.

CRITIQUE OF METHODS

Desiccation Procedure. The desiccation procedure is the most reproducible of all of those studied. Although at least 4 days are required for the estimation of moisture in a sample of powder by desiccation, the time per analysis which is required of the analyst is less than that required for any of the other procedures which were studied.

The results of experiments presented in Table VI, in which samples of desiccated powder were analyzed for moisture by titration with Karl Fischer reagent, indicate that the water not removed by desiccation amounts to no more than 0.02% of the powder. Since the Karl Fischer procedure involves complete solution of the powder prior to titration, and since the Karl Fischer and desiccation procedures give comparable results in analyses of powders containing significant amounts of moisture, it appears very unlikely that the water remaining in powder after desiccation is more than the 0.02% indicated by these experiments.

The experiments presented in Table VI indicate that the loss in weight on redesiccation of a rehumidified sample is equal to but not greater than the gain in weight on rehumidification of the sample after the first desiccation. Since the gain in weight on rehumidification can scarcely be due to any material except water, the experiments indicate that no constituents of the powder except water are removed by desiccation. In order to test this conclusion, the acid from a desiccator which had been used in these experiments was tested for nitroglycerin and diphenylamine, but there was no indication of either substance. Therefore the quantities of these constituents lost during desiccation could not have amounted to more than a few hundredths of a per cent of the powder.

Table III. Estimation of Moisture in JP 198 by Carbon Tetrachloride Distillation

Run No.	Percentage Moisture Detected[a]
1	0.22
2	0.25

[a] A correction of 0.03 ml. was added to volume of water observed before percentage of moisture was calculated. The value of this correction was obtained from a blank determination with a known amount of water and no powder.

Table V. Estimation of Moisture in JP 198

Procedure	Weight of Sample, Grams	No. of Determinations	Average % Water Detected	Maximum Deviation from Average	Mean Deviation from Average
Desiccation	10	6	0.209	0.009	0.007
Cone-and-dish	10	6	0.200	0.022	0.009
CCl_4 distillation	100	2	0.235	0.015	0.015

Table V. Estimation of Moisture in JP 214

Estimation by Desiccation Run No.	Percentage moisture	Estimation by Karl Fischer Procedure Run No.	Solvent	Percentage moisture
1	0.274	1	Ether-methanol	0.29
2	0.267	2		0.29
3	0.260	3		0.27
4	0.262	4		0.28
5	0.286	5		0.29
6	0.283	6	Pyridine–ethyl acetate	0.29
		7		0.29
Av.	0.272		Av.	0.29

Table VI. Estimation of Moisture in JP 214 after Desiccation and Rehumidification

Description of Sample	Approximate % Relative Humidity of Humidifier	% Gain in Weight on Rehumidification	Percentage Moisture Redesiccation	Cone-and-dish	Karl Fischer
Desiccated	0	...	...	0.079	0.020
Rehumidified	25	0.206	0.218	0.234	0.235
Rehumidified	50	0.324	0.319	0.317	0.342
Rehumidified	75	0.498	0.494	0.480	0.496
Redesiccated	0	...	...	...	0.010

All the results indicate that the desiccation procedure for the estimation of moisture in ballistite is simple, accurate, and reproducible; its only disadvantage is the length of time, 4 days, required to complete an analysis.

Cone-and-Dish Procedure. The average of six analyses of JP 198 by the cone-and-dish procedure is in good agreement with the result of six analyses of the same powder by desiccation, but the individual determinations by the cone-and-dish procedure are scattered over a wider range. The data in Table VI suggest that this procedure gives results which are somewhat high for samples containing very little moisture and low for samples containing more than 0.4% of moisture; therefore, it is probable that the success of the procedure for the analysis of ballistites containing 0.2 to 0.4% of moisture is due to a balance between incomplete removal of water and loss through volatilization of other constituents of the powder. The procedure can be recommended only for the rapid but not highly precise analysis of powder samples containing normal amounts of moisture.

Carbon Tetrachloride Distillation Procedure. The carbon tetrachloride distillation procedure yields results rapidly, and errors due to sampling are undoubtedly diminished by the use of a 100-gram sample of powder. However, the results are precise to only about 0.03% of the powder, and the absolute accuracy of the procedure may be somewhat less because of the uncertainties associated with the correction to be applied to the volume of water which is measured. This procedure is suited for control work in which an accuracy of 0.05% is satisfactory.

Karl Fischer Procedure. The results of the first analyses of powders by means of Karl Fischer reagent scattered over a wide range and indicated considerably more moisture than was detected by the desiccation procedure. The data in Tables V and VI indicate that the moisture detected by the Karl Fischer procedure as finally adopted is no more than 0.02% more than that detected by desiccation, and the results are not sufficiently precise to determine whether there is a significant difference between the percentages of moisture detected by the two procedures. Apparently the Karl Fischer procedure is capable of rapid and accurate estimation of moisture in smokeless powder; however, it requires the use of complicated apparatus and the exercise of special precautions in order to obtain satisfactory results.

ACKNOWLEDGMENT

The authors are indebted to Robert B. Corey for his advice and direction during these studies, and to E. E. Hammond, Jr., for some of the analyses, the results of which are described herein.

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Based on work done for the Office of Scientific Research and Development under Contract OEMsr-881 with the California Institute of Technology. Contribution 1052 from the Gates and Crellin Laboratories, California Institute of Technology.

Bromination of Phenols and Phenol Alcohols

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A number of phenols and phenol alcohols were brominated with excess acid bromide—bromate solution at 25°. For each compound the number of positions which brominate is plotted as a function of the bromine excess. The effect of acid concentration, bromination time, and temperature on the extent of bromination is described. While some alkylated phenols brominate quantitatively regardless of the bromine excess used, other alkylated phenols overbrominate to an extent which varies with the magnitude of the bromine excess. The hydroxymethyl groups of phenol alcohols differ widely in the ease with which they are displaced by bromine.

Although the quantitative bromination of phenols by acid bromide-bromate solution, first described by Koppeschaar (*11*) in 1876, has been the subject of numerous investigations, there is much about this reaction that is still not clear. The method is based upon the general assumption that aqueous nascent bromine will replace quantitatively only those hydrogen atoms ortho or para to the hydroxyl group of phenols. It has been found, however, that the presence of certain groups other than hydrogen in the ortho or para positions gives rise to anomalous results.

Numerous experiments by Allen (*1*) and others proved that salicylic acid brominates with the splitting off of the carboxy group and the formation of carbon dioxide and tribromophenol. The bromination of sulfanilic acid was studied by Callan and Henderson (*3*) who, in agreement with previous investigators, found that the sulfo group is eliminated and tribromoaniline is formed. Francis and Hill (*9*) established that the formyl group in *o*- and *p*-hydroxybenzaldehyde is displaced during bromination with the evolution of carbon monoxide and the formation of tribromophenol. Francis (*7*) found that when saligenin is brominated the hydroxymethyl group is displaced and formaldehyde is produced. The displacement of the COOH, HSO_3, CHO, and CH_2OH groups in the phenols studied by the above investigators could be made quantitative, or could be completely inhibited, depending upon the bromination conditions.

There is considerable disagreement in the literature on the accuracy with which alkylated phenols can be determined by bromination. Thus, Fox and Barker (*6*) using the bromide-bromate method observed that phenol and *m*-cresol absorb exactly 3 moles of bromine, but that *o*- and *p*-cresol absorb somewhat more than 2 moles of bromine. Day and Taggart (*4*) likewise found Koppeschaar's method unsatisfactory for the determination of *o*- and *p*-cresol, although phenol, *m*-cresol, β-naphthol, thymol, resorcinol, several nitrophenols, *p*-chlorophenol, salicylic acid, *m*-hydroxybenzoic acid, and a number of salicylates gave good results. In a recent study of the bromide-bromate method, Sprung (*17*) found that phenols which contain substituents in the meta position, or phenols which contain secondary or tertiary alkyl groups in the ortho or para positions, brominate quantitatively. However, phenols which contain primary alkyl groups in the ortho or para positions give results which may be 10 to 150% high. Francis and Hill (*8*) contend that the overbromination of cresols and xylenols observed by Sprung does not occur if only a slight excess of bromine is used, and if the bromination time is very short.

It was the purpose of the investigation reported here to study further Koppeschaar's bromination method with the aim of applying it to the measurement of the rates of condensation of phenols with formaldehyde. For this application it is necessary to know accurately how phenols containing alkyl, hydroxymethyl, and methylene groups brominate. Since no information about the quantitative bromination of phenol alcohols, other than saligenin, could be found in the literature, a number of phenol alcohols were prepared and brominated. The related phenols, as well as *o*-cresol, *m*-cresol, and three isomeric dihydroxydiphenylmethanes were likewise brominated to ascertain the accuracy with which they could be determined. The effect of the magnitude of the bromine excess on the extent of bromination of each phenol and phenol alcohol was studied in detail. The effects of acid concentration, bromination time, and temperature were also investigated in the cases of *p*-cresol and 2-hydroxy-α^1,α^3-mesitylenediol.

SOLUTIONS AND REAGENTS

Sodium Thiosulfate, 0.1 *N*.

Bromide-Bromate Solution, 0.1 *N*. Potassium bromate (5.6 grams) and potassium bromide (30 grams) dissolved in distilled water and made up to 2 liters.

Hydrochloric Acid. Concentrated acid, specific gravity 1.19.

Potassium Iodide, 10% aqueous solution.

Starch Solution, 1% aqueous solution.

Phenol. c.p. grade phenol redistilled three times; melting point 40° C.

Saligenin. Prepared by the reduction of *o*-hydroxybenzaldehyde with sodium amalgam according to the procedure of Lapworth and Schoesmith (*12*). Recrystallized four times from benzene and three times from carbon tetrachloride; melting point 84° C.

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p-Hydroxybenzyl Alcohol. Obtained from phenol-formaldehyde resins by sublimation (*16*). Purified by fractional crystallization from benzene and several recrystallizations from water; melting point 121°.

o-Cresol. Pure *o*-cresol from The Barrett Division redistilled three times; melting point 31°.

m-Cresol. Practical grade material from the Eastman Kodak Company purified by the method of Fox and Barker (*5*); melting point 10°.

p-Cresol. *p*-Cresol (99 to 100%) from The Barrett Division purified by the method of Fox and Barker (*5*); melting point 33°.

2-Hydroxy-α^1,α^3-mesitylenediol. Prepared from *p*-cresol and formaldehyde according to Auwers (*2*) and Ullmann and Brittner (*19*). Recrystallized once from ethyl acetate and once from benzene; melting point 128°.

p-Ethylphenol. A sample from the Reilly Tar & Chemical Corp. redistilled once; melting point 43°.

5-Ethyl-2-hydroxy-α^1,α^3-xylenediol. Prepared from *p*-ethylphenol and formaldehyde (*18*). Recrystallized once from benzene; melting point 84°.

p-Isopropylphenol. A sample from Sharples Chemicals, Inc., recrystallized twice from petroleum ether; melting point 60°.

2-Hydroxy-5-isopropyl-α^1,α^3-xylenediol. Prepared from *p*-isopropylphenol and formaldehyde (*18*). Recrystallized once from benzene; melting point 125°.

p-Cyclohexylphenol. A commercial sample from The Dow Chemical Company recrystallized once from heptane; melting point 130°.

5-Cyclohexyl-2-hydroxy-α^1,α^3-xylenediol. Prepared from *p*-cyclohexylphenol and formaldehyde (*20*). Recrystallized once from benzene; melting point 107°.

p-(1,1,3,3-Tetramethylbutyl)-phenol. A commercial sample from The Resinous Products & Chemical Company recrystallized once from petroleum ether; melting point 84°.

2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)-α^1,α^3-xylenediol. Prepared from *p*-(1,1,3,3-tetramethylbutyl)-phenol and formaldehyde (*14*). Recrystallized three times from petroleum ether; melting point 71°.

4-Chloro-*m*-cresol. A commercial sample from The Barrett Division recrystallized once from petroleum ether; melting point 64°.

6-Chloro-3-hydroxy-α^2,α^4-pseudocumenediol. Prepared from 4-chloro-*m*-cresol and formaldehyde (*13*). Recrystallized twice from 1,2-dichloroethane; melting point 131°.

2,2′-Dihydroxydiphenylmethane. A pure sample furnished by Givaudan-Delawanna, Inc.; melting point 118°.

2,4′-Dihydroxydiphenylmethane. Isolated from an acid-catalyzed

Table 1. Bromination of Some Phenols and Phenol Alcohols

Acidity, 0.75 *N*
Temperature, 25° C.
Time exposed to bromine, 5 minutes

Phenol	Concentration of Phenol Solution	Br Added	$Na_2S_2O_3$ Required	Net Br Absorbed	Residual Br Excess	No. of Reactive Positions Found
	G./l.	*Milli-equivalents*	*Milli-equivalents*	*Milli-equivalents*	*% Br absorbed*	
Phenol	1.507	2.496	0.088	2.407	3.66	3.01
	1.507	2.504	0.098	2.406	4.07	3.01
	0.9490	1.702	0.188	1.514	12.4	3.00
	0.9490	1.922	0.406	1.516	26.8	3.01
	0.9490	2.338	0.817	1.521	53.7	3.02
Saligenin	1.047	1.244	0.013	1.231	1.06	2.92
	1.047	1.282	0.043	1.239	3.47	2.94
	1.047	1.322	0.082	1.240	6.61	2.94
	1.047	1.540	0.282	1.258	22.4	2.98
	1.047	1.736	0.473	1.263	37.5	2.99
	1.047	1.933	0.653	1.280	51.0	3.03
	1.047	2.031	0.754	1.277	59.0	3.03
p-Hydroxybenzyl alcohol	1.004	1.195	0.038	1.157	3.28	2.86
	1.004	1.262	0.099	1.163	8.51	2.88
	1.004	1.793	0.587	1.206	48.7	2.98
	1.004	2.340	1.119	1.221	91.6	3.02
o-Cresol	1.669	1.766	0.156	1.610	9.69	2.09
	1.669	1.803	0.184	1.619	11.4	2.10
	0.8251	0.965	0.133	0.832	16.0	2.18
	0.8251	1.284	0.308	0.976	31.6	2.56
	0.8251	1.440	0.408	1.032	39.5	2.70
	0.8251	1.682	0.601	1.081	55.6	2.83
	0.8251	2.008	0.883	1.125	78.5	2.95
	0.8251	2.380	1.252	1.128	111	2.96
m-Cresol	0.5902	0.837	0.029	0.808	3.59	2.96
	1.146	1.664	0.100	1.564	6.39	2.95
	1.002	1.461	0.090	1.371	6.56	2.96
	0.5902	0.977	0.172	0.805	21.4	2.95
	1.002	1.717	0.344	1.373	25.1	2.96
	1.146	2.067	0.479	1.588	30.2	3.00
	0.5902	1.124	0.302	0.822	36.7	3.01
	1.146	2.287	0.693	1.594	43.5	3.01
	1.002	2.068	0.670	1.398	47.9	3.02
	1.146	2.581	0.974	1.607	60.6	3.03
	0.5902	1.315	0.506	0.809	62.5	2.96
	0.5902	1.407	0.592	0.815	72.6	2.99
	0.5902	1.487	0.666	0.821	81.1	3.01
p-Cresol	1.050	1.033	0.068	0.965	7.05	1.90
	0.9364	0.941	0.076	0.865	8.79	2.00
	1.050	1.361	0.281	1.080	26.0	2.22
	1.050	1.566	0.460	1.106	41.6	2.28
	0.9364	1.569	0.585	0.984	59.5	2.27
	1.050	2.000	0.899	1.101	81.7	2.27
p-Ethylphenol	1.052	0.796	0.063	0.733	8.59	1.70
	1.052	0.931	0.129	0.802	16.1	1.86
	1.052	1.119	0.248	0.871	28.5	2.02
	1.052	1.527	0.586	0.941	62.3	2.19
	1.052	2.039	1.066	0.973	110	2.26
p-Isopropylphenol	1.337	0.915	0.069	0.846	8.16	1.72
	1.337	1.152	0.205	0.947	21.6	1.93
	1.337	1.322	0.307	1.015	30.2	2.07
	1.337	1.524	0.470	1.054	44.6	2.15
	1.337	1.910	0.734	1.176	62.4	2.40
p-Cyclohexylphenol	2.142	1.248	0.038	1.210	3.14	1.99
	2.142	1.369	0.153	1.216	12.6	2.00
	2.142	1.453	0.242	1.211	20.0	1.99
	2.142	1.560	0.322	1.238	26.0	2.04
	2.142	1.867	0.680	1.187	57.3	1.95
p-(1,1,3,3-Tetramethylbutyl)-phenol	3.764	1.890	0.064	1.826	3.50	2.00
	4.025	2.139	0.195	1.944	10.0	1.99
	4.025	2.209	0.267	1.942	13.7	1.99
	4.025	2.204	0.265	1.939	13.7	1.99
	3.764	2.267	0.456	1.811	25.2	1.99
	3.764	2.498	0.673	1.825	36.9	2.00
4-Chloro-*m*-cresol	2.101	1.526	0.051	1.475	3.46	2.00
	1.438	1.042	0.046	0.996	4.62	1.98
	2.101	1.666	0.188	1.478	12.7	2.01
	2.101	1.763	0.273	1.490	18.3	2.02
	1.438	1.237	0.242	0.995	24.3	1.97
	2.101	1.864	0.369	1.495	24.7	2.03
	2.101	1.920	0.427	1.493	28.6	2.03
	2.101	2.009	0.524	1.485	35.3	2.02
	1.438	1.379	0.382	0.997	38.3	1.98
	1.438	1.501	0.487	1.014	48.0	2.01
	1.438	1.641	0.639	1.002	63.8	1.99
	1.438	1.761	0.751	1.010	74.4	2.00
2-Hydroxy-α^1,α^3-mesitylenediol	3.027	1.210	0.053	1.157	4.58	1.29
	2.718	1.064	0.051	1.013	5.03	1.25
	2.687	1.180	0.124	1.056	11.7	1.32
	3.027	1.480	0.254	1.226	20.7	1.36
	2.718	1.373	0.291	1.082	26.9	1.34
	2.687	1.407	0.335	1.072	31.3	1.34
	2.687	1.523	0.445	1.078	41.3	1.35
	2.718	1.636	0.522	1.114	46.9	1.38
	3.024	1.976	0.694	1.282	54.1	1.43
	2.718	1.941	0.781	1.160	67.3	1.44
5-Ethyl-2-hydroxy-α^1,α^3-xylenediol	1.683	0.778	0.034	0.744	4.57	1.61
	1.683	0.908	0.117	0.791	14.8	1.71
	1.683	1.055	0.237	0.818	29.0	1.77
	1.683	1.218	0.385	0.833	46.2	1.80
	1.683	1.683	0.836	0.847	98.7	1.83

phenol-formaldehyde resin by vacuum distillation according to Koebner (*10*). Recrystallized twice from water; melting point 118°.

4,4′-Dihydroxydiphenylmethane. A pure sample supplied by Givaudan-Delawanna, Inc.; melting point 162°.

Table I (Continued).

Phenol	Concentration of Phenol Solution	Br Added	$Na_2S_2O_3$ Required	Net Br Absorbed	Residual Br Excess	No. of Reactive Positions Found
	G./l.	*Milli-equivalents*	*Milli-equivalents*	*Milli-equivalents*	*% Br absorbed*	
2-Hydroxy-5-isopropyl-α^1,α^3-xylenediol	2.020	0.836	0.051	0.785	6.50	1.53
	2.020	0.990	0.132	0.858	15.4	1.67
	2.020	1.199	0.338	0.861	39.3	1.67
	2.020	1.382	0.504	0.878	57.4	1.71
	2.020	1.549	0.655	0.894	73.3	1.74
5-Cyclohexyl-2-hydroxy-α^1,α^3-xylenediol	2.610	0.797	0.093	0.704	13.2	1.28
	2.610	0.930	0.146	0.784	18.6	1.42
	2.610	1.010	0.205	0.805	25.5	1.46
	2.610	1.082	0.283	0.799	35.4	1.45
	2.610	1.295	0.448	0.847	52.9	1.53
	2.610	1.460	0.626	0.834	75.1	1.51
2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)-α^1,α^3-xylenediol	3.708	1.295	0.082	1.213	6.76	1.74
	3.284	1.239	0.113	1.126	10.0	1.83
	3.708	1.416	0.162	1.254	12.9	1.80
	3.284	1.358	0.202	1.156	17.5	1.88
	3.708	1.524	0.249	1.275	19.5	1.83
	3.284	1.534	0.346	1.188	29.1	1.93
	3.284	1.663	0.477	1.186	40.2	1.92
	3.708	1.938	0.573	1.365	42.0	1.96
	3.284	1.881	0.671	1.210	55.5	1.96
	3.284	2.114	0.899	1.215	74.0	1.97
6-Chloro-3-hydroxy-α^2,α^4-pseudocumenediol	3.017	1.471	0.051	1.420	3.59	1.91
	3.017	1.450	0.053	1.397	3.79	1.88
	3.017	1.610	0.162	1.448	11.2	1.95
	3.017	1.717	0.267	1.450	18.4	1.95
	3.017	1.894	0.434	1.460	29.7	1.96
	3.017	2.081	0.598	1.483	40.3	1.99
	3.017	2.293	0.817	1.476	55.4	1.98
	3.017	2.532	1.044	1.488	70.2	2.00
2,2′-Dihydroxydiphenylmethane	1.362	1.048	0.029	1.019	2.85	3.00
	1.362	1.224	0.177	1.047	16.9	3.08
	1.362	1.341	0.287	1.054	27.2	3.10
	1.362	1.742	0.652	1.090	59.8	3.20
2,4′-Dihydroxydiphenylmethane	1.403	1.323	0.027	1.296	2.08	3.70
	1.403	1.514	0.162	1.352	12.0	3.86
	1.403	1.784	0.424	1.360	31.2	3.88
	1.403	2.037	0.666	1.371	48.6	3.91
	1.403	2.269	0.878	1.391	63.1	3.97
4,4′-Dihydroxydiphenylmethane	1.297	1.349	0.065	1.284	5.06	3.96
	1.297	1.524	0.226	1.298	17.4	4.01
	1.297	1.786	0.466	1.320	35.3	4.08
	1.297	2.027	0.688	1.339	51.4	4.13
	1.297	2.525	1.154	1.371	84.2	4.23

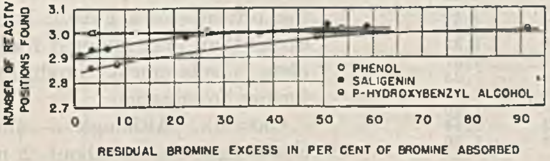

Figure 1. Bromination of Phenol, Saligenin, and *p*-Hydroxybenzyl Alcohol

Acidity, 0.75 *N*
Temperature, 25° C.
Time exposed to bromine, 5 minutes

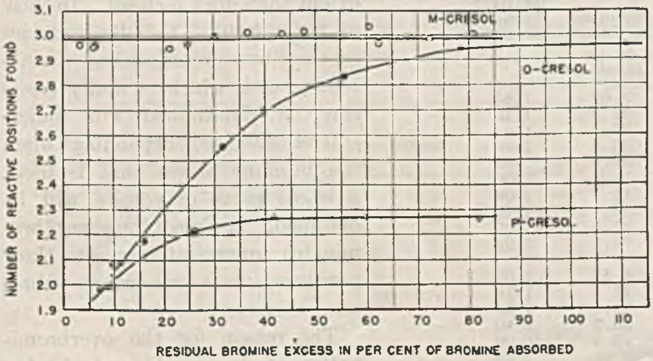

Figure 2. Bromination of *o*-, *m*-, and *p*-Cresol

Acidity, 0.75 *N*
Temperature, 25° C.
Time exposed to bromine, 5 minutes

PROCEDURE

Koppeschaar's method (*11*) as modified by Redman, Weith, and Brock (*15*) was essentially the method used. An accurately weighed quantity of the phenol was dissolved in distilled water containing sufficient sodium hydroxide (about 1 gram) to effect solution, and the solution was made up to 1 liter. A 25-ml. aliquot of the phenol solution was transferred to a 250-ml. glass-stoppered iodine flask, to which were added 25 ml. (or more as indicated below) of water and 5 ml. of concentrated hydrochloric acid. Enough bromide-bromate solution was then run in from a buret to give the desired bromine excess. The flask was quickly stoppered and shaken intermittently for 5 minutes. Ten milliliters of potassium iodide solution were then added to the flask, care being taken to avoid loss of bromine while the stopper was being lifted. The stopper was replaced and the solution again shaken intermittently for 5 minutes. The stopper and sides of the flask were washed down with water, and the solution was titrated with sodium thiosulfate, using starch solution as the indicator. A blank was run on 25 ml. of distilled water. All the brominations were carried out at a temperature of 25° except where otherwise indicated. The acidity of the mixture in the iodine flask after the addition of the bromide-bromate solution was maintained between 0.7 and 0.8 *N* by keeping the sum of the bromide-bromate solution and diluent water added at about 50 ml. Thus, when it was planned to add only 15 ml. of bromide-bromate solution to obtain the desired bromine excess, 35 instead of 25 ml. of water were added.

Aqueous solutions of *p*-(1,1,3,3-tetramethylbutyl)-phenol and 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)-α^1,α^3-xylenediol could not be made, because of the insolubility of their sodium salts. Consequently a weighed amount of each of these phenols was dissolved in 600 ml. of acetone-free reagent grade methanol, and the solution made up to 1 liter with distilled water. In order to avoid precipitation, the aliquots of these solutions were diluted with 25 ml. of methanol instead of water prior to bromination. A series of blanks was run on an aqueous methanol solution with various bromine excesses, and a correction curve for the presence of the methanol was constructed. Acetone-free methanol was found to brominate to an almost negligible extent under the conditions used in this work.

Although aqueous solutions of *p*-cyclohexylphenol and 5-cyclohexyl-2-hydroxy-α^1,α^3-xylenediol could be and were prepared, the addition of hydrochloric acid to the aliquots of these phenols caused them to precipitate, with the result that subsequent bromination was found to be incomplete. This difficulty was overcome by diluting the aliquots with methanol instead of water, and correcting for the presence of the methanol by means of the correction curve discussed above.

With a few phenols, such as *p*-ethylphenol and 4-chloro-*m*-cresol, the use of a large excess of bromine caused the end point to reappear shortly after the analysis had been completed. In such cases thiosulfate solution was added until the end point became stable.

Brominations at 10° and 40° were carried out in a constant-temperature bath up to the point of addition of the potassium iodide.

The number of reactive positions, R, was calculated from the formula

$$R = \frac{EM}{50C}$$

where E is the milliequivalents of bromine absorbed; M is the molecular weight of the phenol, and C is the concentration of the phenol solution in grams per liter.

The residual bromine excess in per cent was obtained by dividing the milliequivalents of sodium thiosulfate used (which is equal to the milliequivalents of unreacted bromine) by the milliequivalents of bromine absorbed, and multiplying the result by 100.

RESULTS AND DISCUSSION

PHENOL, SALIGENIN, AND p-HYDROXYBENZYL ALCOHOL. Figure 1 shows that phenol brominates quantitatively at three positions, regardless of the size of the bromine excess. When a considerable bromine excess is used, three reactive positions are also found for saligenin and p-hydroxybenzyl alcohol, thereby indicating quantitative displacement of the hydroxymethyl groups by bromine; but the presence of a greater bromine excess than that required for complete displacement produces no further bromination.

CRESOLS. Although o- and p-cresol each absorb about 2 moles of bromine when the bromine excess is small, additional absorption of bromine occurs with larger bromine excesses (Figure 2). The curves show clearly that o-cresol overbrominates to a much greater extent than does p-cresol. In view of these results, the discrepancies in the literature regarding the accuracy with which o- and p-cresol can be determined are understandable. For, depending upon the bromine excess that is used, a whole range of results will be obtained. m-Cresol, however, brominates quantitatively at three positions over a wide range of bromine excesses.

The reason for the overbromination of the cresols, and of other phenols discussed below, is not clear. Sprung favors the theory that substitution occurs in the

Table II. Effect of Acidity on Extent of Bromination

Temperature, 25° C.
Time exposed to bromine, 5 minutes

Phenol	Concentration of Phenol Solution	Acid Normality	Br Added	$Na_2S_2O_3$ Required	Net Br Absorbed	Residual Br Excess	No. of Reactive Positions Found
	G./l.		*Milliequivalents*	*Milliequivalent*	*Milliequivalents*	*% Br absorbed*	
p-Cresol	0.9364	0.35	0.903	0.113	0.790	14.3	1.82
	0.9364	0.35	1.042	0.215	0.827	26.0	1.91
	0.9364	0.35	1.272	0.388	0.884	43.9	2.04
	0.9364	0.35	1.491	0.595	0.896	66.4	2.07
	0.9364	0.35	1.708	0.817	0.891	91.7	2.06
	1.050	2.0	0.947	0.018	0.929	1.94	1.91
	0.9364	2.0	0.991	0.128	0.863	14.8	1.99
	1.050	2.0	1.250	0.230	1.020	22.5	2.10
	1.050	2.0	1.465	0.436	1.029	42.4	2.12
	1.050	2.0	1.579	0.518	1.061	48.8	2.19
	0.9364	2.0	1.878	0.909	0.969	93.8	2.24
2-Hydroxy-α^1,α^3-mesitylenediol	2.687	0.35	0.952	0.047	0.905	5.19	1.13
	2.687	0.35	1.062	0.146	0.916	15.9	1.15
	2.687	0.35	1.224	0.298	0.926	32.2	1.16
	2.687	0.35	1.376	0.425	0.951	44.7	1.19
	2.687	0.35	1.590	0.652	0.938	69.5	1.17
	2.687	2.0	1.225	0.043	1.182	3.64	1.48
	2.687	2.0	1.352	0.064	1.288	4.97	1.61
	2.687	2.0	1.554	0.173	1.381	12.5	1.73
	2.687	2.0	2.001	0.558	1.443	38.7	1.81
	2.718	2.0	2.472	0.918	1.554	59.1	1.92

Table III. Effect of Temperature on Extent of Bromination

Acidity, 0.75 *N*
Time exposed to bromine, 5 minutes

Phenol	Concentration of Phenol Solution	Temperature	Br Added	$Na_2S_2O_3$ Required	Net Br Absorbed	Residual Br Excess	No. of Reactive Positions Found
	G./l.	*° C.*	*Milliequivalents*	*Milliequivalent*	*Milliequivalents*	*% Br absorbed*	
p-Cresol	0.9364	10	0.842	0.069	0.773	8.93	1.79
	0.9364	10	0.957	0.160	0.797	20.1	1.84
	0.9364	10	1.106	0.277	0.829	33.4	1.91
	0.9364	10	1.325	0.451	0.874	51.6	2.02
	0.9364	10	1.512	0.643	0.869	74.0	2.01
	0.9364	40	1.046	0.066	0.980	6.73	2.26
	0.9364	40	1.162	0.126	1.036	12.2	2.39
	0.9364	40	1.472	0.336	1.136	29.6	2.62
	0.9364	40	1.696	0.531	1.165	45.6	2.69
	0.9364	40	1.922	0.734	1.188	61.8	2.74
2-Hydroxy-α^1,α^3-mesitylenediol	2.687	10	0.959	0.087	0.872	9.98	1.09
	2.687	10	1.067	0.119	0.948	12.6	1.19
	2.687	10	1.218	0.219	0.999	21.9	1.25
	2.687	10	1.379	0.374	1.005	37.2	1.26
	2.687	10	1.588	0.536	1.052	51.0	1.32
	2.687	10	1.803	0.707	1.096	64.5	1.37
	2.687	40	1.012	0.026	0.986	2.64	1.23
	2.687	40	1.162	0.080	1.082	7.39	1.36
	2.687	40	1.398	0.282	1.116	25.3	1.40
	2.687	40	1.595	0.449	1.146	39.2	1.44
	2.687	40	1.845	0.645	1.200	53.8	1.50

Table IV. Effect of Bromination Time on Extent of Bromination

Acidity, 0.75 *N*
Temperature, 25° C.

Phenol	Concentration of Phenol Solution	Bromination Time	Br Added	$Na_2S_2O_3$ Required	Net Br Absorbed	Residual Br Excess	No. of Reactive Positions Found
	G./l.	*Min.*	*Milliequivalents*	*Milliequivalent*	*Milliequivalents*	*% Br absorbed*	
p-Cresol	1.050	1	0.864	0.064	0.800	8.00	1.65
	1.050	1	0.948	0.098	0.850	11.5	1.75
	1.050	1	1.159	0.247	0.912	27.1	1.88
	1.050	1	1.479	0.525	0.954	55.0	1.96
	1.050	1	1.903	0.940	0.963	97.6	1.98
	1.050	10	1.096	0.125	0.971	12.9	2.00
	1.050	10	1.157	0.157	1.000	15.7	2.06
	1.050	10	1.247	0.204	1.043	19.6	2.15
	1.050	10	1.373	0.296	1.077	27.5	2.22
	1.050	10	1.903	0.811	1.092	74.3	2.25
2-Hydroxy-α^1,α^3-mesitylenediol	2.687	1	0.925	0.057	0.868	6.57	1.09
	2.687	1	1.032	0.109	0.923	11.8	1.16
	2.687	1	1.324	0.325	0.999	32.5	1.25
	2.687	1	1.563	0.526	1.037	50.7	1.30
	2.687	1	1.782	0.754	1.028	73.3	1.29
	2.687	10	1.016	0.033	0.983	3.36	1.23
	2.687	10	1.185	0.084	1.101	7.63	1.38
	2.687	10	1.378	0.268	1.110	24.1	1.39
	2.687	10	1.570	0.467	1.103	42.3	1.38
	2.687	10	1.816	0.673	1.143	58.9	1.43

alkyl groups ortho or para to the phenolic hydroxyl group. Another possible explanation is that methylene quinones are formed, thereby consuming additional bromine over that theoretically required for substitution in the free ortho or para positions. No direct evidence has yet been presented in support of either of these theories.

Alkylated Phenols and Their Hydroxymethyl Derivatives. An examination of Figure 3 reveals that only *p*-(1,1,3,3-tetramethylbutyl)-phenol, *p*-cyclohexylphenol, and 4-chloro-*m*-cresol show two reactive positions regardless of the size of the bromine excess. *p*-Cresol, *p*-ethylphenol, and *p*-isopropylphenol brominate abnormally; the larger the bromine excess, the greater is the number of reactive positions that are found.

Before attempting to explain or generalize these results, it seems desirable to point out that the importance of these data lies not so much in the absolute values as in the trends that are revealed. In other words, while it may be useful to know that 2.96 reactive positions are found for *o*-cresol when the residual bromine excess is 100%, it is more important to know that in the presence of excess bromine *o*-cresol readily absorbs more than 2 moles of bromine, the overbromination depending upon the magnitude of the bromine excess. Aside from the theoretical value, knowing whether a phenol tends to overbrominate is a prerequisite for the establishment of an accurate quantitative bromination method for the phenol. The results obtained for the phenols studied lead to the following generalizations, which extend and modify those proposed by Sprung. Phenols having primary or secondary alkyl groups ortho or para to the phenolic hydroxyl group tend to overbrominate in the presence of excess bromine, the extent of overbromination depending upon the magnitude of the bromine excess. Phenols having ortho, meta, or para tertiary alkyl groups brominate quantitatively, regardless of how large the bromine excess is.

p-Cyclohexylphenol is an exceptional case, for although it has a secondary alkyl group, it brominates quantitatively. The cyclohexyl group possibly introduces sufficient steric hindrance to prevent overbromination.

Figure 3 also shows that only with 2-hydroxy-5-(1,1,3,3-tetramethylbutyl)-α^1,α^3-xylenediol and 6-chloro-3-hydroxy-α^2,α^4-pseudocumenediol does quantitative displacement of both hydroxymethyl groups by bromine take place, and even with these dialcohols large bromine excesses are required for complete displacement. Only partial elimination of the hydroxymethyl groups occurs when 2-hydroxy-α^1,α^3-mesitylenediol, 5-ethyl-2-hydroxy-α^1,α^3-xylenediol, 2-hydroxy-5-isopropyl-α^1,α^3-xylenediol, and 5-cyclohexyl-2-hydroxy-α^1,α^3-xylenediol are brominated. The data concerning these dialcohols are not only of value in indicating the relative ease with which the hydroxymethyl groups are displaced, but they also demonstrate clearly that it cannot be assumed that bromination conditions under

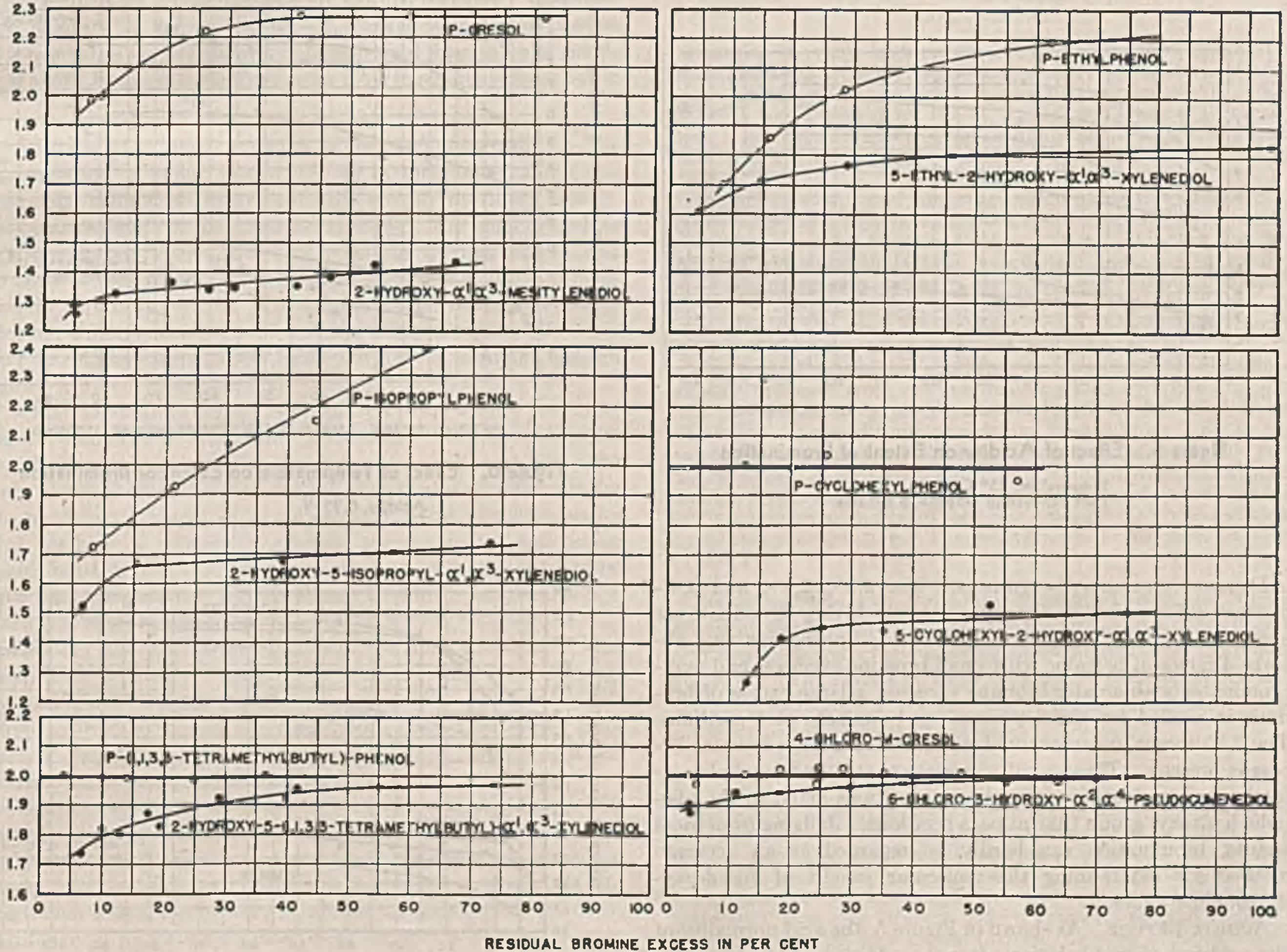

Figure 3. Bromination of Some Alkylated Phenols and Their Hydroxymethyl Derivatives

Acidity, 0.75 *N*
Temperature, 25° C.
Time exposed to bromine, 5 minutes

which an alkylated phenol brominates quantitatively will give quantitative bromination of the dialcohol of this phenol. It appears that para-alkylated phenol dialcohols whose alkyl groups are tertiary lose their 2 hydroxymethyl groups during bromination much more easily than do para-alkylated phenol dialcohols whose alkyl groups are primary or secondary.

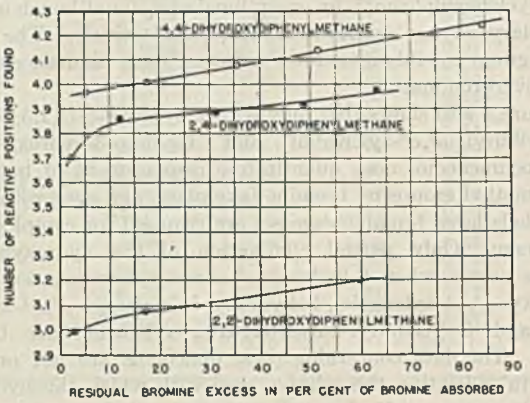

Figure 4. Bromination of 2,2'-, 2,4'-, and 4,4'-Dihydroxydiphenylmethane

Acidity, 0.75 *N*
Temperature, 25° C.
Time exposed to bromine, 5 minutes

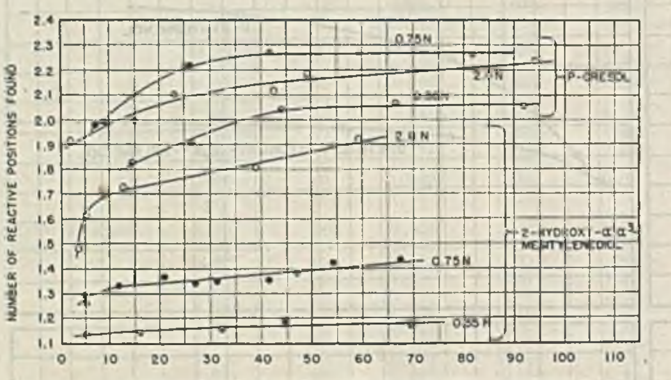

Figure 5. Effect of Acidity on Extent of Bromination

Temperature, 25° C.
Time exposed to bromine, 5 minutes

DIHYDROXYDIPHENYLMETHANES. The 2,2'-, 2,4'-, and 4,4'-isomers differ widely in the extent to which they brominate, as shown in Figure 4. While 4,4'-dihydroxydiphenylmethane absorbs 4 moles of bromine with small bromine excesses, and overbrominates with greater bromine excesses, a large excess of bromine is needed for the 2,4'-isomer to brominate at 4 positions. The 2,2'-isomer underbrominates even when a large bromine excess is present. These results indicate that dihydroxydiphenylmethanes brominate more readily at positions ortho to the phenolic hydroxyl group than at para positions. Judging from these results, bromination can hardly be regarded as an accurate method for determining the molecular weight of dihydroxydiphenylmethanes.

ACIDITY EFFECT. As shown in Figure 5, the acid normality of the acidified phenol solution after the addition of the bromide-bromate solution has an appreciable effect on the extent of bromination of *p*-cresol. Reducing the acidity from 0.75 *N* to 0.35 *N* decreases the amount of overbromination of *p*-cresol, but the differences which result from increasing the acidity from 0.75 *N* to 2.0 *N* may be due more likely to experimental error than to a significant trend.

The acidity has an even more pronounced effect on the displacement of the hydroxymethyl groups of 2-hydroxy-α^1,α^3-mesitylenediol by bromine. The higher the acid normality is, the greater is the displacement of hydroxymethyl groups.

TEMPERATURE EFFECT. Figure 6 shows that the extent to which *p*-cresol brominates depends greatly upon the temperature. At 10° no overbromination takes place even in the presence of a large excess of bromine. The displacement of the hydroxymethyl groups of 2-hydroxy-α^1,α^3-mesitylenediol is similarly retarded by low temperatures, although the magnitude of the temperature effect is not so great as it is in the case of *p*-cresol.

TIME EFFECT. A change in the bromination time from 1 minute to 5 minutes produces a significant increase in the number of reactive positions found for *p*-cresol and for 2-hydroxy-α^1,α^3-mesitylenediol, as may be seen from Figure 7. Increasing the bromination time beyond 5 minutes does not affect the results appreciably.

No universal bromination procedure can be recommended at this time which can be used with confidence for the quantitative bromination of phenols, phenol alcohols, dihydroxydiphenyl-

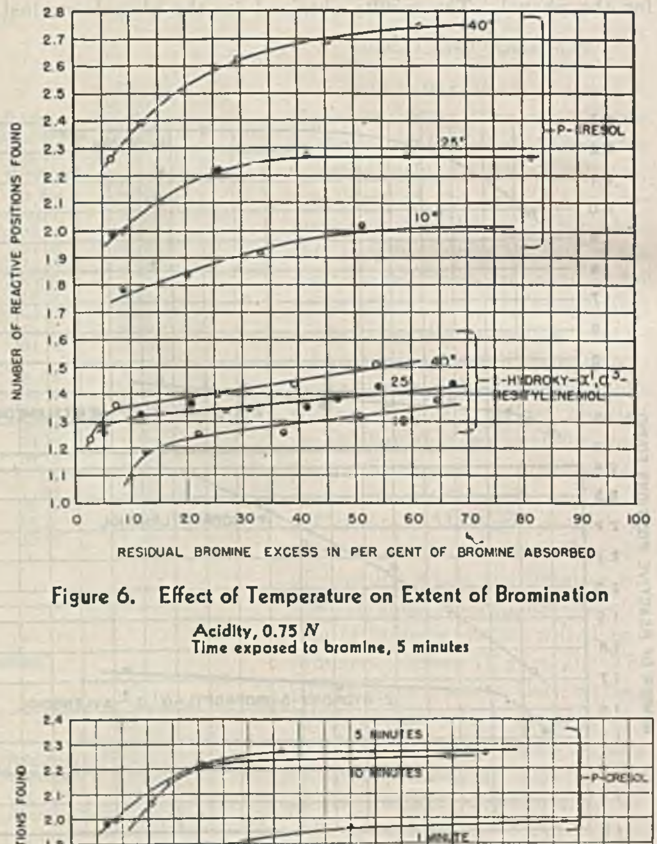

Figure 6. Effect of Temperature on Extent of Bromination

Acidity, 0.75 *N*
Time exposed to bromine, 5 minutes

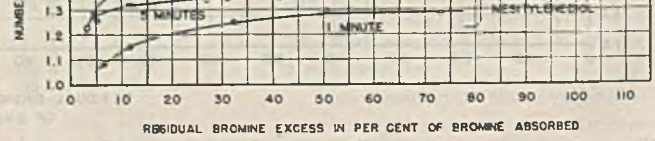

Figure 7. Effect of Bromination Time on Extent of Bromination

Acidity, 0.75 *N*
Temperature, 25° C

methanes, and higher polymers, much less mixtures of these compounds. However, knowing which compounds brominate normally, and which brominate abnormally, and how various bromination conditions affect the results, it should be possible to determine accurately a large number of compounds by modifying the procedure where necessary. Further research is needed before bromination can be used for the quantitative analysis of the complex mixtures which result from the reaction of phenols with formaldehyde.

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Determination of Calcium in Magnesite and Fused Magnesia

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A method for the determination of calcium oxide in materials containing a high magnesium oxide content is proposed, whereby a separation of the magnesium from the lime is first effected. This procedure is the reverse of the usual technique employed. Mannite is used to prevent precipitation of the calcium during precipitation of the magnesium as hydroxide. The method is direct, requiring fewer preliminary separations than the existing methods. Quantitative recovery of the lime is assured. Spectrographic examination of a number of the precipitates of lime showed them to be of analytical purity, free from contamination by other impurities in the samples.

EXTREMELY small amounts of calcium, especially in the presence of much magnesium, as in magnesites and fused magnesia, cannot be determined satisfactorily by direct precipitation as oxalate (*3*). In material of this type, the usual procedure is to precipitate the calcium first as sulfate, then as oxalate, and to treat the residual sulfates so that a saturated solution of magnesium sulfate is formed. To this are added mixtures of ethyl alcohol, methyl alcohol, and sulfuric acid, in which the magnesium sulfate is appreciably soluble, while the insoluble calcium sulfate is removed by filtration.

While the calcium sulfate is purported to be wholly insoluble, careful study shows that results obtained by these procedures are usually somewhat low. The precipitation as sulfate is successful only in the absence of alkali metals, the sulfates of which are for the most part difficultly soluble in alcohol. This, of course, makes this method of separation entirely unsuitable for substances which must be first attacked by an alkali fusion—e.g., some fused and high-temperature fired periclase in which recrystallization has occurred.

In other methods for the separation of small amounts of lime from large amounts of magnesium, such as may occur in magnesium alloys (*2*, *5*), a sugar solution is used to dissolve the calcium hydroxide, leaving the magnesium hydroxide almost completely precipitated in strong alkali solution, from which the calcium may be separated by filtration.

The alloys, however, are relatively free of the impurities usually found in appreciable amounts in magnesite.

During work in this laboratory involving many thousands of boron analyses, solutions containing a polyhydric alcohol, in this particular case mannite, were titrated to an approximate pH of 11. Although in many cases rather large quantities of calcium were present as the chloride, no calcium hydroxide was precipitated. If, however, these solutions contained magnesium chloride, an appreciable precipitate of magnesium hydroxide occurred, rendering the boron analyses useless and making removal of the magnesium ion obligatory.

These phenomena suggested a possible new means of separating calcium from appreciable magnesium, providing conditions could be found which would yield a quantitative separation of the calcium from either all or a major portion of the magnesium.

EXPERIMENTAL

Samples of very high-grade, specially prepared magnesium oxide obtained from the high-temperature calcination of magnesium hydroxide were used in the preliminary study. This material was supplied by the J. T. Baker Chemical Company. Both chemical and spectrographic analysis showed that various shipments of this material contained from 0.04 to 0.08% calcium oxide.

Two-gram samples of this magnesium oxide were dissolved in hydrochloric acid and various amounts of reagent grade mannite from the Hercules Powder Company were added to the acid solution contained in 500-ml. volumetric flasks. The solution was then made alkaline with carbonate-free sodium hydroxide, diluted to 500 ml., mixed, and allowed to stand overnight. Examination of the clear supernatant liquid showed that from 95 to 99% of the magnesium had been removed.

The next step consisted of adding various amounts of a chloride solution prepared from calcium oxide purified by triple precipitation as oxalate after preliminary separation of the interfering elements. The additions of calcium ranged from 2 to 20 mg., calculated as oxide per 100 ml. of solution contained in the volumetric flask. After treatment of this solution with mannite and sodium hydroxide, as described in the general procedure, the calcium was separated from the clear supernatant liquid as oxalate by double precipitation. The recoveries obtained were excellent (Table I).

Following these tests, the sample of calcined magnesite No. 104 issued by the National Bureau of Standards, and a series of magnesite samples from various sources were analyzed by the method described. The results in Table I indicate excellent recoveries of the lime with accuracy equal to, or better than, some of the present generally accepted methods.

GENERAL PROCEDURE

Weigh out 2-gram samples of the magnesite or fused magnesia into 100-cc. porcelain casseroles, add 35 to 40 cc. of 1 to 1 hydrochloric acid, and warm until solution is effected. In the event that the material is not entirely soluble in the dilute hydrochloric acid, place the 2-gram sample in a 20-cc. platinum crucible and intimately mix with it about 3 to 5 grams of sodium carbonate. Place the crucible in a muffle furnace, or over a Fisher burner, sinter for about 30 minutes at 900° to 1000° C., cool, and dissolve in the casserole with 50 to 60 cc. of 1 to 1 hydrochloric acid.

After solution has been brought about by either method, evaporate the solution to dryness on a steam bath and bake the residue in a drying oven for one hour at 120° C. Add 5 cc. of concentrated

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Table I. Gravimetric Determination of Calcium in the Presence of Large Amounts of Magnesium

Substance	CaO Present	CaO Found by Usual Alcohol Method	Error, CaO	CaO Found by Proposed Method	Error, CaO
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
MgO + CaO[a]	4.0	3.7	−0.3	3.9	−0.1
	8.0	7.8	−0.2	8.1	+0.1
	12.5	12.1	−0.4	12.4	−0.1
	16.0	15.6	−0.4	16.0	0.0
	20.0	19.8	−0.2	19.8	−0.2
	25.0	24.5	−0.5	25.0	0.0
	31.0	31.1	+0.1	31.1	+0.1
	36.0	35.5	−0.5	35.8	−0.2
	40.0	39.4	−0.6	40.1	+0.1
	40.0	39.5	−0.5	40.1	+0.1
India magnesite	8.5[b]	7.7	−0.8	8.9	+0.4
	9.1[b]	8.4	−0.7	9.2	+0.1
	9.7[b]	9.4	−0.3	10.0	+0.3
	9.9[b]	9.5	−0.4	9.9	0.0
Magnesite 104[c]	26.8	26.2	−0.6	27.4	+0.6
	26.8	26.6	−0.2	27.2	+0.4
	26.8	26.1	−0.7	27.4	+0.6
	26.8	26.1	−0.7	26.9	+0.1
	26.8	26.2	−0.6	27.3	+0.5
	26.8	26.4	−0.4	26.4	−0.4
	26.8	26.5	−0.3	26.2	−0.6
	26.8	26.0	−0.8	26.9	+0.1
	26.8	26.0	−0.8	27.0	+0.2
	26.8	26.1	−0.7	27.1	+0.3
Sea-water magnesite	18.0[b]	17.5	−0.5	17.9	−0.1

[a] Pure calcium oxide additions to magnesium oxide.
[b] Averaged values reported by chemical laboratory of Norton Co., Chippawa.
[c] U. S. National Bureau of Standards burned magnesite sample 104.

hydrochloric acid to the baked residue and then about 50 to 75 cc. of hot water, and digest until salts are in solution. Filter off the silica, washing the precipitate 4 to 5 times with hot 1 to 4 hydrochloric acid wash and finally with hot water. The silica content of the sample may be determined by the usual ignition and treatment of the precipitate with hydrofluoric acid, although very accurate determinations require two dehydrations. If the precipitated silica has been properly washed, no calcium will be found in the residue after hydrofluoric acid treatment.

To the cooled filtrate contained in a 500-cc. volumetric flask add 15 to 25 grams of mannite. When solution of the mannite has been effected, add 6 drops of phenolphthalein indicator and a solution of 9.0 *N* carbonate-free sodium hydroxide dropwise until the pink color of the indicator appears. The sodium hydroxide used must be carbonate-free because of the possibility of forming calcium carbonate, which is insoluble in the polyhydric alcohol solution and would lead to low lime results. Now add an excess of 5 cc. of the sodium hydroxide solution by dropwise additions while the solution in the flask is agitated to ensure prompt mixing of the two solutions. Cool the flasks to room temperature, dilute to 500 cc. with distilled water, shake the flask well, and allow to stand for 6 to 8 hours, or overnight. Pour the solution through a loose, dry, filter paper until a 200-cc. aliquot can be obtained. The aliquot may be removed by means of a pipet from the clear supernatant liquid in the flask, although in many cases this method is not satisfactory.

To the aliquots contained in 400-cc. beakers add 5 drops of methyl red indicator and acidify with hydrochloric acid, adding 5 cc. in excess. An addition of 5 grams of ammonium chloride at this point is desirable should, for some reason, an undue amount of magnesium remain in the solution. To the boiling solution add 0.5 gram of ammonium oxalate and, when dissolved, add ammonium hydroxide until the solution is neutral. Digest on a steam bath until the calcium oxalate precipitate is well formed. Remove, add 2 cc. of ammonium hydroxide dropwise, and allow precipitate to stand for 4 hours. Filter the solution through a No. 40 Whatman paper and wash with a cold 1% solution of ammonium oxalate.

Dissolve the washed precipitate through the paper with 50 cc. of hot 1 to 2 hydrochloric acid and reprecipitate, filter, and wash the calcium exactly as described for the initial precipitation. Convert the calcium oxalate to the oxide by ignition at 1100° to 1200° C. in tared platinum crucibles to constant weight, observing all of the usual precautions necessary for the weighing of this hygroscopic precipitate (*4*).

The 200-cc. aliquot taken for this analysis represents an 0.8-gram sample. The percentage of calcium oxide in the sample may be calculated as follows:

$$\frac{\text{Weight of precipitate} \times 100}{0.8} = \%\ \text{CaO}$$

The authors prefer weighing the lime as oxide as described, but there is no objection to using the volumetric oxalate-permanganate titration to obtain the lime values. The described procedure is less subject to errors than the volumetric method.

DISCUSSION OF RESULTS

In this investigation, samples of magnesium oxide with various additions of pure calcium oxide in amounts equivalent to samples containing from 0.5 to 5.0% were analyzed by the above procedure.

In addition, ten separate and individual analyses of the sample of calcined magnesite No. 104, issued by the Bureau of Standards, four samples of India magnesite, and one sample of magnesite from sea water were analyzed by the same method. These latter samples were then analyzed by precipitation of the calcium as sulfate and then as oxalate after solution of the sulfate by the mixed alcohols.

The results of these investigations, which are shown in Table I, indicate that the values obtained by this new procedure are accurate and reliable. In general, as expected, the results are slightly higher than those found by the so-called alcohol method, probably because of the slight solubility of the calcium sulfate in the alcohol mixture.

The number of milligrams of calcium oxide present in the Bureau of Standards burned magnesite sample 104 is taken from the averaged certificate value of 3.35% calcium oxide (*1*). Four of the eight cooperating analysts reported higher values for lime than the averaged value. If the value obtained by the Bureau of Standards analyst were substituted for the value shown in the table, the calcium oxide present would be 27.0 mg. instead of 26.8 mg. Substitution of this value would show greater deviations for the analyses obtained by the alcohol, while the results obtained by the procedure proposed herein would show better agreement in eight of the ten analyses. While there is no justification for assuming that this value is better than the average reported value, the results obtained by the proposed method are in very close agreement with those reported by excellent analysts using the existing procedures.

The aluminum oxide content of standard sample 104 is given in the certificate as 0.84%. One might expect the aluminum to be a possible source of error in this method. Because of the solubility of the aluminum hydroxide in the sodium hydroxide solution, it might later be expected to coprecipitate partially or completely with the calcium. No trouble from this source was encountered.

A number of the calcium oxide precipitates obtained by the use of the proposed method were examined spectrographically for purity. In these examinations the spectra obtained using a large Bausch & Lomb Littrow type prism spectrograph were inspected critically. Only the usual spectrographic traces of impurities which are always detectable in the most precise chemical separations were present. The precipitates of calcium oxide obtained were judged, therefore, to be free from any coprecipitated constituents of the sample.

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A DISSERTATION submitted in partial fulfillment of the requirements for the degree of master of science to the faculty of the Graduate School of Niagara University.

Effect of Uniform versus Intermittent Product Withdrawal from Distillation Columns

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It has long been tacitly assumed that the best way to operate high-efficiency distillation columns is with as nearly continuous a product-withdrawal rate as possible. The relative effectiveness of intermittent *vs.* continuous product withdrawal for the separation of α- and β-pinene was tested with a heligrid-packed, a helices-packed, and a gauze-plate column. Especially with the heligrid-packed column distinctly better separation was obtained by product withdrawal once every hour than once every 30 seconds.

FRACTIONAL distillation is one of the most important laboratory tools in the field of hydrocarbon research. It would be impossible to enumerate here all the publications dealing with laboratory and commercial fractionating columns. Special mention should be made, however, of the excellent review of the literature on the construction, testing, and operation of laboratory fractionating columns made by Ward (*9*) and of two more recent papers on distillation practices and methods by Othmer (*4*) and Podbielniak (*8*). Despite these numerous publications and the real progress made, usually empirically, in the development of efficient laboratory fractionating columns, relatively little has been published on the practical operation of such columns. There remains to be established a scientific basis for certain operational techniques now in common use, such as the preflooding technique, which have been developed through practical experience. That many differences of opinion exist concerning the preferred mode of operation, even for major elements, is revealed by the following excerpts from Ward's review (*9*):

> The usual distillation practice is to keep the distillation rate constant. . . .Some operators, however, increase the rate when collecting a pure component and decrease the rate between components. . .Most investigators use the term "reflux ratio" to designate the quantity of reflux per unit weight of product. . . McMillan's results show higher efficiency with medium rather than high or low reflux ratio. Calingaert and Huggins, with a coke-packed column, found the efficiency was proportional to the reflux ratio at constant vapor velocity. . .The usual practice is to maintain a constant reflux ratio; however, some investigators decrease the reflux while collecting pure compounds and increase it at the critical points between compounds. . . Judging from their results, Hill and Ferris concluded the peak efficiency of a packed column was at a rate just below flooding. Podbielniak found maximum efficiency when the packing is barely wet. This is verified by Bruun and Schicktanz, whose results show efficiency decreased materially near the flooding point.

Podbielniak (*8*) pointed out the possibility that intermittent product withdrawal might be superior to uniform product withdrawal:

> The measurement and control of reflux ratio for high efficiency columns are most important in obtaining best possible separation with a column in a given time of distillation. . . It has long been tacitly assumed that the best way to operate any column is with as nearly continuous a product-withdrawal rate as possible. . .However, in operating the high-efficiency column and packing here described, on close-boiling binary test mixtures at high reflux ratios, very much better separations have been obtained by holding the column at total reflux for periods of 30 minutes or more, and then withdrawing a quota of product almost instantaneously, again holding the column at total reflux, and so on, than by withdrawing the product continuously at the same average rate as in the intermittent operation. . .This unexpected advantage of intermittent product withdrawal, so outstanding as to merit the nickname "the free-wheeling effect" in the author's laboratory, still is without theoretical explanation.

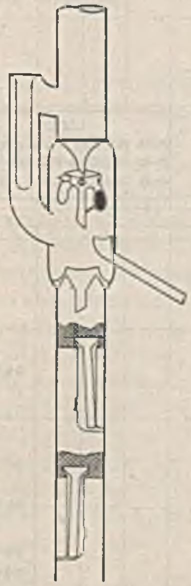

Figure 1. Reflux Controller and Top of Gauze Plate Column

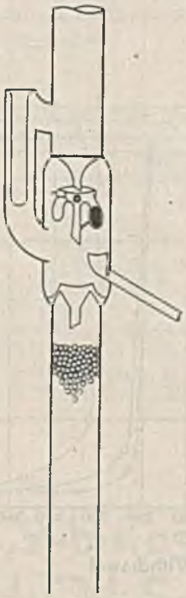

Figure 2. Reflux Controller and Top of Helices-Packed Column

In the laboratory of the Naval Stores Research Division complex mixtures of terpene hydrocarbons are often carefully fractionated into individual pure components. For this purpose, three different types of columns are available: a vacuum-jacketed Podbielniak type, 1 inch (2.5 cm.) in diameter, containing 4 feet of packing; an insulated, heat-compensated column, 1 inch in diameter, packed with $^3/_{16}$ inch Fenske-type glass helices for 7 feet; and a Palkin type (*5*), containing 45 individual gauze plates 1 inch in diameter, approximately 2 inches apart. Distillations are generally carried out at reduced pressure (usually at 20.0 mm. of mercury) to minimize thermal isomerization and at high reflux ratio to ensure maximum purity of product. Mixtures rich in α-pinene (boiling point at 20 mm. = 52.2° C.) and β-pinene (boiling point at 20 mm. = 59.7° C.) are frequently distilled. It was thought worth while, therefore, to investigate the utility of the "free-wheeling effect" in these distillations, especially since mixtures of pure α- and β-pinene can be analyzed conveniently and accurately simply by measurement of the optical rotation, Biot's relationship holding closely for these terpenes (*3*). Accordingly, two series of distillations were planned to test this free-wheeling effect.

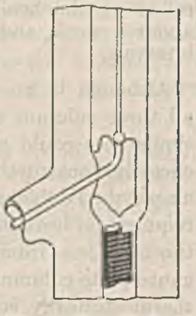

Figure 3. Reflux Controller and Top of Heligrid Column

EXPERIMENTAL PROCEDURE

In the first series of distillations each of the three columns was operated so that the product withdrawal, or take-off, was "uniform"; in the second series, so that the withdrawal was "intermittent". It was planned that in so far as possible the operation of all the columns in a series would be alike, thus permitting evaluation of the response of the various columns both with respect to each other and with respect to the manner of product withdrawal.

All three columns were operated simultaneously from a single control panel and "column line" manifold maintained at 20.0

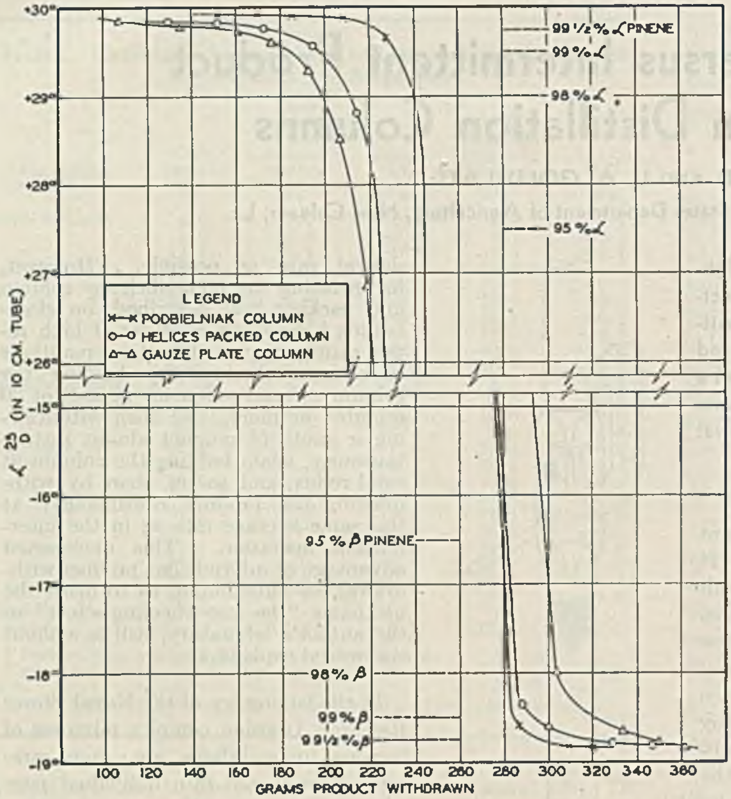

Figure 4. Uniform Product Withdrawal

mm. of mercury pressure by means of a modified Palkin-type dual pressure control assembly system (*6*). Throughput was maintained at 300 cc. per hour (at the head) by heating the still pots electrically. Current was supplied to Variacs through constant-voltage transformers and the Variacs were adjusted manually from time to time to maintain the desired throughput. Active ebullition was maintained by means of an electrically heated boiling promoter (*7*). Product take-off was maintained at 3 cc. per hour by suitable electrically operated timing devices. Each still pot was charged with 500 grams of a stock mixture of 50% α-pinene and 50% β-pinene (by weight), and distillation was continued without interruption until the β-pinene plateau had been reached or until reflux at the head ceased. Each distillation lasted about a week, and fractions were cut at 6- or 8-hour intervals.

Although it was desired to condition and operate all three columns as similarly as possible, certain dissimilarities could not be avoided, owing to the differences in construction of the three columns. For example, the Podbielniak column, being vacuum-jacketed, required no heat compensation for the jacket, whereas the heat loss from both the helices-packed and the gauze-plate columns was partially compensated by four thermostatically controlled, electrically heated resistance units in each column. In order to minimize possible differences arising from different manipulation of the thermostats, they were preset, so that each column would be losing a slight amount of heat at the boiling point of α-pinene and were left unchanged throughout the distillations. To obviate the possibility of differences in efficiency arising from any difference in degree of thoroughness of preflooding none of the columns was flooded.

Each column was allowed to reflux for approximately 5 hours before product withdrawal was begun. In the case of the helices-packed column and the gauze-plate column, each fitted with a modified head of the type described by Carter and Johnson (*2*) (Figures 1 and 2), "uniform" withdrawal was arranged for by use of an electric time switch operating on a 30-second cycle and set at 1%. In the case of the Podbielniak column (Figure 3) since the smallest portion of product that could be withdrawn reliably was about 0.2 cc., the "uniform" withdrawal was arranged for by use of an electric time switch operating on a 5-minute cycle and set at 0.13%. This gave a take-off of 3.0 cc. per hour when the reflux was 300 cc. per hour. In the case of the "intermittent" withdrawal, all the columns had a product withdrawal period of 36 seconds followed by a shut-in period of 59 minutes and 24 seconds. This could be arranged for by use of a time switch operating on a 1-hour cycle and set at 1%. The optical rotation of each fraction (about 20 cc.) was measured and then plotted against grams of product withdrawal from each column.

RESULTS AND DISCUSSION

Figure 4 shows such plots for some of the intermediate fractions obtained by uniform product withdrawal for all three columns operated simultaneously. Figure 5 illustrates similar plots obtained using intermittent product withdrawal. These plots permit a direct comparison of the effectiveness of all three columns, as well as an evaluation of the effect of uniform versus intermittent product withdrawal. [The performance of a column measured in theoretical plates at atmospheric pressure cannot be interpreted as the plateage of that column operating under vacuum. Thus Byron, Bowman, and Coull (*1*) point out that "a 50-plate column (at atmospheric pressure) would realize only half a plate at 7.6 mm. of mercury".] The fractions with the highest rotation, for both α- and β-pinene, were obtained from the Podbielniak column. Table I shows for all six distillations the size in grams of the intermediate portions between α- and β-pinene at various levels of purity—i.e., 95, 98, 99, and 99.5%. Also shown in this table is the difference in the

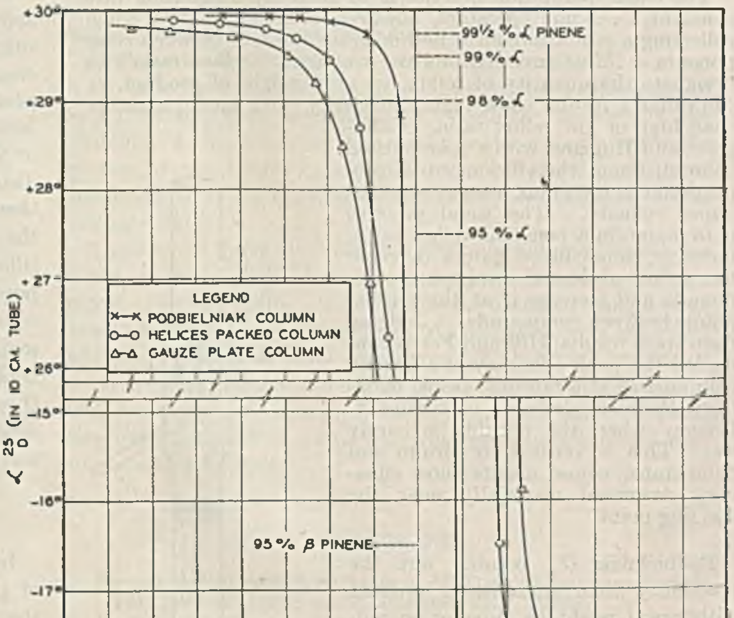

Figure 5. Intermittent Product Withdrawal

Table I. Comparison of Uniform and Intermittent Product Withdrawal

	Grams of Product between α- and β-Pinene of Indicated Purity			
	99.5%	99%	98%	95%
Podbielniak column				
Uniform	72	55	43	35
Intermittent	52	37	27	23
Decrease	20	18	16	12
Helices-packed column				
Uniform	138	97	74	58
Intermittent	121	95	73	56
Decrease	17	2	1	2
Gauze-plate column				
Uniform	184	138	105	87
Intermittent	171	130	103	72
Decrease	13	8	2	15

quantity of material of intermediate purity obtained when operating under uniform as against intermittent withdrawal. Of the three columns tested the Podbielniak column, when operated under the conditions of this test, made the best showing; the gauze-plate column, the poorest. Furthermore, for the Podbielniak column, when intermittent rather than uniform product withdrawal was used, the improvement was very marked and consistent, showing a decrease in size of intermediate fractions of approximate 35% at all levels of purity. Although some improvement was also apparent in the operation of the other two columns, this improvement in several cases was within the limits of possible experimental error.

It may, therefore, be concluded that when operating high-efficiency columns at high reflux ratios it is not necessary to use as nearly continuous product withdrawal as possible. In fact, when a reflux ratio of 100 to 1 is used, better separations are obtained by product withdrawal once every hour than once every 30 seconds.

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Determination of 1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane in DDT Dusts and Oil Solutions

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A method is described for the determination of 1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT) in commercial dusts and oil solutions. The method is based upon the dehydrochlorination of the sample at 25.0° ± 0.1° C. in 95% ethyl alcohol solution for dust mixtures, and in kerosene solution for oil solutions, for 15 minutes, using 20 ml. of *N* ethanolic sodium hydroxide. Comparative results are given for the crystallization method and the method described. Possible sources of error are discussed.

THE insecticidal value of an economic poison containing DDT is believed primarily due to its content of the para-para' isomer, 1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT); and in enforcement of the Agricultural Code of the State of California pertaining to labeling and sale of agricultural chemicals, it is necessary to determine the percentage of this compound in commercial dusts and sprays. Several useful methods have been developed (*6, 7, 8, 13, 15*) for determining or detecting total DDT, but they are not applicable to the quantitative estimation of the individual principal isomers occurring in commercial DDT. The crystallization method of Cristol, Hayes, and Haller (*5*) has proved most valuable for the determination of *p,p'*-DDT in the technical product and straight DDT dust formulations, but it is not applicable to oil solutions, such as fly sprays, or dusts containing pyrethrum powder or concentrates and is time-consuming when applied to low percentage dust mixtures. The complex mixtures making up modern commercial insecticides cause serious interference in most colorimetric methods (*1, 3, 10*).

Cristol (*4*) has suggested that the difference in reaction rates of *p,p'*-DDT and *o,p'*-DDT to dehydrochlorination might be used for determination of the para-para' isomer in technical DDT. This reaction was investigated by the author, and procedures were developed applicable to most commercial DDT dusts and sprays. [Since the submission of this paper an article on the determination of *p,p'*-DDT in technical DDT has been published (*12*).]

EXPERIMENTAL

A number of commercially available technical and purified grade DDT samples of known *p,p'*-DDT content, as determined by the Cristol, Hayes, and Haller crystallization method (*4*), were dehydrochlorinated under strict conditions of temperature and concentration.

A 1.000-gram sample was dissolved in 75.0 ml. of 95% ethyl alcohol, and reacted 15 minutes with 20.00 ml. of *N* ethanolic sodium hydroxide at 25.0° ± 0.1° C. A graph of the per cent chloride ion formed, as ordinate, and per cent *p,p'*-DDT of the samples as abscissa, gave a straight line, which could be expressed by the formula:

$$(\%\ \text{chloride} \times 11) - 9.30 = \%\ p,p'\text{-DDT}$$

A 0.500-gram sample was dissolved in kerosene, made up to 100.0 ml. with kerosene, and reacted 15 minutes with 20.00 ml. of *N* ethanolic sodium hydroxide at 25.0° ± 0.1° C., while being stirred at 700 to 800 r.p.m. A graph of the per cent chloride ion formed and per cent *p,p'*-DDT of the samples gave a straight line, expressible by the formula:

$$(\%\ \text{chloride} \times 23) - 16.90\% = \%\ p,p'\text{-DDT}$$

REAGENTS AND APPARATUS

Ethyl alcohol, commercial 190-proof, 95% by volume.

Ethanolic sodium hydroxide, 1.000 *N*. Dissolve 41 to 42 grams of C.P. sodium hydroxide pellets in about 350 ml. of ethyl alcohol with the aid of heat, cool, and filter into a 1-liter volumetric flask. Add alcohol almost to mark, and mix. Standardize against 0.5 or 0.2 *N* hydrochloric acid, using methyl orange indicator.

Ethanolic potassium or sodium hydroxide, approximately 1 *N*. Dissolve 56 grams of C.P. potassium hydroxide or 40 grams of C.P. sodium hydroxide in about 250 ml. of ethyl alcohol, filter, and make to 1 liter with ethyl alcohol.

Nitric acid, 1 to 1, 1 volume of C.P. concentrated nitric acid plus 1 volume of distilled water.

Nitric acid, 1 to 3, 1 volume of C.P. concentrated nitric acid plus 3 volumes of distilled water.

Silver nitrate 0.1 *N*, 16.989 grams of silver nitrate per liter of solution. Standardize by precipitating and weighing as silver chloride.

Ammonium thiocyanate, 0.1 *N*, 7.611 grams of ammonium thiocyanate per liter solution. Standardize against the 0.1 *N* silver nitrate.

Ferric alum indicator, 10%, 10 grams of C.P. ferric ammonium sulfate dissolved in a minimum of distilled water. Filter, decolorize with concentrated nitric acid, and dilute to 100 ml.

Nitrobenzene, purified grade mononitrobenzene.

Acetone, C.P. reagent grade.

Kerosene, a good quality water-white kerosene or deodorized kerosene.

Constant-temperature bath, capable of maintaining a temperature of 25.0 ± 0.1° C., and large enough to hold two 250-ml. flasks.

Electric stirrer, fitted with a 18- to 20-mm., two-blade glass stirrer, speed adjustable to 700 to 800 r.p.m.

Interval timer, "minute minder", or clock with sweep-second hand.

Parr bomb.

PROCEDURE FOR DRY MATERIALS

TECHNICAL AND PURIFIED DDT (96 to 100% from total chlorine). A 1.000-gram sample of the material is placed in a 250-ml. Ŧ Erlenmeyer flask, 75.0 ml. of 95% ethyl alcohol are added, and the flask is heated under reflux until the sample is dissolved. The solution is cooled and maintained at 25.0° ± 0.1° C. in a thermostatically controlled bath, 20.00 ml. of 1.000 *N* ethanolic sodium hydroxide, also maintained at 25.0° ± 0.1° C., are added, and the contents are mixed by rotating. The flask is rotated about every 5 minutes. At the end of 15 minutes the reaction is quickly stopped by the addition of 15 ml. of nitric acid, 1 to 3. The flask is removed from the bath, and 30.00 ml. of 0.1 *N* silver nitrate, 3 ml. of 10% ferric alum indicator, and 5 ml. of nitrobenzene are added. The flask is stoppered and shaken a few seconds to coagulate the precipitate and coat the particles of silver chloride (*2*). The stopper is washed down and the excess silver nitrate is titrated with 0.1 *N* ammonium thiocyanate. The per cent chloride ion formed is calculated:

$$\text{Ml. of } 0.1\ N\ \text{AgNO}_3 \times 0.3546 = \%\ \text{chloride}$$

The per cent of *p,p'*-DDT is calculated from the per cent chloride:

$$(\%\ \text{chloride} \times 11) - 9.30 = \%\ p,p'\text{-DDT in sample}$$

DDT DUST MIXTURES NOT CONTAINING SULFUR OR ORGANIC THIOCYANATES. *Total DDT*. Dust mixtures containing unknown amounts of DDT must first be analyzed for percentage of total DDT.

Samples containing 5 to 80% of total DDT can be ignited in a Parr peroxide bomb, or refluxed with metallic sodium and isopropyl alcohol (*14*) and total DDT calculated from total chlorine:

$$\frac{\text{Ml. of } 0.1\ N\ \text{AgNO}_3 \times 0.7092}{\text{sample weight}} = \%\ \text{total DDT}$$

Samples containing 1 to 5% of DDT are most conveniently analyzed by the Gunther method (*7*), using 5 to 10 grams of sample which is refluxed 15 minutes with 30 ml. of *N* ethanolic potassium or sodium hydroxide. The flask is cooled and the solution acidified with dilute nitric acid. An excess of 0.1 *N* silver nitrate, 3 ml. of ferric alum solution, and 5 ml. of nitrobenzene are added and the flask is shaken to coagulate and cover the silver chloride particles. The excess 0.1 *N* silver nitrate is titrated with 0.1 *N* ammonium thiocyanate:

$$\frac{\text{Ml. of } 0.1\ N\ \text{AgNO}_3 \times 3.546}{\text{sample weight}} = \%\ \text{total DDT}$$

p,p'-DDT. The per cent total DDT divided into 100 yields the sample weight in grams equivalent to 1.000 gram of total DDT. This sample weight is run through the same procedure used for technical and purified DDT. Dusts of high DDT content can usually be titrated for the chloride produced by the dehydrochlorination reaction without first filtering.

Add 30.00 ml. of 0.1 *N* silver nitrate, 3 ml. of ferric alum indicator, and 5 ml. of nitrobenzene, shake, and titrate with 0.1 *N* ammonium thiocyanate. Calculate the per cent chloride formed and from this the percentage of *p,p'*-DDT.

Example. If total DDT is 5.68%, then 100/5.68 = 17.606 grams equivalent to 1.000 gram of total DDT subject to dehydrochlorination.

30.00 ml. of 0.1 *N* AgNO_3 − 9.60 ml. of 0.1 *N* NH_4SCN = 20.40 ml. of 0.1 *N* AgNO_3 used.

20.40 × 0.3546 = 7.23% chloride ion formed during dehydrochlorination.

(7.23 × 11) − 9.30 = 70.23% of the total DDT is *p,p'*-DDT.

5.68% total DDT in sample multiplied by 0.7023 = 3.99% *p,p'*-DDT in sample.

The inert fillers usually do not obscure the end point. Dusts of low DDT content containing a large amount of insoluble filler must usually be filtered following the dehydrochlorination reaction, carefully washing all soluble chloride from the filler. Suction should not be used because of the possibility of losing chloride from the acid solution.

DDT DUST MIXTURES CONTAINING SULFUR. *Total DDT*. Samples containing 10% or more total DDT are first analyzed for total DDT by using a Parr bomb. Low percentage DDT-sulfur mixtures containing 1 to 10% DDT and 50 to 90% sulfur can be analyzed by the Gunther method (*7*) if modified as follows:

A sample weight large enough to give an accurate titration—i.e., 5 grams of a dust containing 5% total DDT—is refluxed 10 minutes with 25 to 40 ml. of acetone. The flask is cooled in an ice bath or refrigerator for about an hour to reduce the solubility of sulfur in acetone. The sulfur is filtered off, using a small Büchner funnel and suction, and washed twice with cold acetone. The acetone in the filtrate, containing the DDT, is boiled off on a steam bath with the aid of a stream of air, being heated only long enough to remove the acetone. The DDT residue is refluxed with 30 ml. of *N* ethanolic potassium or sodium hydroxide for 15 minutes and cooled. A measured excess of 0.1 *N* silver nitrate, 50 ml. of distilled water, and a few Carborundum chips are added to the flask, and the flask is boiled gently on a hot plate until most of the alcohol is boiled off. The flask is cooled slightly, 20 ml. of 1 to 1 nitric acid are added, and the solution is boiled until all silver sulfide is decomposed. Care must be taken to prevent loss through bumping. The flask is cooled, 3 ml. of ferric alum solution and 5 ml. of nitrobenzene are added, the flask is stoppered and shaken, and the excess silver nitrate is titrated. The per cent total DDT is calculated using the factor 3.546.

p,p'-DDT. A sample weight equivalent to 1.000 gram of total DDT, calculated from the total DDT percentage, is refluxed with 40 ml. of acetone for 10 minutes, then cooled in an ice bath or refrigerator. The sulfur is filtered off by suction, and the filtrate is caught in a 250-ml. Ŧ Erlenmeyer flask. The filter is washed twice with cold acetone. The acetone is boiled off on a steam bath using an air stream (avoid heating after the removal of acetone). The DDT residue is then refluxed with 75.0 ml. of 95% ethyl alcohol, cooled, and dehydrochlorinated at 25.0° ± 0.1° C. for 15 minutes with 20.00 ml. of 1.000 *N* ethanolic sodium hydroxide. The reaction is stopped by adding 15 ml. of 1 to 3 nitric acid. The flask is removed from the bath, 30.00 ml. of 0.1 *N* silver nitrate, 50 ml. of distilled water, and Carborundum chips are added to the flask, and the flask is heated on a hot plate until most of the alcohol has boiled off. Then 20 ml. of 1 to 1 nitric acid are added and the solution is boiled until all silver sulfide is decomposed. The flask is cooled, and after addition of ferric alum solution, and nitrobenzene and shaking, the excess 0.1 *N* silver nitrate is titrated. The percentage chloride and *p,p'*-DDT are calculated as in DDT dust mixtures not containing sulfur.

DDT DUST MIXTURES CONTAINING ORGANIC THIOCYANATES. *Total DDT*. Total DDT in the sample can be determined from total chloride by using a Parr bomb. The Gunther method (*7*) can be used on low percentage DDT samples if modified. Alkali hydroxides react with organic thiocyanates to form cyanides and cyanates (*9*), which react with silver nitrate, causing high results.

The sample is refluxed with ethanolic potassium or sodium hydroxide, cooled, and filtered into a separatory funnel; the filter is washed thoroughly. The filtrate is acidified slightly with dilute nitric acid and extracted twice with 25-ml. portions of petroleum ether to remove the dichloroethylene derivative of DDT. The subsequent boiling with nitric acid would yield chloride if the DDT olefin was not removed. The lower aqueous layer is drained into a 400- or 600-ml. beaker. The petroleum ether layers are washed twice with water, and the washings are added to the beaker. A measured excess of 0.1 *N* silver nitrate is added to the beaker, followed by 25 ml. of concentrated nitric acid and a few boiling chips. The beaker is covered with a watch glass, boiled down on a hot plate almost to dryness, and cooled slightly, 10 ml. more of nitric acid are added, and the contents are again boiled down almost to dryness. Silver cyanate and cyanide are decomposed by boiling nitric acid (*11*). The beaker is cooled and the contents are washed into a 250-ml. ₸ Erlenmeyer flask. After the addition of ferric alum and nitrobenzene and shaking, the excess 0.1 *N* silver nitrate is titrated and the per cent total DDT calculated as described for mixtures not containing sulfur.

p,p'-DDT. Using a sample weight equivalent to 1.000 gram of total DDT, the sample is dehydrochlorinated with 20.00 ml. of 1.000 *N* ethanolic sodium hydroxide for 15 minutes at 25.0° ± 0.1° C., stopping the reaction with 15 ml. of 1 to 3 nitric acid. The contents of the reaction flask are filtered through a coarse paper into a separatory funnel. The use of suction is to be avoided because of possible chloride loss. The filter is washed with water sufficiently to remove soluble chloride. The combined filtrate and washings are extracted twice with petroleum ether to remove DDT olefin, and the lower layer is drained into a 600-ml. beaker. The petroleum ether layers are washed twice with water and the washings are added to the beaker. Then 30.00 ml. of 0.1 *N* silver nitrate, 25 ml. of concentrated nitric acid, and a few boiling chips are added. The beaker is covered with a watch glass and the solution boiled down almost to dryness on a hot plate. The beaker is cooled slightly, 10 ml. of nitric acid are added, and it is again boiled down. The beaker is cooled and the contents are washed into a ₸ Erlenmeyer flask. Ferric alum and nitrobenzene are added, the flask is shaken, and the excess silver nitrate titrated. The per cent *p,p'*-DDT is calculated.

PROCEDURE FOR OIL SOLUTIONS

Total DDT. The Gunther method (*7*) is the most convenient method for determining the percentage of total DDT in oil solutions.

A sample of the DDT oil solution, weighing 5 to 20 grams, is refluxed with 30 ml. of approximately *N* ethanolic potassium or sodium hydroxide for 15 minutes. The flask is cooled and acidified slightly with dilute nitric acid, and the contents are washed into a separatory funnel. The lower layer is drained into a 250-ml. ₸ Erlenmeyer flask, and the upper layer is washed twice with water, the washings being added to the flask. A measured amount of 0.1 *N* silver nitrate, known to be an excess, is added to the flask along with 3 ml. of ferric alum solution and 5 ml. of nitrobenzene. The flask is stoppered and shaken, and the excess 0.1 *N* silver nitrate titrated with 0.1 *N* ammonium thiocyanate. Total DDT is calculated using the factor 3.546, as for DDT dust mixtures.

When organic thiocyanates are present, the method must be modified as follows:

The weighed sample is refluxed as described above, cooled, and transferred to a separatory funnel. It is then acidified with dilute nitric acid, and extracted twice with 25-ml. portions of petroleum ether to remove the dichloroethylene derivative of DDT. The lower layer is drained into a 600-ml. beaker. The oil layer is washed twice with water and the washings are added to the beaker. A measured excess of 0.1 *N* silver nitrate, 25 ml. of concentrated nitric acid, and a few boiling chips are added to the beaker. The beaker is covered with a watch glass, and boiled down almost to dryness on a hot plate. The beaker is cooled, and 10 ml. more nitric acid are added and the contents boiled down again. After cooling, the contents are washed into a 250-ml. ₸ Erlenmeyer flask. On adding ferric alum and nitrobenzene and shaking, the excess silver nitrate is titrated with 0.1 *N* ammonium thiocyanate. Total DDT is calculated using the factor 3.546.

p,p'-DDT. A sample weight equivalent to 0.500 gram of total DDT, calculated from the per cent total DDT, is weighed into a 250-ml. Erlenmeyer flask. The volume of this weight of sample is calculated by dividing the sample by the density. This volume is subtracted from 100, giving the number of milliliters of kerosene to be added to the flask to make a total solution volume of 100.0 ml. The flask is placed in a thermostatically controlled bath and maintained at 25.0° ± 0.1° C. An 18- or 20-mm. glass, two-blade stirrer, is placed in the flask, so that the blades are just off the bottom of the flask. While the oil solution is stirred at 700 to 800 r.p.m., 20.00 ml. of 1.000 *N* ethanolic sodium hydroxide, also maintained at 25.0° ± 0.1° C., are added and the reaction is allowed to continue 15 minutes. The reaction is stopped by the addition of 15 ml. of 1 to 3 nitric acid. The stirrer is stopped and the contents of the flask are washed into a separatory funnel. The lower layer is drawn off into a 250 ml. ₸ Erlenmeyer flask. The oil layer is washed twice with water and the washings are added to the flask. The per cent chloride formed is determined by adding 10.00 ml. of 0.1 *N* silver nitrate, 3 ml. of ferric alum solution, and 5 ml. of nitrobenzene, shaking, and titrating the excess silver nitrate with 0.1 *N* ammonium thiocyanate:

$$\frac{\text{Ml. of 0.1 } N \text{ AgNO}_3 \times 0.3546}{0.5} = \%\text{ chloride}$$

$$(\%\text{ chloride} \times 23) - 16.90 = \%\ p,p'\text{-DDT in total DDT}$$

$$\frac{\%\text{ total DDT} \times \%\ p,p'\text{-DDT}}{100} = \%\ p,p'\text{-DDT in sample}$$

If organic thiocyanates are present, the above procedure is modified.

The sample and kerosene are dehydrochlorinated as described above, 20.00 ml. of 1.000 *N* ethanolic sodium hydroxide are added while stirring at 700 to 800 r.p.m., the reaction is allowed to proceed 15 minutes and then stopped by adding 15 ml. of 1 + 3 nitric acid. The reaction mixture is washed into a separatory funnel, and extracted twice with 25-ml. portions of petroleum ether. The lower layer is drained into a 600-ml. beaker. The oil layers are washed twice with water and the washings are added to the beaker. Then 10.00 ml. of 0.1 *N* silver nitrate, 25 ml. of concentrated nitric acid, and a few boiling chips are added to the beaker. The beaker is covered with a watch glass and the solution boiled down almost to dryness on a hot plate. The beaker is cooled, 10 ml. more of concentrated nitric acid are added and the solution is again boiled down. When cool, the contents are washed into a 250-ml. ₸ Erlenmeyer flask. Ferric alum solution and nitrobenzene are added, the flask is shaken, and the excess 0.1 *N* silver nitrate is titrated with 0.1 *N* ammonium thiocyanate. The per cent chloride formed, and per cent *p,p'*-DDT are calculated as described for regular oil solutions of DDT.

DISCUSSION

Preliminary tests indicated that a sample weight of 1.000 gram of total DDT was about optimum for dry materials. Larger sample weights gave only slightly more chloride ion on dehydrochlorination, which was offset by an increase in interfering substances.

Tests were run to determine the effect of agitation during dehydrochlorination of DDT dust samples. Identical results were obtained when the reaction mixture was stirred continually at 700 r.p.m., or just mixed by rotating the flask three times during the 15-minute period.

Most DDT oil sprays contain at least 1% total DDT by weight. In order to keep the solution volume to a minimum, a sample weight equivalent to 0.500 gram of DDT was used. The addition of alcohol to the oil solution was found inadvisable because the alcohol dilutes the ethanolic sodium hydroxide, producing less chloride ion during dehydrochlorination.

Attempts to use 1.000 *N* butanolic sodium hydroxide in place of ethanolic sodium hydroxide for the dehydrochlorination of DDT in oil solutions were unsuccessful.

The Gunther method (*7*) gives slightly higher results for total DDT than total DDT calculated from total chlorine. Tests indicated that the percentage of *p,p'*-DDT, in samples containing 5% or less of DDT was closer to theoretical when total DDT was determined by the Gunther method (*7*) than when total DDT was calculated from total chlorine.

An accuracy of 2% *p,p'*-DDT can be expected for most dry DDT mixtures, and 4% *p,p'*-DDT oil sprays. Pyrethrins can

Table I. Determination of p,p'-DDT in Dust Mixtures of Known Composition

Sample No.	Composition	% p,p'-DDT In Sample	% p,p'-DDT Found	% Recovery
1	20% DDT (total) 80% talc	15.41	15.40 15.36 Av. 15.38	99.81
2	10% DDT (total) 90% talc	7.88	7.85 7.82 Av. 7.84	99.49
3	5% DDT (total) 50% sulfur 45% talc	3.85	3.91 3.90 Av. 3.91	101.56
4	5% DDT (total) 50% sulfur 45% talc	3.94	4.05 4.03 Av. 4.04	102.54
5	10% DDT (total) 85.25% talc 4.75% Lethane 60[a]	7.34	7.32 7.26 Av. 7.29	99.32
6	10% DDT (total) 88.8 % talc 0.2 % pyrethrins 1.0 % oil	7.63	7.22 7.21 Av. 7.22	94.63
7	10% DDT (total) 89.4 % talc 0.1 % pyrethrins 0.5 % oil	7.88	7.52 7.54 Av. 7.53	99.56

[a] Contains β-thiocyanoethyl esters of aliphatic fatty acids averaging 10 to 18 carbon atoms.

Table II. Comparative Analyses of Commercial DDT Samples

Sample No.	Per Cent p,p'-DDT Found: Crystallization method	Per Cent p,p'-DDT Found: Dehydrochlorination method	Difference
Technical and Purified Grade DDT Samples			
1	75.07	74.85	0.22
2	77.07	76.28	0.79
3	77.95	78.04	0.09
4	78.76	78.36	0.40
5	86.04	85.74	0.30
6	89.10	88.82	0.28
7	97.00	96.85	0.15
8	99.45	98.74	0.71
		Average difference	0.37
Commercial DDT Dust Mixtures (Not Containing Sulfur)			
45106[a]	5.36	5.44	0.08
44398	8.19	8.12	0.07
44239	13.22	12.95	0.27
44327	18.17	18.89	0.62
44889	37.34	37.47	0.13
43929	39.11	39.20	0.09
43923	39.63	38.82	0.81
		Average difference	0.30
Commercial DDT Dusts Containing 50% Sulfur			
45110	3.43	4.28	0.85
45072	3.83	4.03	0.20
45114	3.97	4.16	0.19
45111[b]	4.95	4.36	0.59
		Average difference	0.46

[a] Contains β,β'-dithiocyanodiethyl ether.
[b] Contains basic sulfates of copper and zinc and 2.10% sulfur.

cause an error of 5% p,p'-DDT in dust formulations. Duplicate results should agree within 0.5% p,p'-DDT.

The values of p,p'-DDT obtained by the method described are relative to the crystallization method as a standard. There is no method known to give the true values of p,p'-DDT in technical DDT, though the crystallization method gives results which are believed to be closest to the truth.

Table III. Determination of Known Amounts of p,p'-DDT in Oil Solutions

Sample No.	Composition	% p,p'-DDT In sample	% p,p'-DDT Found	% Recovery
1	Kerosene solution[a]	1.53	1.55	101.31
2	Spray oil solution[b]	4.23	4.45	105.20
3	Kerosene solution 0.1% pyrethrins	1.55	1.61	103.87
4	Kerosene solution 5% Lethane 60[c]	2.68	2.58	96.27

[a] Specific gravity 0.7940 at 20.0° C.
[b] Light-medium emulsible spray oil, specific gravity 0.8729 at 20.0° C.
[c] Contains β-thiocyanoethyl esters of aliphatic fatty acids averaging 10 to 18 carbon atoms.

Table IV. Effect of Time on Dehydrochlorination

Reaction Time	Chloride Formed
Min.	%
5	6.45
7	7.09
10	7.52
15	7.77
20	7.91

Table V. Effect of Stirring Speed on Dehydrochlorination of DDT in Oil Solutions

Stirring Speed	Chloride Formed
R.p.m.	%
500	3.79
700	4.03
800	4.04

SOURCE OF ERROR

A source of error is the presence of water-soluble chlorides in some types of commercial DDT dusts. The presence of 0.1% water-soluble chloride will cause a positive error of 1.0% total DDT if the Gunther method (*7*) is used. This would lower the sample weight equivalent to 1.000 gram of total DDT and cause an error in p,p'-DDT content. Only four samples of the many analyzed were found to contain appreciable amounts of water-soluble chlorides. Their presence, once established, can usually be determined quantitatively and a correction made. If large amounts are found present it might be easier to extract the DDT with benzene and determine the total DDT in the benzene extract. Dust of unknown composition should be checked qualitatively for water-soluble chloride ions before beginning a quantitative determination of DDT.

A graph of Table IV will show that any error due to the measurement of time during the dehydrochlorination reaction will be less at 15 minutes than at any shorter period. This relationship holds for both DDT dusts and oil solutions.

In the analysis of DDT-sulfur mixtures it is imperative that all silver sulfide be decomposed before back-titrating with thiocyanate: otherwise an appreciable error will be introduced. A positive error in total DDT will cause a negative error in the p,p'-DDT percentage. If the error occurs only during the p,p'-DDT determination, the results will be high.

ACKNOWLEDGMENT

The author wishes to thank Herbert A. Rooney, of this laboratory, for his work on DDT in the presence of organic thiocyanates.

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Rapid Electrometric Determination of the Alkalinity of Sea Water

Using a Glass Electrode

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On the basis of glass electrode pH measurements of solutions to which known amounts of dilute hydrochloric acid have been added, "empirical coefficients" have been calculated, and the normality of a dilute solution of sodium bicarbonate containing a mixture of salts has been determined with a precision of about 1%. The operations are illustrated in connection with determination of the alkalinity of sea water. One measurement of pH yields the normality or alkalinity directly and a direct-reading pH instrument could be scaled to read normality, molarity, or alkalinity directly. The factors that affect the accuracy of the determination are listed and their magnitudes indicated. All steps are indicated that must be performed in developing a similar procedure for systems other than sea water. Industrial control determinations, and clinical investigations where large numbers of determinations are made, can be similarly standardized.

THE term "alkalinity" has been adopted by the International Association of Physical Oceanography (1939) as the standard designation to replace the terms "titratable base", "excess base", "titration alkalinity", and "buffer capacity" of sea water. It is defined as being the number of milliequivalents of hydrogen ion neutralized by 1 liter of sea water at 20° C. The alkalinity of sea water is primarily due to the presence of bicarbonates, though borates, phosphates, arsenites, and silicates are present in lesser amounts to form a complex buffered system with a pH of about 8. Information concerning the total concentration of salts of these weak acids as well as the available alkali cannot be acquired from a single pH measurement but must be determined otherwise.

The methods for the determination of alkalinity of sea water have been well summarized by Sverdrup, Johnson, and Fleming (*3*). Because of the variety of results obtained by the different methods, there is a definite need for a standard procedure yielding accurate and precise results which can be universally understood and compared. None of the methods involves any assumptions as to the nature of the buffers present in sea water, but all take into account the variation in salt content. The work of Mitchell and Rakestraw (*2*) was based upon a titration procedure and yielded excellent results. In the method of Thompson and Bonnar (*5*) an excess of standard acid was added to the sea-water sample. The amount of the acid that had been effectively neutralized by the sea water was readily determined by measuring the amount of excess acid colorimetrically, by comparison with a series of standard tubes. Though the method is convenient, the standard comparison tubes were difficult to prepare and rather unstable.

Some time ago the glass electrode was used at this laboratory by Thompson and Anderson (*4*) for making routine pH and alkalinity measurements of sea water. This eliminated some of the difficulties of the earlier methods, but new considerations arose. Further investigation of the use of the glass electrode by the present authors in determining the concentration of the excess acid has demonstrated the necessity of a knowledge of the relationship between the pH of the solution and the amount of acid added to sea water of various salinities. This involves the experimental determination of coefficients which are empirical, having significance only when applied to this determination with the specified conditions.

DETERMINATION OF EMPIRICAL COEFFICIENT

The empirical coefficients were determined from a series of titrations of natural and artificial sea-water samples. Sea water is alkaline to about the same extent as a 0.002 *N* sodium bicarbonate solution. One hundred milliliter samples were titrated with 0.01000 *N* hydrochloric acid until the pH was about 3.0. The equivalent point was taken as occurring with the greatest change in e.m.f. per unit volume of added acid, at a pH of about 4.5. The pH of the solution was measured at frequent intervals beyond the equivalence point. From the known amount of acid added and the experimentally determined alkalinity, it was possible to determine the excess acid present. The empirical coefficient, f_{H^+}, was calculated by dividing $C_{H^+}f_{H^+}$ obtained from the pH measurement of the solution by the concentration of excess strong acid, C_{H^+}, as shown under calculations. From this coefficient, C_{H^+} in other similar solutions can be calculated.

EXPERIMENTAL EQUIPMENT. The pH measurements were made with Leeds & Northrup glass electrodes No. 1199-12 and reference electrodes No. 1199-13. These were connected with a Leeds & Northrup vacuum tube amplifier to a Type K2 potentiometer.

EXPERIMENTAL PROCEDURE. The electrodes were standardized according to the method recommended by Dole (*1*) against a potassium acid phthalate solution, which was prepared from salt obtained from the National Bureau of Standards according to directions supplied by the bureau. An additional check was made as recommended by Dole against sodium borate. The $E°$ values were determined before each series of titrations, using Equation 1:

$$E^\circ = E. - \frac{2.3RT}{nF}\,\text{pH} \tag{1}$$

A concentrated synthetic sample of sea water having the following composition was prepared from carefully purified salts: NaCl, 0.4920 *M*; $MgCl_2$, 0.0646 *M*; Na_2SO_4, 0.0338 *M*; $CaCl_2$, 0.0138 *M*; KCl, 0.0123 *M*; $NaHCO_3$, 0.0026 *M*. Solutions for titration were prepared by dilution of this concentrated solution.

Eight samples of natural and four samples of artificial sea water ranging in ionic strength from about 0.07 to 1.0, were titrated. The chlorinity range was from about 2.0 to 29 grams of halides per liter of sea water. The pH of the sea water varied between 7.8 and 8.2. During titrations the solution temperature was maintained constant within 1° between 22° and 25° C.

CALCULATIONS. The pH was calculated using Equation 1, the "glass electrode hydrogen-ion activity", $C_{H^+}f_{H^+}$, according to Equation 2

$$\text{pH} = -\log C_{H^+}f_{H^+} \tag{2}$$

and the normality of the excess strong acid according to Equation 3

$$C_{H^+} = \frac{(\text{ml. of excess HCl})(N\ \text{HCl})}{(\text{ml. of sample} + \text{ml. of HCl})} \tag{3}$$

Example. A 100-ml. sample of sea water plus 25.93 ml. of

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Table I. Coefficient Data for Sample, Cl = 18.83 Grams per Liter

HCl, Ml.	pH	$(C_{H}{}^{+}f_{H}{}^{+})(10^5)$	$(C_{H}{}^{+})(10^5)$	$f_{H}{}^{+}$
23.93	4.370	4.266	3.31	1.29
24.13	4.280	5.248	4.91	1.07
24.33	4.195	6.397	6.51	0.984
24.53	4.125	7.465	8.12	0.920
24.93	4.015	9.638	11.3	0.854
25.43	3.900	12.62	15.2	0.836
25.93	3.810	15.49	19.2	0.807
26.92	3.670	21.38	26.8	0.798
29.94	3.420	38.11	49.3	0.773
34.91	3.195	63.83	84.4	0.756
39.90	3.050	88.92	117.0	0.760
44.80	2.950	112.5	147.3	0.764

Table II. Summary of $f_{H}{}^{+}$ Data

Sample	Cl, Grams per Liter	pH Range	$f_{H}{}^{+}$	Average Deviation
1	2.09	4.07-2.93	0.844	0.010
2	2.84	4.00-3.04	0.798	0.006
3	7.03	3.95-2.98	0.764	0.007
4	9.60	4.09-3.03	0.757	0.005
5	12.31	3.62-3.01	0.748	0.007
6	15.38	4.01-2.95	0.740	0.009
7	15.86	3.92-3.03	0.763	0.010
8	16.97	3.69-3.01	0.766	0.016
9	18.83	3.81-2.95	0.777	0.016
10	10.56	3.94-3.08	0.763	0.007
11	23.44	3.98-2.93	0.777	0.011
12	28.93	3.99-3.02	0.768	0.005

0.00999 *N* hydrochloric acid yielded a solution with a pH of 3.81. The equivalence point occurred at 23.52 ml. of the acid. Therefore,

$$C_{H}{}^{+} = \frac{(25.93 - 23.52)(0.00999)}{(100 + 25.93)} = 19.2 \times 10^{-5} \text{ equivalent per liter} \qquad (4)$$

$$C_{H}{}^{+}f_{H}{}^{+} = 15.49 \times 10^{-5} \text{ at pH } 3.81 \qquad (5)$$

$$f_{H}{}^{+} = \frac{C_{H}{}^{+}f_{H}{}^{+}}{C_{H}{}^{+}} = \frac{15.5 \times 10^{-5}}{19.2 \times 10^{-5}} = 0.807 \qquad (6)$$

The $f_{H}{}^{+}$ values were not constant throughout the pH range investigated; the variations in the values are given for one sample in Table I.

The data for the twelve samples titrated are given in Table II and in Figure 1. The pH range over which the coefficients were sensibly constant is given for each sample.

In these measurements the limiting factor was pH. The reproducibility of the pH measurements was ±0.005 pH unit, which amounts to a 1.2% variation in the $f_{H}{}^{+}$ values.

The variation of $f_{H}{}^{+}$ with pH is considered to be due to the decreasing ionization of the carbonic acid as the amount of excess hydrochloric acid increases. It is possible, making certain assumptions, to correct for the ionization of the carbonic acid. When this is done the $f_{H}{}^{+}$ values at the higher pH values are lowered and the results are in agreement with those at lower values where the excess hydrogen ion is sufficient to repress the ionization of the carbonic acid. However, this must not be done for the present application of the $f_{H}{}^{+}$ results.

In Figure 1 the size of the circle indicates the extent of deviation of the individual measurements. From this figure the values of $f_{H}{}^{+}$ in Table III have been taken.

Table III. Interpolated Values of $f_{H}{}^{+}$

Chlorinity, grams per liter	2	4	6	8	10
Ionic strength	0.072	0.143	0.215	0.287	0.359
Coefficient	0.845	0.782	0.770	0.760	0.755
Chlorinity, grams per liter	12	14	16	18	20
Ionic strength	0.430	0.502	0.574	0.646	0.717
Coefficient	0.752	0.752	0.754	0.754	0.758

DETERMINATION OF ALKALINITY OF SEA WATER

Exactly 25.00 ml. of 0.01000 *N* hydrochloric acid are placed in a clean dry 135-ml. glass-stoppered bottle that has been aged for several months with hydrochloric acid having a pH of about 3.5. A 100-ml. sample of sea water is pipetted into the bottle, the sample is brought to the desired temperature, and the pH is measured. This measurement may be made aboard ship, but the treated sample may be safely retained and the pH measured more conveniently ashore. As indicated in Equation 7, the normality of the excess strong acid, C_H, is calculated by dividing $C_{H}{}^{+}f_{H}{}^{+}$ obtained from the pH measurement of the solution by the appropriate coefficient, f_H, for the water being analyzed.

$$\frac{C_{H}{}^{+}f_{H}}{f_{H}{}^{+}} = C_{H}{}^{+} \qquad (7)$$

By substituting the $C_{H}{}^{+}$ value in the following equation, developed by Thompson and Bonnar, the alkalinity may be calculated:

$$\text{Alkalinity} = \left[\left(\frac{1000}{\text{ml. of sample}}\right)(\text{ml. of HCl})(N\ \text{HCl})\right] - \left[\left(\frac{1000}{\text{ml. of sample}}\right)(\text{ml. of sample + ml. of HCl})(C_{H}{}^{+})\right] \qquad (8)$$

Since all the above factors are fixed except the alkalinity and the $C_{H}{}^{+}$, Equation 8 becomes

$$\text{Alkalinity} = 2.500 - (1250)\left(\frac{C_{H}{}^{+}f_{H}{}^{+}}{f_{H}{}^{+}}\right) \qquad (9)$$

and it is possible to prepare tables or graphs which will relate pH or the $C_{H}{}^{+}f_{H}{}^{+}$ and alkalinity for a certain chlorinity range where no significant variation in $f_{H}{}^{+}$ occurs. Furthermore, it is possible to scale a pH meter so that it will be a direct-reading instrument for the alkalinity or for the normality of the sea water.

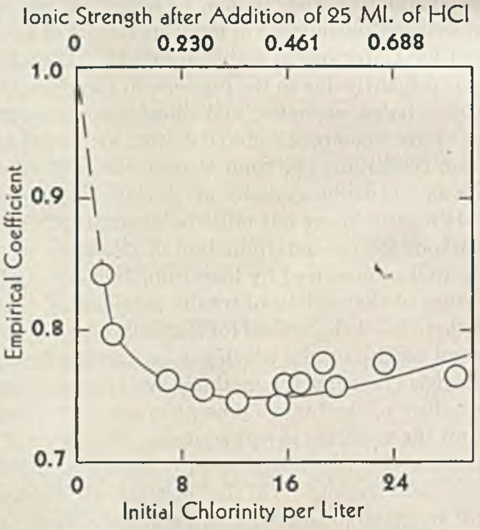

Figure 1. Variation of Coefficient of Hydrogen Ion with Initial Chlorinity of Sample and Ionic Strength after Addition of 25 ml. of Acid

To test the proposed method three samples representing a chlorinity of 18.83, 12.31, and 7.03 were treated with several different amounts of standard hydrochloric acid. The alkalinities were calculated and compared with the values obtained by titration; the results are shown in Table IV.

These results indicate a probable error in the neighborhood of 1%, which is not an unreasonable or unusually high value, considering that the concentration of the solution is only about 0.002 molar with respect to the bicarbonate ion.

The major factors that influence the results of the determination have been investigated and the following conclusions obtained. If the pH varies by ±0.01 unit at 3.60 the alkalinity will vary by ±0.5%. This same percentage variation results from a change of ±3° or a change of ±2.5% in the value of f_{H^+}. An error in measuring the volume of the standard acid of ±0.05 ml. and an error of ±2 parts in 1000 in the normality of the standard acid produce a change of ±0.25%, while an error of ±0.1 ml. in measuring the volume of the sample produces an error of only ±0.15% in the alkalinity values.

At this laboratory the acid is measured with calibrated automatic pipets and the sample bottles are usually prepared before the ship is under way. The sample is measured using a measuring pipet described by Thompson and Anderson (*4*). The pH values usually encountered are around 3.6. Under abnormal conditions they may rise to 4.0 and higher, but this can be remedied by adding more acid, which is a desirable thing to do, as this brings the f_{H^+} values into the region where they are more nearly constant.

The method described for determining the alkalinity of sea water routinely should be applicable to a number of other systems, such as wash waters, effluent from manufacturing operations, urines, blood, and other biological fluids.

If the procedure is to be applied successfully to other systems, the test solutions must be fairly uniform as to ionic strength and the concentration of the unknown material. Then by using a standard size sample and a fixed amount of reagent, the relationship between the constituent whose concentration is being determined and the pH, or any electrode e.m.f. that is related to the test substance, can be determined. Once the relationship has been established, the laborious titration process can be eliminated. Obviously, where only an occasional determination is to be made, no benefits are found. However, where large numbers of samples are examined in routine industrial or clinical work, a considerable saving of time is effected.

Table IV. Summary of Calculated Alkalinity Values

Sample	pH of Treated Sample	Alkalinity, Milliequivalents per Liter		Percentage Error
		Calculated	By titration	
A	3.05	2.35		
	3.67	2.33		
	4.13	2.33		
	4.37	2.32		
		Av. 2.33	2.35	1
B	3.01	1.74		
	3.39	1.72		
	3.91	1.70		
		Av. 1.72	1.71	0.5
C	2.98	1.22		
	3.47	1.22		
	3.65	1.21		
		Av. 1.22	1.21	1

ACKNOWLEDGMENT

The authors are especially grateful to T. G. Thompson for his contribution to the preliminary phases of this investigation and to E. C. Lingafelter for his very valuable suggestions and criticisms.

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Accelerated Ozone Weathering Test for Rubber

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Light-energized oxidation and cracking by atmospheric ozone are the agencies chiefly responsible for the deterioration of rubber outdoors. Since these processes are separate and distinct, it is proposed to distinguish between them in the evaluation of rubber for resistance to weathering. An accelerated test for susceptibility to atmospheric ozone cracking is discussed. Apparatus for conducting the test and for measurement of ozone in minute concentration is described in detail.

IT HAS been previously shown by the authors (*1*) that two separate and distinct factors are responsible for the changes which rubber compounds undergo when exposed outdoors: a light-energized oxidation and attack by ozone which is normally present in the atmosphere in minute concentration. The former acts independently of stress in the rubber, the latter only when the material is stretched.

Since sunlight, ozone, and temperature vary hourly, daily, seasonally, and with locality, the over-all result to the exposed material will depend on the balance between the causative factors and will be unique, since any given combination of such factors will not be duplicated. It is therefore essential that the susceptibilities of a given compound to damage by these two factors be determined separately. The information thus furnished will then permit of an estimate of the durability of the compound under any given set of conditions.

Damage by light-energized oxidation can be mitigated to any great extent only by physical protection from light, which can be partially achieved by incorporation of carbon black or ferric oxide. It is likely to be the major factor in the case of light-colored goods. Susceptibility can be readily gaged by measurement of the oxygen absorbed when the material is irradiated in air or oxygen under controlled conditions. The present obstacle to formulation of a standard test is the lack of a constant and reproducible light source simulating sunlight.

This article is principally concerned with the ozone factor. In the case of rubber goods containing appreciable loadings of carbon black, such as insulated cable jackets and hose, by far the most important cause of deterioration is the familiar cracking at stressed locations by the ozone of the atmosphere, popularly and erroneously referred to as "light cracking".

Many workers have attempted to use ozone-cracking in the laboratory as a measure of outdoor-cracking, only to abandon the method because of failure to duplicate outdoor ratings. The probable cause of this failure has been found by the authors to be the use of too high concentrations of ozone. Small additions of wax, for example, which would confer substantial protection to cracking at atmospheric concentrations of ozone, are quite without effect in most cases at concentrations one hundred times greater. If ozone concentrations approximating that of the atmos-

Table I. Effect of Temperature on Time Taken to Crack

Compound	Wax %	80 Hours	110 Hours	120 Hours	130 Hours	140 Hours	150 Hours
		Temperature, Degrees Fahrenheit					
GR-S cable jacket	0	10	3	1	1	1	1
	1	72	5	2	1	1	1
	2	400	30	6	2	1	1
	3	[a]	[a]	18	5	2	1
	4	[a]	[a]	60	20	3	2
	5	[a]	[a]	240	60	8	3
Natural rubber cable jacket	0	3	1.5	1	1	..	..
	1	100	2	1	1	..	..
	2	300	4	1	1	..	..
	3	450	40	1	1	..	..
	4	[b]	60	1	1	..	..
	5	[b]	85	2	1	..	..
Natural rubber gum compound	0	4	2	1	..	..	..
	1	110	3	1	..	..	..
	2	200	3	1	..	..	..
	3	340	4	1	..	..	..
	4	[c]	5	1	..	..	..

[a] Good after 6 months.
[b] Good after 3 months.
[c] Good after 1 month.

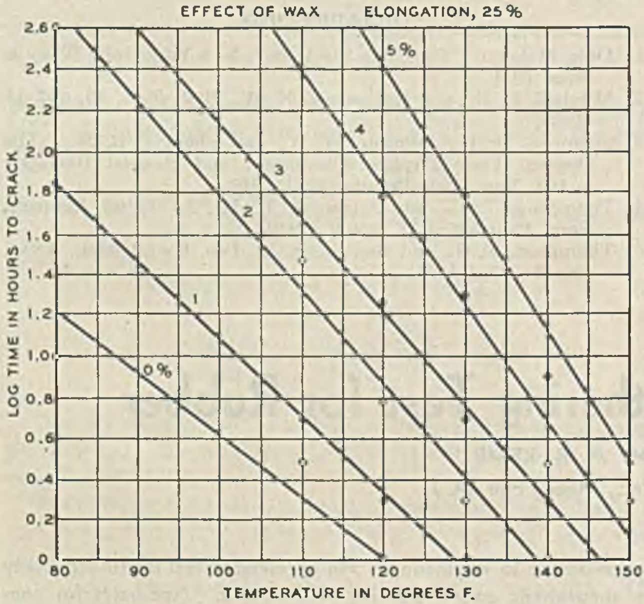

Figure 1. Effect of Temperature on Time Taken to Crack a GR-S Cable Jacket Compound Containing Different Amounts of Protective Wax

Ozone concentration 25 parts per 10^8, elongation 25%

phere be used (around 3 parts per 100,000,000 by volume) outdoor exposures can be closely duplicated. Rubber compounds designed principally as wire and cable insulations for outdoor use have been rated in this way in these laboratories for some time with considerable success.

The nature and degree of cracking of a given compound on exposure to dilute ozone depend on the concentration, the temperature, the degree of elongation, and whether this is static or dynamic (*1*).

TEST CONDITIONS

For accelerated aging in the laboratory the authors have currently adopted a concentration of 25 ± 2 parts of ozone per 100,000,000 of air by volume as the test atmosphere and the expiration of time for the first appearance of cracks in the stressed sample at the chosen degrees of elongation (usually 20 and 30%) and temperature as the measure of performance. The specimen is examined under magnification of 7 to 10 times, which not only gives results more quickly but greatly reduces errors due to any visual defects of the observer.

Ozone concentrations up to 100 parts per 100,000,000 can be satisfactorily used in many cases of highly weather-resistant compounds but are not permissible for general use. Unfortunately in ozone at 25 parts per 10^8, the time taken to crack such compounds at room temperature is too long to be practicable for an accelerated test; so resort is taken to the effect of increased temperature.

In the absence of protective wax, increase in temperature results in more but much finer cracks which in many cases can be recognized only under magnification. In the presence of wax, cracks when formed are few but large and well defined. Raising the temperature reduces progressively the effects of the waxes in current usage till a point is reached at which they are ineffectual. For a given wax this temperature increases with its concentration and is higher for GR-S compounds then for natural rubber compounds. For example, a GR-S cable jacket, a natural rubber cable jacket, and a natural rubber gum compound containing various additions of a certain wax, at 25% elongation in an ozone atmosphere of 25 parts per 100,000,000 gave the results shown in Table I in hours to crack.

These values, plotted in Figures 1, 2, and 3 on a semilog basis, reveal a distinct connection between temperature and wax content. As the temperature rises a progressive decrease in cracking time occurs, the gap between low and high wax additions being gradually closed, more rapidly in the case of natural rubber compounds than in GR-S compounds. It is this feature that is suggested as the basis of accelerated testing of susceptibility to atmospheric ozone cracking. The temperature of test chosen for a given type of compound is such that the highest economically practicable addition of protective wax can be made to fail in a reasonable time, say 3 or 4 days. This temperature is obviously lower for natural rubber than for GR-S, 70° to 80° and 110° F. being suggested for the former and 120° or 125° for the latter. The proposed concentration of ozone is 25 to 30 parts per 100,000,000 and the degree of elongation 20 or 25%. The criterion of

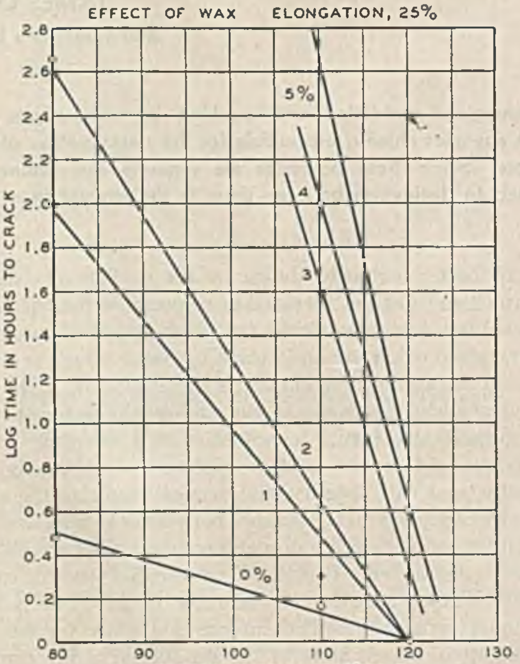

Figure 2. Effect of Temperature on Time Taken to Crack a Natural Rubber Cable Jacket Compound Containing Different Amounts of Protective Wax

Ozone concentration 25 parts per 10^8, elongation 25%

performance is the time taken for the first sign of cracking to appear.

It is not suggested that the ratio of performance between low and high wax additions remains the same with change in temperature, so that the lower temperature life may be determined by extrapolation from the higher. Compounds of known weathering performance must be used as controls. It is considered that as data accumulate over a wider range of compounds it will be possible to establish definite performance requirements under specified conditions similar to those outlined above. The room temperature test is intended to cover compounds of low weathering resistance and to detect anomalies, as, for example, a certain wax examined by the authors which is actually highly efficient at 120° F. but performs poorly at room temperature (Figure 4).

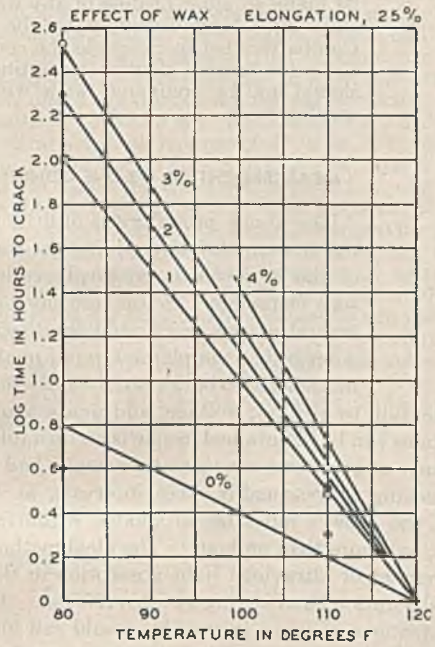

Figure 3. Effect of Temperature on Time Taken to Crack a Natural Rubber Gum Compound Containing Different Amounts of Protective Wax

Ozone concentration 25 parts per 10^8, elongation 25%

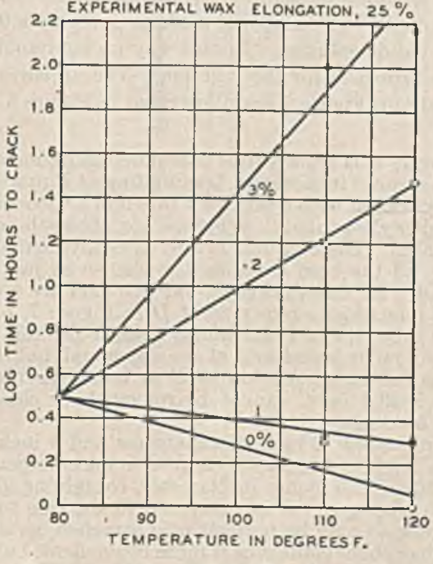

Figure 4. Anomalous Behavior of an Experimental Wax–Natural Rubber Gum Compound

Ozone 25 parts per 10^8, elongation 25%

TEST APPARATUS

Essential to the test are means of furnishing and maintaining uniformly an atmosphere of ozone of the required concentration. This is readily and most conveniently accomplished by passing air or oxygen over a mercury vapor lamp having an envelope of quartz or glass transmitting short-wave ultraviolet light. Ozone is formed from the oxygen by the short-wave ultraviolet light.

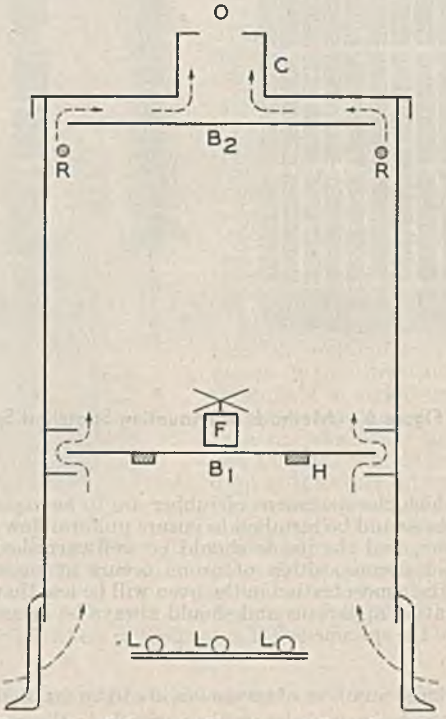

Figure 5. Schematic Drawing of Test Chamber

For laboratory use modifications of the apparatus shown in Figure 16 of the previous paper (*1*) are used. With this arrangement a flow ranging up to 1 cubic meter of air per hour can be supplied at concentrations from 5 to several hundred parts of ozone per 10^8. The higher the flow the lower the concentration. The ozone produced will decrease rather rapidly at first but more slowly after a hundred hours or so, permitting a very uniform output, providing temperature and voltage are kept uniform and the humidity of the air supply has no extreme variations. The lamps should burn continuously. Used in this way they function for several months.

In the past the authors have made considerable use of the G.E. germicidal lamp as ozone generator, since the yield was much less and easier to control than with the quartz tube. However, the nature of the glass in this lamp has recently been modified so as to reduce the ozone output, making it practically useless as an ozone generator. The lamp in current use for the purpose is the Hanovia Safe-t-aire lamp, a mercury vapor discharge tube in quartz. This lamp (Catalog No. 2851) has normally a 30-cm. (12-inch) column and even when operated at as low a voltage as possible generates far too much ozone for easy control. The output can, however, be regulated nicely by covering part of the column with aluminum foil or other opaquing means. Only about 5 cm. (2 inches) of exposed column are needed for a laboratory generator. The tube is held concentric by waxed or shellacked corks or rubber stoppers in a glass tube 2 or 3 inches in diameter provided with side tubes for inlet and outlet of air. This lamp operates at a low temperature and has a very long life. [Currently (August, 1946) a small 12-volt lamp recently developed by the Westinghouse Electric Corp. (Sterilamp WL-794) is being tested. This lamp, of automobile headlight bulb size and intended for use in household refrigerators, is a most convenient source for a laboratory generator delivering from 0.5 to 1.0 cubic meter per hour. Enough experience has not been gained to determine its useful life.]

The flow of ozonized air from these generators is conducted to the base of a laboratory-type oven maintained at the tempera-

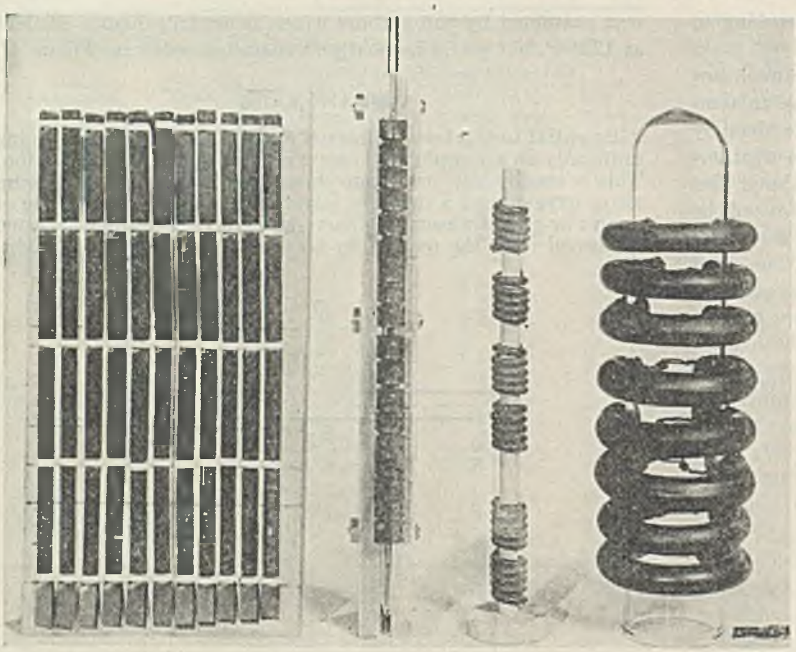

Figure 6. Methods of Mounting Stretched Specimens for Test

ture at which the specimens of rubber are to be exposed. Suitable baffles should be installed to ensure uniform flow at all parts of the oven, and the inside should be well varnished or waxed, since rapid decomposition of ozone occurs at metal surfaces. Even so, the concentration in the oven will be less than that from the generating apparatus and should always be measured at the location of the specimens.

Where large numbers of specimens are to be exposed a different arrangement is used, depicted schematically in Figure 5.

This consists of a drum or tank, 2 feet in diameter and 3 feet high on legs, open at the bottom and closed at the top, with a loosely fitting lid furnished with a short chimney. The inside is divided into 2 compartments by baffle B_1 12 inches from the bottom. This baffle is 2 inches less in diameter than the drum, the two rings shown acting as a light-lock to prevent light from reaching the upper chamber. Another similar baffle is mounted just below the lid. The lower chamber houses an aluminum plate on which is mounted a single Hanovia No. 2851 Safe-t-aire lamp operated, after aging for a few hundred hours at approximately 750 volts alternating current. Ozone in suitable concentration is thus generated in this chamber. This air rises into the upper chamber through the opening between the edges of baffle B_1 and the sides of the drum, escaping to the outer air around baffle B_2 and through the chimney, C. The amount and concentration of air thus circulating can be readily controlled by adjusting the size of the opening, O, of the chimney or installing a damper in the chimney. A small fan rotating slowly on reduced voltage may advantageously be mounted on baffle B_1 to ensure uniformity of composition and temperature of the air in the upper chamber. The fan blades should be adjusted to generate only a horizontal disturbance.

If the device is to be operated at an elevated temperature, a ring heater is mounted on the under side of baffle B_1, regulated by a thermostat mounted in the upper chamber. A 500-watt heater will maintain a temperature of 110° F. and a 750-watt heater a temperature of 120° F. When used at these elevated temperatures the drum is insulated with a layer of thick felt or other suitable material. The specimens to be exposed are suspended by wires from rail R around the inside walls of the upper chamber. The drum should preferably be of aluminum, which is less active as a decomposition catalyst of ozone than copper, iron, or zinc. In any event the inside should be painted with a thin layer of wax. In the units used in these laboratories a full chimney opening gives a concentration of ozone in the upper chamber of 25 parts per 10^8, using the lamp referred to. The opening is reduced in size as the activity of the lamp decreases with age.

Specimens for exposure are mounted as shown in the photograph of Figure 6.

Sheets are mounted as strips stapled to a waxed board, a, at elongations chosen, usually 20, 25, 30, and 50%, though GR-S compounds usually break at the staple with 50% elongation. Alternatively strips are mounted bent around a mandrel of a diameter calculated to give the required elongation, the ends secured between 2 wooden strips, b. Wires, c, are wound around waxed dowels or glass rods of the necessary diameter and cables, d, similarly wound on glass tubing. Specimens must not be exposed immediately after mounting, but must stand for a uniform time of at least 24 hours to allow healing of any wax film that may have been disrupted by the stretching. Comparison between sample and control should be on the basis of identical mountings. Sheets should not be compared with wires, for example.

MEASUREMENT OF OZONE CONCENTRATION

The above procedure is of little value without a means of determining the concentration of the ozone in the atmospheres in the exposure chambers. In the routine operation of several of the accelerated weathering devices described, a simple and rapid method of estimation had to be devised, because although with careful attention to air flow, voltage, and temperature, uniform concentrations can be maintained, ozone is an unstable substance and assurance of a uniform concentration can be had only by repeated checking at reasonably close intervals, at least daily. Moreover, the answer must be obtainable within a relatively short time, not more than an hour. The ideal method would be by measurement of ultraviolet light absorption in the region of the ozone absorption band having a peak at 2550 Å. However, at the concentrations of ozone in use this would call for a path at least 50 feet long to give a practicable measure and is thus inconvenient.

The method currently used reverts to the classical method of estimation by absorption by a solution of potassium iodide in water and estimation of the iodine liberated. To furnish sufficient iodine for measurement in the short time allotted a large volume of air must be dealt with. To ensure absorption of the ozone, the air to be measured is made to generate a fine spray of potassium iodide solution. In this way an enormous surface of solution is furnished for the reaction. The apparatus is shown schematically in Figure 7 and illustrated in Figure 8.

In Figure 7, A is a glass tube 0.375 inch in diameter (approximate) and about 4 inches long, terminating at B in a short length of capillary tubing with a bore of 1 to 2 mm. Concentric within A is a smaller glass tube, C. (Figure 7, a, shows this assembly on a larger scale.) The end of C is first carefully heated in a blowpipe flame till the bore is reduced in size so as just to admit a No. 69 drill. At this thickened end two flats are ground off on a sheet of fine Aloxite paper as at D in Figure 7, b. When in position in tube A, end D fits snugly against the hole in capillary B. C may now be sealed to A at the upper end, but it is better to rely on the rubber connection at E to hold the tubes in place, since once sealed in, C cannot be removed for cleaning in the event of a blockage.

F is a trap about 2 inches in diameter and 4 inches long, requiring no further description, and G is an enlargement in the exit tube, about 1.5 inches in diameter, containing glass wool to trap spray passing F. F is connected to the side tube of A by rubber tubing or may be permanently attached, as shown in the figure. The rubber connector is more convenient, but the tubing used must first be soaked for a long period in dilute iodine solution and thoroughly washed, or iodine may be taken up from the reagent. H is a 1-liter three-necked Woulff's bottle in which A and F are secured by Pyrex ground joints, A occupying the center opening with B protruding just below the neck and tube J

reaching to within 0.5 inch of the bottom of the bottle. The third neck serves to introduce and remove the reagent.

A is connected through rubber joints and glass or plastic tube *K* to rotameter *L*, graduated from 0 to 1.0 cubic meter of air per hour. The entrance to the rotameter is connected to the atmosphere whose ozone content is to be determined and the exit from *F* is connected to a vacuum line. After 75 ml. of reagent are introduced into *H*, the stopper is replaced, and the vacuum gradually applied. Almost the entire body of liquid will enter *F*, furnishing a head of reagent at *B*, where the entering air resolves it into a fine mist which fills the entire bottle. At the end of the run the vacuum is disconnected and the liquid transferred to the titration vessel. For atmospheres containing around 25 parts of ozone per 10^8 of air, ample iodine for titration will be obtained in 0.5 to 1 hour. When runs longer than 1 hour are called for, it is necessary to add distilled water at intervals to make up for evaporation. This is most conveniently done through the air intake. The liberated iodine is determined by titration with sodium thiosulfate. Since the amount is so small, 0.002 *N* to 0.001 *N* solutions must be used, and since the end point using starch as indicator is uncertain, the electrometric method of Foulk and Bowden (*3*) is resorted to, in which use is made of the depolarizing effect of iodine on a polarized electrode.

In the authors' practice the titration vessel is a 250-cc. wide-mouthed extraction flask having a hole in the side near the neck. A two-hole rubber stopper carries into the flask 2 glass tubes into which are sealed the two electrodes, in this case stout platinum wires (0.1 inch thick) with circular loops at the ends to increase the areas exposed to the liquid. Sensitivity is increased by increasing the surface area of the electrode, but this form is used because it is rugged and not disturbed by agitation of the liquid. To the electrodes is applied a potential of 30 to 40 millivolts. This is readily obtained by connecting suitable resistors—e.g., 30,000 and 1000 ohms—in series across an ordinary 1.5-volt dry cell and picking off the voltage across the resistor of lower value. A galvanometer is connected in series. The authors use a Rubicon 3402-H.H. with an Ayrton shunt, but a less sensitive type is probably sufficient.

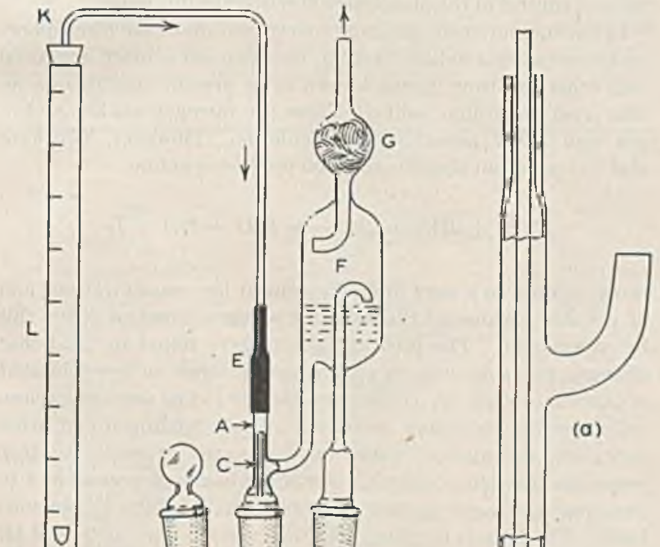

Figure 7. Ozone-Absorbing Device

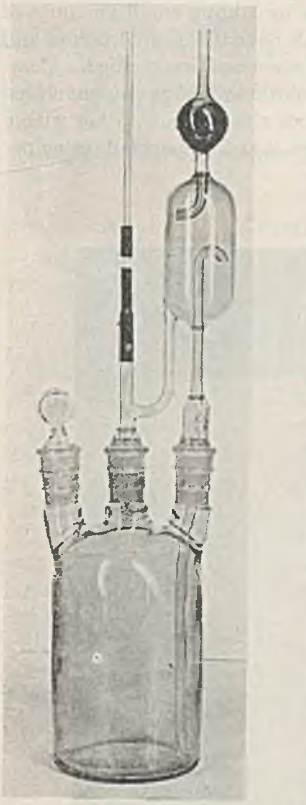

Figure 8. Ozone-Absorbing Device

Fifteen grams of potassium iodide are dissolved in 75 ml. of buffer solution (equal volumes of 0.025 *N* disodium hydrogen phosphate and 0.025 *N* potassium dihydrogen phosphate). The solution is introduced into the titration flasks, the electrodes are inserted, and the liquid is swirled vigorously over them. Following an initial kick the galvanometer spot will return to zero if no iodine is present, because polarization of the electrodes will prevent passage of current. Presence of an oxidizing agent such as iodine removes the polarizing hydrogen from the cathode and current flows. Addition of thiosulfate (through the hole in the side of the flask) till the iodine is removed restores the polarized state and returns the galvanometer deflection to zero. The reagent will usually require the addition of 2 to 5 drops of 0.002 *N* thiosulfate, depending on the batch, to bring this about.

After the ozone run the iodide solution containing the iodine is placed in the titration vessel and thiosulfate is added until only a barely perceptible yellow remains; then the electrodes are inserted and thiosulfate is added drop by drop at intervals till no deflection is obtained, the liquid being vigorously swirled meanwhile. The liquid is then returned through the trap to rinse the apparatus and the titration is completed. One cc. of 0.001 *N* thiosulfate represents 0.0112 cc. of ozone at S.T.P.

A little difficulty may be encountered at first in identifying the end point to within one drop of thiosulfate solution at this low concentration. It will be found easier if the titration is made to a small residual deflection of the galvanometer.

Neither the form nor dimensions of the apparatus described are critical. Those given are of the apparatus in current use. Duplicate apparatus reproduces results within ±5%, which is good enough at these low concentrations. It has been found that reducing the concentration of the potassium iodide solution below 20% gives low results. The system described passes about 0.3 cubic meter of air per hour, but this can be changed by changing the size of the air jet, *C*. With a given jet there may be considerable leeway in the size of the capillary nozzle. The criterion is a reaction vessel filled with a mist of reagent. The authors have compared reaction vessels ranging in size from 125 ml. to 12 liters and find a tendency to low results with a capacity of less than 500 ml. A larger vessel than this yields no advantage.

A most important point to remember is that potassium iodide in solution is photochemically oxidized to iodine in presence of light, even in neutral or alkaline solution. Therefore titration must not be conducted in bright daylight and during the ozone run the whole of the absorption apparatus must be enclosed in a light-tight box as shown in Figure 9. Failure to observe this precaution will result in utterly erroneous findings.

The 0.002 *N* thiosulfate should be standardized at frequent intervals, as such dilute solutions lose strength through oxidation.

Since the iodine in solution has a vapor pressure, some will be carried away in the exhausted air; a correction must therefore be applied to the result obtained. The amount of this has been determined in two ways: (1) by making determinations over a range of increasing periods of time, plotting the ozone found against time, and extrapolating to zero time which gives the true value; (2) by operating the apparatus with a stream of nitrogen and simulating the ozone reaction by adding small amounts of 0.001 *N* iodine at frequent intervals over the desired period and in amount equivalent to the ozone concentration studied. Comparison of the iodine remaining in solution with the amount added gives the error. These two methods checked each other within ±5% at any concentration between 3 and 25 parts of ozone per 10^8. The percentage loss with time is shown by Figure 10. The determinations were made over a period of only 2 hours at the highest concentration, since measurement time in practice never exceeds 1 hour. With decreasing concentration the period was increased progressively up to 8 hours for the lowest.

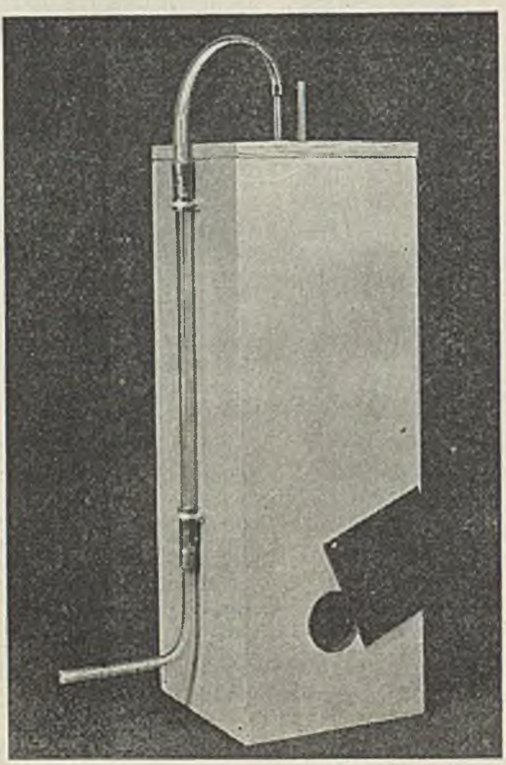

Figure 9. Dark Housing for Ozone Absorber

The curve applies only to the particular conditions employed—viz., a flow of 0.27 to 0.30 cubic meter per hour and a vacuum of 60 cm. of mercury. For other conditions the correction must be determined experimentally.

The absorption of ozone is assumed to be complete, since increasing the concentration of potassium iodide up to 80% gave no higher values. Further, dilution experiments, in which ozone of concentrations up to 100 parts per million was diluted with a known volume of air and the dilution simultaneously measured, when carefully conducted, checked within ±5%. This is not a definite proof but a reasonable assumption.

It might be thought that the loss of iodine could be reduced by cooling the reaction vessel in ice. The reduction has proved on trial to be insignificant. Expansion of the air at the nozzle and some evaporation of the water results in cooling the reagent to around 60° F., depending on the duration of the run. Where room temperatures are high as in summer months, however, immersion in ice would ensure more uniform conditions.

The principal merit of this method lies in the rapidity with which ozone concentrations at the level suggested for use in the accelerated weathering methods described can be made. Since variations in the rubber compounds tested and the personal errors in recognizing the first appearance of cracking are often large, it is felt that this method is well within the over-all accuracy possible in weathering values. It is planned to check the method further against light-absorption determinations.

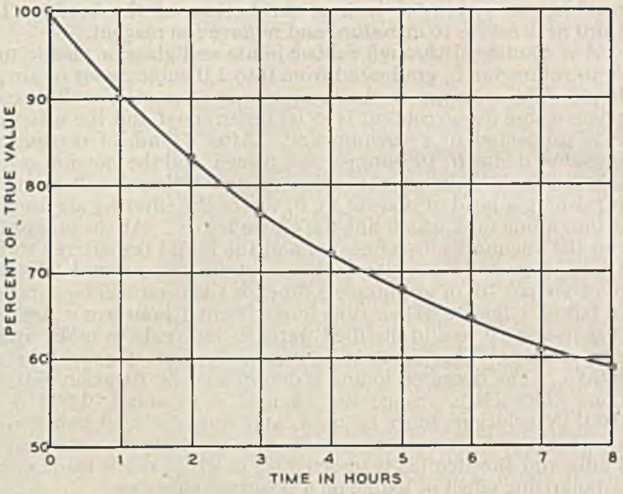

Figure 10. Correction Curve for Ozone Estimation Described in Text

An apparatus for the continuous recording of ozone concentration, employing the above principles, has been described by Gluckauf *et al.* (*4*). The output of such an apparatus could readily be arranged to maintain a constant concentration of ozone in a test chamber by adjustment of the voltage to the ultraviolet lamp. It is possible, however, that the effort involved in maintenance of such apparatus would exceed that called for by intermittent control in the procedures described in this paper.

In the measurement of ozone concentrations of the atmosphere by the potassium iodide reaction, the criticism is often advanced that other oxidizing agents known to be present also liberate iodine from potassium iodine. These are nitrogen oxides, hydrogen and other peroxides, and chlorine. However, Gluckauf *et al.* (*4*) point out that the reaction producing iodine

$$NO_2 + 2H^+ + 2I^- \longrightarrow H_2O + NO + I_2$$

proceeds only to a very limited extent at low concentrations and at pH 7.0, because of the lack of hydrogen ions and prove this by experiment. The present authors have found by trial that nitrogen peroxide even in concentration three- or fourfold that of the atmosphere (*2*, *5*) does not liberate iodine from potassium iodide by the procedure described. As for hydrogen and other peroxides, the authors have made repeated attempts to trap suspended particles of organic peroxides in a water spray and to freeze out hydrogen peroxide in traps cooled by a dry ice–acetone bath. The liquids so obtained from several cubic meters of air have invariably failed to liberate titratable amounts of iodine from buffered potassium iodide solution. Free chlorine apparently is absent from the atmosphere at the location of these laboratories. Nevertheless, in this connection the possibility of the presence of these or other oxidizing agents in the atmosphere of industrial locations should be borne in mind.

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Determination of the Relative Acidity of Wood and Adhesive Joints

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Problems involving the assessment of the pH of wood glue and plywood sections are discussed. The use of fluorescent dyes and ordinary color indicators has been investigated and very interesting observations are described. Dye indicators are shown to be satisfactory for differentiative pH measurement.

ONE of the important considerations in investigating the character of the glue line in plywood bonding is the acidity of the actual glue and the adherent wood. It is known that corrosion of the wood takes place when the glue used is either too acid or too alkaline (*1*, *5*, *6*), but, as yet, research workers on the subject have found no suitable solution of the problem of assessing the actual acidity at the glue line after pressing and curing the plywood. This paper discusses some of the problems involved and proposes a method which, for all practical purposes, gives the pH of the finished plywood glue line.

The "reference pH" used by Campbell (*4*), grinding up the plywood and suspending it in water or acid, is not suitable for attacking most problems concerning glue lines because too many factors affect its determination. For example, the thickness of the veneer, the quantity of the resin used, the degree of dilution, the leaching out of salts from the wood, and the possible hydrolysis on dilution would all have an influence on the final pH measured with the glass electrode. At best, the reference pH gives an over-all average of the acidity of the veneers and the glue together, but affords no specific information as to the actual acidity at the wood-glue interface. Campbell said that the pH of the moisture condition of air-dry wood could not be measured directly because wood in this condition is not moist enough to wet the glass electrode. He overlooked, however, the possibility of using suitable indicators to determine acidity by the colorimetric method.

Table I. Fluorescent Dyes

	Dye	Manufacturer	Color Change
1.	Coumarin	Dr. Theod Schuchardt-Gorlitz C.P.	None
2.	Fluorescein sodium	B.D.H.[a]	Very slight
3.	Eosin	Eastman Kodak	None
4.	Erythrosin	Eastman Kodak	None
5.	1 - Naphthol - 4 - sulfonic acid	C.A.F. Kahlbaum, Chemische Fabrik Adlershof bei Berlin	Slight
6.	2 - Naphthol - 6 - sulfonic acid	Eastman Kodak	None
7.	Naphthionic acid	Eastman Kodak	None
8.	Amino G acid, 2-naphthylamine - 6,8 - disulfonic acid	C.A.F. Kahlbaum	Good
9.	R acid, 2-naphthylamine-3,6-disulfonic acid	C.A.F. Kahlbaum	Good
10.	1 - Naphthylamine - 4,8-disulfonic acid	C.A.F. Kahlbaum	Good
11.	2-Naphthol	Du Pont	None
12.	2-Naphthol	C.A.F. Kahlbaum	None
13.	1-Naphthylamine	Du Pont	None
14.	Acridine	B.D.H.	Slight
15.	Auramine	Du Pont	Slight
16.	Potassium thiocyanate	B.D.H.	None
17.	Uranyl nitrate	Schering Kahlbaum	None
18.	Phenol red	B.D.H.	None
19.	Rhodamine B	B.D.H.	None
20.	Rhodamine 6DGN extra	Du Pont	None
21.	Basic orange 3 RN	Du Pont	None
22.	Dihvdrothio-*p*-toluidine	Du Pont	None
23.	Berberine sulfate	B.D.H.	Slight
24.	Ammonium salt of phenyl per acid	Du Pont	None
25.	Erythrosin bluish	National Aniline & Chemical Co.	Good
26.	Eosin bluish (alcohol solution)	National Aniline & Chemical Co.	Good
27.	Auramine	B.D.H.	None
28.	Rhodamine 6G	B.D.H.	None
29.	Tetrahydroxyflavonal	B.D.H.	None

[a] British Drug Houses.

FLUORESCENT INDICATORS

Some of the more common titration indicators gave very poor and indistinct color changes when applied to wood and therefore the use of ordinary color indicators was at first discarded. D. H. Hamly of the Department of Botany suggested the use of fluorescent dyes, and was of invaluable assistance in the subsequent work in fluorescent microscopy.

The working principle was that the fluorescent color of the dyes under ultraviolet rays would not be affected by the color of the wood. Little information could be found in the literature regarding fluorescent dyes which manifested a change in color with a change in pH. Consequently, the work began with a search for fluorescent dyes that might be suitable as indicators.

All known available fluorescent dyes (see Table I) were investigated.

A solution of each dye was made up, 1 to 1000 where possible and more dilute when necessary, and kept in a stock bottle. Strips of birch veneer 3 × 0.5 × 0.0625 inch were used as test pieces and their pH was controlled by soaking in solutions of different acidities. Standard buffers, hydrochloric acid, sulfuric acid, and sodium hydroxide, were employed in making the standard pH solution. After soaking for 24 hours, the test pieces were allowed to dry in air. A drop of the dye was put on the surface of each of several test pieces of varying pH, and when the dye was dry, the resultant color was observed under the fluorescent microscope.

Five dyes (Table I) showed some appreciable change in color with varying pH, but in each case the color change was not sharp, but gradual; furthermore, there was actually only a change in shade of color rather than a distinct change from one color to another. Attempts to set up standards in order to determine the actual range of the color variation failed because there was no method of determining the true pH of the birch test pieces. The use of a material other than wood as a background for the dyes was found to be impractical because the character of the background has a marked effect on the fluorescence. In view of these facts, it was decided to abandon the investigation on the use of fluorescent dyes for the examination of the glue line. Research was continued, however, with the ordinary color indicators and some very interesting results were obtained.

COLOR INDICATORS

It was first noticed that B.D.H. (British Drug Houses) Universal indicator, which is green in its ordinary state, changed to red immediately when it came in contact with filter paper. The dye was applied to a strip of birch, and again a red color indicated acid constituents. The acidity cannot be due to the carbon dioxide in the air, because Universal indicator does not turn red when left for a long period of time in distilled water exposed to the atmosphere. The actual pH of the birch could not be determined with this indicator because it is not suitable for pH's lower than 4. A search was begun for an indicator with the proper pH range, which would also exhibit a good color change on wood.

BROMOPHENOL BLUE AND THE pH OF BIRCH. Investigation of all the dyes with a color change below pH 4 showed that bromophenol blue was the only one suitable for measuring the acidity of birch. This dye has a range from 3.0 (yellow) to 4.6 (blue) with a gradation of the combination of these two colors between the limits.

A series of buffers was made which covered the pH range from 3.0 to 4.6 in steps of 0.1 unit. Strips of birch veneer were cut and soaked in these buffers for 1.5 hours. This period was long enough to condition the test pieces, since longer soaking had no influence on the final pH of the strip. It will be assumed that the pH of these strips attains the same value as the buffer, because the color indicated on the wood with bromophenol blue compared very favorably with the color in the buffer solution, and since the amount of buffer used was great in comparison with the size of the test piece, the pH of the wood must eventually, by leaching and impregnation, reach the pH of the buffer. The wood constituents are not sufficient to affect the pH of the buffer.

The soaked strips, when dry, were painted with bromophenol blue and served as standards for the comparison of color changes of the dye on wood. The pH of birch was then determined by painting a clean birch strip with the indicator and comparing the resulting color with the standards.

Because the dye solution was thought to have an effect on the pH of the wood, experiments were carried out using various concentrations of dye and varying alcohol-water mixtures as the solvents. It was found that a concentration of 1.2 grams of bromophenol blue per liter was sufficient to give a good color on wood. The optimum solvent proved to be 70% alcohol by volume, since this gives a dye solution with a pH very close to that of the wood itself. With this solvent the indicator reaches a permanent color in a minimum time. Other solvents with more or less water percentages give the same results, but longer time is required to obtain a reading.

The wood test pieces should be clean or preferably recently planed, because handling of the wood has a ready and pronounced effect on the pH at the surface. Another interesting observation was that a test strip, even when clean, shows a slight variance in pH over different areas. This led to the investigation of moisture content of the wood.

MOISTURE CONTENT OF WOOD

In sapwood, the moisture is present in three conditions: (1) as the chief constituent of the sap, (2) absorbed in the cell walls, and (3) filling, completely or partially, the intercellular cavities (*2*). In heartwood, however, it occurs only as condition 3. It is obvious, then, that the moisture content of wood varies over different areas. If moisture content has an effect on the pH of the wood, it should not be surprising that bromophenol blue shows varying pH in a sample of wood. Experiments were carried out to find the effect of moisture content on the pH of wood.

A newly planed test piece was painted with the indicator and then cut into three equal sections. One section was put in a closed box saturated with water vapor; the center section was allowed to stand in the atmosphere; and the third section was put in an oven at 70° C. After 24 hours, the colors of the three sections were compared. As was expected, the pH of the heated section dropped, and the pH of the humidified section rose, while the center section remained the same and served to show that there was a definite change in each of the other two.

Quantitative values of the pH could not be determined because the color limits of the indicator were approached. This proved, however, that oven-dry wood and the "saturated" wood had a difference of at least 1.5 pH units in the case of yellow birch. In a matter of a few hours, the surface of the wood regained its original air-dry moisture content.

The establishment of a definite relation between moisture content and pH of wood is not practical, in view of the fact that the moisture content varies in different woods and in different parts of the same wood. The fact remains, however, that the value of the pH is very sensitive to moisture content. Even the changing humidity conditions of the atmosphere from day to day produce a corresponding change in the pH of the wood. This indicates that the buffering system in wood mentioned by Campbell and Packman (*4*) cannot be very effective in regard to humidity changes.

pH IN DIFFERENT WOODS

Samples of several different woods were obtained from the Department of Forestry and tested with bromophenol blue. The intrinsic dark colors of some species made it difficult, but, for the most part, readings were possible. Values ranged from 3.2 (B.C. cedar) to 4.5 (white ash) (see Table II). Values are by no means absolute, because pH may vary in each species and readings were made using the buffered birch samples as standards.

No relation could be found between pH and the listed moisture content of various species, nor was there any relation between pH and specific gravity. There was no appreciable difference in the average pH of the two types—i.e., coniferous and deciduous.

pH OF THE GLUE

The pH of the glue before application can usually be measured with the glass electrode. Data relating to the effect of the pH of the glue on the strength of plywood are tabulated by Dowling (*5*), but his measurements were made before pressing and he did not attempt to measure the ultimate pH of the glue after curing and setting.

Experiments were carried out with color indicators in an attempt to add the dye in the glue mixture and determine the pH after setting. With dark-colored glues like phenol-formaldehyde the method was impractical, but with cold-setting glues like urea formaldehyde favorable results were obtained. It was observed that, because of reaction of the catalyst, the pH dropped as polymerization progressed in the case of urea-formaldehyde. No change was noticeable in the pH of casein on setting.

pH AT THE GLUE LINE

Experiments were then carried out involving the application of color indicators to the glue and wood in cross sections of plywood.

Table II. Relative pH of Different Wood Species

Species	Specific Gravity	Moisture Content, %	pH
Coniferous			
Balsam (eastern)	....	....	4.0
Cedar (B.C.)	....	....	3.2
Cedar (eastern)	....	....	3.5
Cypress	....	....	3.9
Fir (B.C.)	0.53	4.55	3.4
Hemlock (eastern)	....	....	3.8
Hemlock (western)	0.45	....	3.6
Larch (white)	....	....	3.6
Pine (eastern white)	0.42	....	3.4
Pine (jack)	0.51	....	3.7
Pine (red)	....	7.3	3.7
Redwood	....	....	3.6
Spruce (black)	0.43	....	3.4
Spruce (Sitka)	0.54	....	3.5
Spruce (white)	0.42	....	3.9
Tamarack (eastern)	0.59	....	3.6
Deciduous			
Ash (black)	....	....	3.7
Ash (white)	0.66	....	4.5
Basswood	....	....	3.4
Beech	....	....	3.3
Birch	0.64	5.7	3.8
Cherry	....	....	3.5
Chestnut	....	....	3.2
Elm (white)	0.59	....	3.6
Hickory	0.80	....	3.2
Maple (hard)	0.78	....	3.6
Maple (soft)	....	....	3.8
Oak (red)	....	....	3.3
Oak (white)	0.72	6.2	3.5
Poplar	0.43	5.8	3.9
Sycamore	0.56	....	4.1
Walnut	....	5.4	3.5
Whitewood	....	....	3.9
Willow	0.40	....	4.4

Chlorophenol red was painted on the cross section of a finished sample of three-ply birch bonded with alkaline phenol formaldehyde. After the dye was dry the specimen was examined under the microscope. Beautiful distinction was manifested between the glue line and the veneers. The glue line itself and the wood at the interface turned a bright red color (indicating a pH of approximately 9), while the wood not in contact with the glue was yellow. Penetration of the glue into the veneer became apparent and single tendrils of resin stood out clearly. Thus a good picture of the glue line and veneers in cross section was produced, showing the distribution of the glue and the effect of the alkaline constituents of the glue on the wood in contact with it.

The same indicator was applied to the surface of a veneer in the same sample of plywood. Penetration areas were well defined and in some cases penetration not visible without the indicator was brought out.

With urea-formaldehyde the effect was not so clear, because the pH of the birch itself is too nearly that of the glue line and no clear distinction was visible. Bromophenol blue was found more suitable for urea resins. With casein both chlorophenol red and bromophenol blue are satisfactory.

The application of bromophenol blue to the glue line readily distinguished an alkaline glue. Urea-formaldehyde and casein can thus be differentiated, even though they are similar in appearance. The phenolics are distinguishable by their dark color.

Color photographs were taken of typical specimens and good results were obtained. The authors will be pleased to make the films available to interested readers.

SUMMARY

The use of fluorescent dyes as pH indicators for plywood has been investigated and found to be impractical. It is possible to determine the relative pH of wood by the use of ordinary color indicators.

Experiments have proved that the pH of any wood species is closely related to its moisture content and wood structure. The pH of light-colored glues was measured even after setting.

Color indicators have yielded valuable information regarding pH and glue penetration in plywood.

LITERATURE CITED

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Determination of Dipentaerythritol in Mixtures of Pentaerythritol and Dipentaerythritol

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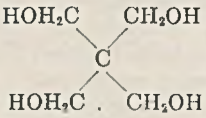
BECAUSE pentaerythritol and dipentaerythritol are now established as raw materials for the resin chemist, greater accuracy in the analysis of commercial pentaerythritols is becoming of prime importance.

Pentaerythritol (also called monopentaerythritol) has the formula

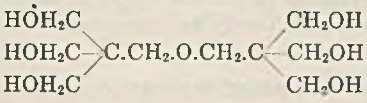


and is usually sold as a "pure" product or in admixture with varying proportions of dipentaerythritol.

The purest form of pentaerythritol usually sold commercially contains about 2 to 3% of dipentaerythritol and about 0.1 to 0.2% of tripentaerythritol. It usually consists of clear, colorless octahedrons melting at about 254+° C. Strictly pure pentaerythritol melts at 260.6° C.

The purest form of dipentaerythritol sold commercially contains about 8 to 10% of tripentaerythritol, a minute amount of tetrapentaerythritol, and possibly a few tenths per cent of monopentaerythritol. It usually exists in the form of colorless, opalescent, platelike crystals of melting point about 218-220° C. Strictly pure dipentaerythritol melts at 221° C.

The chemical formula for dipentaerythritol is:



In addition to pure pentaerythritol (which is also often referred to as nitration grade or as high melting point pentaerythritol) and pure dipentaerythritol, various mixtures of pentaerythritol and dipentaerythritol, such as the 90-10, 85-15, 75-25, and 70-30 mixtures, have found their way into industry. Consequently, there is a real need for a satisfactory method for the determination of dipentaerythritol in such mixtures.

The benzilidine, the various acetyl procedures, and other methods based on the determination of hydroxyl groups have been tested and found wanting in some important respect.

The method described below has been developed and used in the laboratories of the Trojan Powder Company for a number of years, with results which have been more reliable and meaningful than those obtained by any heretofore known procedure. An understanding of certain phenomena related to aqueous solutions of the pentaerythritols will aid the chemist using the method in obtaining reasonably accurate and duplicatable results.

Aqueous solutions of the pentaerythritols are not what the physicist would call ideal solutions, but are very complex mixtures, depending upon their proportions, concentrations, and temperatures. Consequently, such properties as the solubility of each pentaerythritol in water, the solubility of dipentaerythritol in aqueous solutions of monopentaerythritol, the solubility of tripentaerythritol in solutions already containing monopentaerythritol and dipentaerythritol, etc., and the nature of the crystals obtained from these solutions are not expressible in simple terms. There is no doubt that molecular complexes and equilibrium mixtures play an important function in aqueous solutions of pentaerythritols and the phenomenon of hydrogen-bonding seems to be an underlying cause.

The present method for the determination of dipentaerythritol is based upon the precipitation of dipentaerythritol from aqueous solutions containing a mixture of monopentaerythritol and dipentaerythritol, such precipitation being effected by ensuring the presence of at least a certain minimum ratio of dipentaerythritol to pentaerythritol in the clear solution before any precipitation, or crystallization, is allowed to take place. This minimum ratio of dipentaerythritol to pentaerythritol is provided in many cases by actually adding a weighed amount of pure dipentaerythritol to the sample and then applying a corresponding correction on the final, weighed dipentaerythritol crystals obtained, to allow for this added dipentaerythritol. In terms of units of weight, the minimum proportion of dipentaerythritol to pentaerythritol which has been found operative in this method is about 1 part of dipentaerythritol to 1 part of pentaerythritol—to a 2.5-gram sample consisting of 2.0 grams of pentaerythritol and 0.5 gram of dipentaerythritol, one should add at least 1.5 grams of pure dipentaerythritol before proceeding with the analysis. The procedure given below is recommended as generally applicable over a wide range of commercial pentaerythritol products.

METHOD

Exactly 2.500 grams of the sample (in a tared aluminum dish) and 2.500 grams of pure dipentaerythritol are weighed out. The sample is transferred to a weighed (to the nearest 0.1 gram) 125-cc. Erlenmeyer flask, 60 grams of distilled water are added and the flask is shaken gently, and heated (on an electric hot plate) to take all the sample into solution. To prevent undue loss of water during this heating, a clean rubber stopper should be placed in the neck of the flask and loosened a few times to relieve any excess pressure in the flask. The heating and shaking should be continued 3 to 5 minutes, until a clear solution results.

If an undue amount of water has been driven out of the flask during this dissolving stage, the flask with its contents should be placed upon a balance and water added, drop by drop, to ensure the presence of 60 grams of water. The flask should be allowed to stand in the room for at least 0.5 hour, with occasional gentle shaking, then transferred to a water bath at a temperature of 18° C. (not less than 15° C.), and allowed to remain here overnight.

The next morning the total weight of the flask and its contents is checked to be certain that 60 ± 0.1 grams of water are present in the mixture. Usually the addition of a few drops of water is necessary.

The flask with its contents is now placed in a water bath at 25° C. and gently shaken; the stopper is removed, and the crystals of dipentaerythritol which have separated are stirred by means of a glass rod, keeping the contents at 25° C. When the crystals have been broken up and the mixture has been at 25° C. for at least 10 minutes they are transferred to a weighed 15-ml. Gooch-type, fritted-glass crucible of medium porosity. This transfer should be made by means of 40 ml. (measured) of denatured alcohol (Formula 1) applied by means of a small wash bottle. The crystals are then washed with 10 ml. of ethyl ether and dried at 110° C. for 1 to 2 hours, or to constant weight.

CALCULATIONS

The weight of dipentaerythritol actually in the original sample is calculated from the final dry weight obtained by first deducting the weight of pure dipentaerythritol added and then applying a correction for the amount of dipentaerythritol remaining in the filtrate and alcohol washings. This correction has been carefully determined and found to be 0.145 gram for the conditions specified above. If these conditions are altered, this value will be different.

METHOD OF CALCULATION.

$$\%\ \text{dipentaerythritol} = \frac{A - 2.500 + B}{2.500} \times 100$$

where A = weight of dry crystals obtained and B = solubility correction, or in this case, 0.145 gram

The 2.500 figure in the numerator is the weight, in grams, of the added dipentaerythritol. The 2.500 figure in the denominator is the weight of original sample.

In an actual test, A was found to be 2.857 and 2.850 grams for separate determinations. Hence, the per cent dipentaerythritol in the sample is:

$$\frac{2.857 - 2.500 + 0.145}{2.5} \times 100 = 20.08\%$$

and

$$\frac{2.850 - 2.500 + 0.145}{2.5} \times 100 = 19.80\%$$

The mixture used in this analysis was made from weighed quantities of pure pentaerythritol and pure dipentaerythritol in the proportions of 80 to 20.

Table I. Determination of Dipentaerythritol

Mixture No.	Known Composition of Original Mixture: Pentaerythritol %	Known Composition of Original Mixture: Dipentaerythritol %	Composition Found by Analysis: Pentaerythritol (by difference) %	Composition Found by Analysis: Dipentaerythritol %
1	99	1	98.6	1.1, 1.4, 1.7, 1.3 Av. 1.4
2	98	2	98.1	1.6, 2.3, 1.9, 1.8 Av. 1.9
3	97	3	96.8	3.2, 2.9, 3.5, 3.3 Av. 3.2
4	93	7	93.1	7.0, 6.5, 7.2, 6.8 Av. 6.9
5	90	10	90.15	9.85, 9.85 Av. 9.85
6	80	20	80.07	20.05, 19.80 Av. 19.93
7	70	30	70.02	29.85, 30.10 Av. 29.98
8	45	55	45.08	54.92, 54.92 Av. 54.92
9	40	60	40.03	60.04, 59.90 Av. 59.97
10	35	65	35.00	64.92, 65.08 Av. 65.00

REMARKS

An idea of the accuracy and precision of this method can be obtained from Table I.

As it is necessary to have at least 1 part of pure dipentaerythritol for each part of pure pentaerythritol, there is no necessity for using an added amount of dipentaerythritol, when working with mixtures containing more than 50% of dipentaerythritol. In the results listed in Table I, beginning with mixture 8, no dipentaerythritol was added and a 5-gram sample of the mixture was used for analysis instead of 2.5 grams.

Unless the dipentaerythritol used for this method is of the highest purity, serious errors result, particularly in the solubility correction factor.

In extreme cases, a blank using a known mixture of pentaerythritol and dipentaerythritol, having about the same composition as the unknown, should be run simultaneously with the sample under test, in order to establish the solubility correction value for this specific set of conditions.

The importance of uniform technique throughout this method cannot be overemphasized.

The conditions mentioned for the cooling and rewarming to 25° C. must be strictly adhered to, since they have a considerable effect upon the precipitation of the dipentaerythritol.

The crystals which form in the flask should not be permitted to cake to a hard mass, but should be present as relatively fine, individual plates readily removable by means of a stirring rod and a stream of alcohol from a wash bottle.

It is very important that the sample taken for analysis be representative of the mixture under examination. Dipentaerythritol has a very low packing density and a pronounced tendency to segregate when in admixture with the denser and more compact pentaerythritol crystals.

This method has been used on thousands of samples of commercial pentaerythritol products and has, in the hands of skilled technicians, given satisfactory and meaningful results.

ACKNOWLEDGMENT

The author gratefully acknowledges the assistance of many persons on the technical staff of the Trojan Powder Co., particularly of Victor Ginsler, Kenneth Stripp, and E. A. Wernett, in the development of this method.

Measurement and Analysis of Gases in Vacuum-Packed Food Containers

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An apparatus and method for determining the quantity and composition of gases in vacuum-packed and gas-packed food containers are described. The method is applicable to both large and small containers, flexible, semirigid, or rigid. Gas contents as small as 1 cc. may be measured and analyzed with fair accuracy, and gas contents of 5 cc. or more permit accuracy of the order of ±5% or better. Results obtained on a number of vacuum-packed foods, particularly coffee and dry whole milk, are presented, and application of the method to detection of leakage, determination of oxygen and nitrogen permeabilities of packaging materials, and determination of true densities of dry foods is described.

IN THE evaluation of various packaging materials, methods and conditions for vacuum packing, especially of dry or dehydrated food products in flexible containers, means of determining the amount and composition of residual gases in the packages, as well as the changes in these gases, whether through sorption, desorption, generation, permeation, or leakage during storage, have proved of great value. Strachan and Embree (*5*) have described a device and method for sampling and analysis of the gas in large cans of gas-packed dehydrated foods, while a U. S. Department of Agriculture circular (*1*) has described a similar method. Unpublished work is being done in other laboratories on the measurement and analysis of gases in canned food products. All these methods, however, appear to lack the versatility and sensitivity achieved with the author's design of equipment and procedure, especially as applied to small packages containing 113.4 grams (4 ounces) or less of dry food products.

BELL-JAR METHOD OF MEASURING VACUUM

A widely used approximate method for determining the residual vacuum in canned goods is to reduce the external pressure until the cans begin to bulge. This method was readily applicable to flexible packages with considerably greater accuracy because of the much smaller pressure differential required to bulge the flexible package walls noticeably. Essentially, the method consists merely of placing the package under a glass bell jar connected to a vacuum pump and a vacuum gage or a manometer, reducing the pressure in the bell jar to the point at which the first swelling or bulging of the package is visible, and reading the gage or manometer to obtain a direct measure of the residual vacuum or absolute pressure in the package. This has been used as a very rapid method, capable of testing from one to three packages individually per minute, using a small glass bell jar, a dial vacuum gage calibrated in inches of mercury, a 42.5-liters (15 cubic feet) per minute vacuum pump, and quick-acting control and release valves. Comparison of residual vacuum determinations by this method with more reliable values on the same packages obtained by calculation from total residual gas content and gas space volume, as described below, indicates an over-all probable error of not more than ±25.4 millimeters (1 inch), and usually not more that ±0.5 inch, for the rapid bell-jar method, without correction for ordinary variations in room temperature and barometric pressure.

DETERMINATION OF GAS CONTENT OF PACKAGES

Although the amount and composition of gases have been determined in 1-pound cans of vacuum-packed coffee, with gas pressures often greater than 1 atmosphere due to evolution of gases by the coffee after packing, the system used appeared not to be directly applicable to the problem. The author was dealing with packages mostly containing from 3 to 5 ounces of product, and some of the products evolved very little gas after vacuum packing, so that he often had to deal with 1 cc. or less of gas per package. Furthermore, the flexible packaging materials with which he was working, usually laminated sheets such as paper to foil with a heat-sealing inner coating, offered difficulties in the way of attaching a gas-collection system.

After several trial procedures, an apparatus was designed and constructed which not only effectively overcame most of the previous difficulties, but had a number of other useful applications. This apparatus includes a gas-measuring system, with means for connecting a wide variety of hermetically sealed packages to the system in such manner as to sample their gas contents without loss or contamination, and a gas-analysis system. The essential details of the apparatus are illustrated in Figure 1. In practice, the glass parts were made to order of Pyrex and the entire assembly was mounted for convenient manipulation on a specially constructed stand of wood and metal.

The semimicro gas-analysis buret, *G*, is approximately 70 cm. long. It is marked, from the 1-mm. inside diameter capillary tip, by 0.02-cc. divisions along a 5-mm. inside diameter barrel to 10 cc., whence marking continues by 0.2-cc. divisions along a 15-mm. inside diameter barrel to 20 cc. just above the stopcock. This buret is interchangeable with another of similar design and

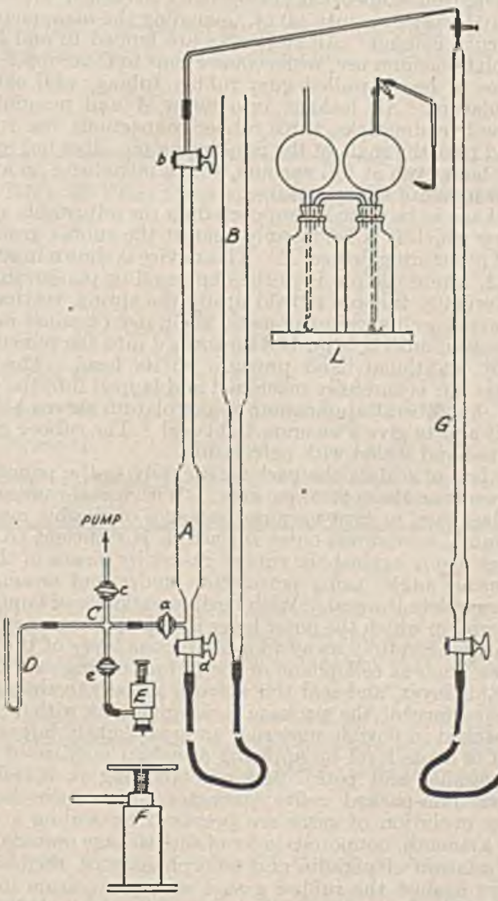

Figure 1. Apparatus for Measuring and Analyzing Gases in Food Packages

the same length, but of 100-cc. capacity, marked by 0.05-cc. divisions from the 1-mm. tip along an 8-mm. inside diameter barrel to 10 cc. and by 0.5-cc. divisions along a 24-mm. inside diameter barrel from there to 100 cc. just above the stopcock. The same leveling tube, *H*, for acidulated water, is used with either buret.

Gas analysis is conducted by means of a number of Richards' pipet assemblies, *L*, with suitable reagents for determination of various gases as desired. The author has used 33% potassium hydroxide solution for carbon dioxide, Fieser's solution for oxygen, and ammoniacal cuprous chloride for carbon monoxide when present, the residue being nitrogen. The specially designed 2-mm. inside diameter transfer tubes, sloping upward and reduced to 1-mm. near their carefully tapered tips, permit alternate connection of the tube from the gas-collection system and those from the several Richards' pipet assemblies to the gas-analysis buret, through a short piece of 2-mm. inside diameter gum rubber tubing fitted with a pinchclamp, without significant loss or contamination of the gas sample or interchange of the reagents in the Richards' pipets with the acidulated water in the buret. Careful operative technique with the equipment described permits determination of the oxygen in a 1-cc. sample of ordinary air with an accuracy of about ±10%, or in a 10-cc. sample with an accuracy of about ±1%.

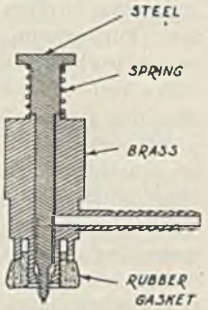

Figure 2. Package-Puncturing Device

The special gas-collection and measuring buret, *A*, has a 2-mm. inside diameter tip above the upper stopcock, is marked by 0.05-cc. divisions from this stopcock along an 8-mm. inside diameter barrel to 10 cc., and by 0.5-cc. divisions along a 24-mm. inside diameter barrel to 100 cc. at a point between the side arm and the lower stopcock, *d*, where the barrel is reduced to 5-mm. The mercury leveling tube, *B*, is similar in size and shape to *H*. The connecting manifold, *C*, and manometer *D* are 2 mm. in inside diameter and as short as convenient. The volume of the capillary system, from stopcock *a* to stopcock *c* to surface of package attached to device *E*, is just 3.0 cc., including the manometer up to its mercury column. All stopcocks are lapped in and lubricated for high-vacuum use, while connections to *C* are made with short pieces of heavy-walled gum rubber tubing, well covered with petrolatum. Air leakage into buret *A* and manifold *C*, through the five stopcocks, three rubber connections, one rubber gasket, and past the shaft of the puncturing pin, does not exceed 0.1 cc. per hour even at full vacuum, which introduces no appreciable error in use of the apparatus.

The package to be tested is supported on the adjustable spring table, *F*, by which it is held firmly against the rubber gasket of the special puncturing device, *E*. This device is shown in section in Figure 2, where the pin is in the depressed or puncturing position. Normally this pin is held up by the spring, so that the tip is retracted well within the metal shell, even against atmospheric pressure, until it is pushed downward into the puncturing position by additional hand pressure on its head. The steel shaft of this pin is carefully machined and lapped into the brass barrel, so that liberal application of petrolatum serves both to lubricate it and to give a vacuum-tight seal. The rubber gasket is also seated and sealed with petrolatum.

The method of sealing the package securely to the puncturing device depends on the type of package. With metal cans, metal-covered glass jars, or firm vacuum packages of flexible material with a smooth, nonporous outer surface, it is sufficient to press the package firmly against the rubber gasket by means of the adjustable spring table, using petrolatum under and around the gasket to complete the seal. With flexible packages of laminated sheet material in which the outer layer is paper, it is necessary to strip the paper carefully away to a nonporous layer of the laminated sheet, such as cellophane or metal foil, taking care not to puncture this layer, and seal this smooth surface to the gasket. When the surface of the package is irregular, as with peanuts vacuum-packed in flexible material, an area slightly larger than the gasket is made level by applying a molten mixture of equal parts of paraffin and petrolatum and allowing it to solidify. Flexible vacuum-packed coffee packages which have become swollen by evolution of gases are prepared by sealing a metal washer to a smooth, nonporous layer of the package material with a molten mixture of paraffin and amorphous wax, then sealing this washer against the rubber gasket with petrolatum in such position that the puncturing pin can pass through the hole in the washer.

The tightness of the seal between the package and the puncturing device is checked, before puncturing the package, by drawing a full vacuum on the 3-cc. capillary system, closing the stopcock to the pump, and observing the manometer. Since leakage of only 0.002 cc. of air into this system raises the pressure by 0.5 mm., even a very slight leak is detected in a few minutes and eliminated by application of more petrolatum around the gasket or puncturing pin.

When the tightness of these seals has been verified, the entire gas-collection system is vacuumized, including the transfer tube to the gas-analysis buret. Then, with the several stopcocks in appropriate positions, the package is punctured by pressing firmly on the head of the puncturing pin, and the gas from the package is allowed to expand into the vacuumized system. If there is very little gas in the package, it is first admitted only to the 3-cc. capillary system, and the equilibrium pressure is read on the manometer. Then it is admitted to the 100-cc. gas-measuring buret, and the manometer is read again. In the absence of complicating factors, such as an equilibrium water-vapor pressure or progressive desorption of gas from the packaged product, these two manometer readings, together with the known volumes of the capillary system and gas buret, permit calculation of the unknown gas-space volume of the package.

The stopcock in the buret side arm is now closed, and the volume of gas in the buret is measured at 1-atmosphere pressure. Part or all of this gas, depending on its amount, is passed through the transfer tube to the gas-analysis buret. It may be held there for subsequent analysis, or successive portions of gas from the same package may be added to it, if necessary to obtain a larger sample for analysis. Each successive portion of gas is withdrawn from the package by lowering the mercury leveling tube until the mercury falls below the side arm, opening the side-arm stopcock to allow the remaining gas to expand into the buret, closing the side-arm stopcock, measuring the gas in the buret at 1 atmosphere, then transferring this gas to the gas-analysis buret, or discarding it, as desired.

GAS MEASUREMENT CALCULATIONS

When dealing with dry powdered or granular packaged materials which do not exhibit significant sorption or desorption of gases, the gas-measurement calculations are relatively simple.

Remembering that the volume of the gas-measuring buret is 100 cc., and of the capillary system 3 cc., let V_0 be the gas-space volume of the package in cubic centimeters, V be the total gas content of the package measured in cubic centimeters at room temperature and 1 atmosphere, P_0 be the total gas pressure in atmospheres in the package before puncturing, and r_1, r_2, r_3--- be the buret readings as each successive portion of gas from the package is measured at 1 atmosphere. From the simple PV relationship, $V = P_0V_0$, $0.01r_1(V_0 + 103) = P_0V_0$, $0.01r_2(V_0 + 103) = 0.01r_1(V_0 + 3)$, $0.01r_3(V_0 + 103) = 0.01r_2(V_0 + 3)$, etc. It readily follows that $r_1 = 100V/\ V_0 + 103)$, $r_2 = 100V(V_0 + 3)/(V_0 + 103)^2$, $r_3 = 100V \times (V_0 + 3)^2/V_0 + 103)^3$, etc. From this, it is apparent that $r_2/r_1 = r_3/r_2 --- r_n/r_{n-1} = (V_0 + 3)/(V_0 + 103) = k$, a constant. Obviously, V is the sum of a geometric series whose first term is r_1 and whose ratio is the constant, k. Therefore, $V = r_1 + r_2 --- + r_n/(1 - k)$, and $V_0 = (103k - 3)/(1 - k)$.

In practice, if there is a substantial amount of gas in the package, and no significant desorption of gas occurs during removal of successive portions, we take the average value of k from the inverse ratios of successive r values, and obtain the values of P_0, V_0, and V from the above relationships. Random variations in successive k values indicate experimental error, while progressive increase in successive k values generally indicates either desorption of gas from the packaged product or a leak in the package or system.

If the amount of gas in the package is very small, or a significant amount of gas is desorbed, a more accurate determination of V_0 is made, after sampling the gas for analysis.

In one case, air is admitted to the package and capillary system to exactly 1 atmosphere, while the buret is vacuumized. Then this air is allowed to expand into the buret, trapped off, and measured at 1 atmosphere as r_a. Again, from the PV relationship, $0.01r_a(V_0 + 103) = V_0 + 3$, or $0.01r_a = (V_0 + 3)/(V_0 + 103) = k$, the constant previously derived. Then, by substitution, $V_0 = (103r_a - 300)/(100 - r_a)$. In the other case, which is generally more convenient, the package and capillary systems are thoroughly pumped out to remove all sorbed gas, then the pump stopcock is closed, and air at 1 atmosphere in the 100-cc. gas-measuring

Table I. Relationship of V_0 to k and to r_r

k	r_r	V_0	k	r_r	V_0	k	r_r	V_0	k	r_r	V_0
0.11	89	9.4	0.31	69	41.9	0.51	49	101	0.71	29	242
0.12	88	10.6	0.32	68	44.1	0.52	48	105	0.72	28	254
0.13	87	11.9	0.33	67	46.3	0.53	47	110	0.73	27	267
0.14	86	13.3	0.34	66	48.5	0.54	46	114	0.74	26	282
0.15	85	14.6	0.35	65	50.8	0.55	45	119	0.75	25	297
0.16	84	16.0	0.36	64	53.2	0.56	44	124	0.76	24	314
0.17	83	17.5	0.37	63	55.7	0.57	43	130	0.77	23	332
0.18	82	19.0	0.38	62	58.3	0.58	42	135	0.78	22	352
0.19	81	20.5	0.39	61	60.9	0.59	41	141	0.79	21	373
0.20	80	22.0	0.40	60	63.7	0.60	40	147	0.80	20	397
0.21	79	23.6	0.41	59	66.5	0.61	39	153	0.81	19	423
0.22	78	25.2	0.42	58	69.4	0.62	38	160	0.82	18	453
0.23	77	26.9	0.43	57	72.4	0.63	37	167	0.83	17	485
0.24	76	28.6	0.44	56	75.6	0.64	36	175	0.84	16	522
0.25	75	30.3	0.45	55	78.8	0.65	35	183	0.85	15	564
0.26	74	32.1	0.46	54	82.2	0.66	34	191	0.86	14	611
0.27	73	34.0	0.47	53	85.7	0.67	33	200	0.87	13	666
0.28	72	35.9	0.48	52	89.3	0.68	32	210	0.88	12	730
0.29	71	37.9	0.49	51	93.1	0.69	31	220	0.89	11	806
0.30	70	39.9	0.50	50	97.0	0.70	30	230	0.90	10	897

buret is allowed to expand into the vacuumized package and capillary system. At equilibrium the side-arm stopcock is closed and the air remaining in the buret is measured. Calling this reading r_r, we have, from the PV relationship, $100 = 0.01r_r (V_0 + 103)$ and $100 - r_r = 0.01r_r(V + 3)$. Dividing the second of these equations by the first, we find $k = 1 - 0.01r_r$, and, by substitution, $V_0 = (100/0.01r_r) - 103$. Table I gives V_0 for various values of k and r_r.

DETERMINATION OF TRUE DENSITY

This apparatus permits reasonably accurate determination of the true density of dry powdered or granular materials, such as coffee, milk powder, and dehydrated soups, which are not well suited to true density determinations by liquid displacement. In this case, density is actually determined by gas displacement. It is merely necessary to determine the weight of the package contents and divide this by the total net volume less the gas space volume, to obtain the true density of the packaged product.

In the case of flexible vacuum packages, where there is no free head space, and the package contents are firmly compressed by external atmospheric pressure, the apparent or bulk density of the product is given by dividing the net weight by the total net volume. There is then, of course, a definite relationship between true density, apparent density, net weight, and gas space volume. When working with a packaged material that is very uniform in apparent and true densities, it is convenient to use this relationship for checking the accuracy of V_0 determinations on individual packages, or indeed as a means of obtaining the most reliable value of V_0 for the individual package.

As an example of this, standard Ottawa test sand was used in work on experimental flexible vacuum packaging to test the effectiveness of different packaging materials and methods. This sand, being substantially pure quartz, has a true density of 2.65 grams per cc. In the 50- to 70-mesh size, found most suitable for this experimental packaging work, its apparent density is consistently 1.62 grams per cc. The gas space volume per gram of packaged sand is then $1/1.62 - 1/2.65 = 0.24$ cc.

ACCURACY OF VOLUME AND PRESSURE DETERMINATION

In addition to experimental errors in reading the buret, other errors may be introduced through failure to level the mercury tube properly, leaks in the system, variations in temperature, failure to establish complete pressure equilibrium before closing the side-arm stopcock, sorption or desorption of water vapor or gases, and in various other ways. However, with careful technique, and by conducting all measurements in a room maintained at 75° ± 2° F., the author has obtained reasonably accurate and reproducible results over a considerable range of gas-space volumes and pressures.

In order to check the accuracy of the method, it has been applied to known conditions from time to time. As an example, a small round-bottomed, ring-necked flask was tightly fitted with a rubber stopper carrying a short capillary connecting tube. The volume was determined, by weight of water contained, as 128.6 cc. This flask, clean and dry, was then connected to the capillary system in place of the special puncturing device, and its gas-space volume was determined repeatedly by the methods described. Typical data for a number of repeat runs, with varying amounts of air in the flask at the start of the run, are given in Table II.

Table II. Gas-Space Volume Results on a Known Volume

Run 1			Run 2			Run 3			Flask Vacuumized, Buret at 1 Atmosphere	
r	k	V_0	r	k	V_0	r	k	V_0	r_r	V_0
55.5			45.0			30.5				
	0.568	129		0.567	128		0.574	132	43.0	130
31.5			25.5			17.5				
	0.572	131		0.569	129		0.560	124	43.5	127
18.0			14.5			9.8				
	0.562	125		0.570	130		0.566	128	53.2	129
10.1			8.25			5.55				
	0.565	127		0.570	130		0.567	128	43.3	128
5.7			4.7			3.15				
	0.570	130		0.564	126		0.572	131	43.2	129
3.25			2.65			1.80				
Av.	0.567	128.2		0.568	128.8		0.568	128.8		128.6

The true density of 50- to 70-mesh Ottawa test sand was found to be 2.65 grams per cc. by displacement of water, in excellent agreement with the literature values of 2.653 to 2.660 grams per cc. for the density of quartz. Then 175.0 grams of this sand, clean and dry, were placed in the flasks described above, and its gas-space volume was again determined. The results are given in Table III.

Table III. True Density of Sand by Gas Displacement

Run 1			Run 2			Run 3			Flask Vacuumized Buret at 1 Atmosphere	
r	k	V_0	r	k	V_0	r	k	V_0	r_r	V_0
38.0			29.0			31.5				
	0.395	62.3		0.397	62.9		0.397	62.9		
15.0			11.5			12.5			60.5	62.3
	0.394	62.0		0.396	62.6		0.396	62.6		
5.90			4.55			4.95			60.3	62.9
	0.398	63.1		0.395	62.3		0.394	62.0		
2.35			1.80			1.95			60.5	62.3
Av.	0.396	62.5		0.396	62.6		0.396	62.5		62.5

True volume of 175.0 grams of sand = 128.6 − 62.5 = 66.1 cc.
True density of sand = 175.0 ÷ 66.1 = 2.65 grams per cc.

Table II shows that V_0 values based on single k values deviated as much as 3% and V_0 values based on single r_r values deviated more than 1% from the known value, but that average determined V_0 values were in excellent agreement with the known value. Deviations of individual V_0 values in Table III from the average are somewhat less, and the true density of sand based on the average V_0 values is in complete agreement with that obtained by displacement of water.

APPLICATION TO FOOD PRODUCTS SEALED IN RIGID CONTAINERS

Although primarily interested in the gas content of flexible vacuum packages, the author has applied the apparatus and

Table IV. Peanuts Vacuum-Packed in a Can

Weights, Grams		Gas Measurement			Gas Analysis	True Density
		r	k	V_0		
Gross	181.6	7.25			Sample, 9.24 cc.	$\frac{125.3}{213-94}$ = 1.05 grams per cc.
Tare	56.3		0.496	95.4	CO_2 1.10 = 12.6%	
Net	125.3	3.00			O_2 0.00 = 0.0%	
			0.486	91.6	N_2 8.08 = 87.4%	$P_0 = V/V_0$ = 0.156 atm.
Volumes, Cc.		1.75				Vacuum = 25.3 inches
					Av. V_0 = 94.0	Oxygen reacted with peanuts during storage[a] = 3.4 cc. = 0.025 N.T.P. cc. per gram
Gross	220.2	Av.	0.491	93.5		
Tare	7.2				$V = \frac{r}{1-k}$ = 14.7 cc.	
Net	213.0	Package Vacuumized, Buret at 1 Atmosphere			CO_2 = 1.85 cc.	
					N_2 = 12.85 cc.	
Temperature, 75°F.		r = 50.5 cc.				
Barometer, 760 mm.		rV_0 = 95.0 cc.				

[a] Assuming all nitrogen present in residue from air sealed in package.

Table V. Whole Milk Powder Gas-Packed in a Can

Weights, Grams		Gas Measurement			Gas Analysis	True Density
		r	k	V_0		
Gross	184.9	21.5			Sample 20.0 cc.	$\frac{124.0}{199.2-93.1}$ = 1.17 grams per cc.
Tare	60.9		0.490	93.1	CO_2 17.0 = 85.0%	
Net	124.0	10.5			O_2 0.08 = 0.4%	
			0.495[a]	95.0[a]	N_2 2.92 = 14.6%	$P_0 = V/V_0$ = 0.454 atm.
Volumes, Cc.		5.20[a]			Av. V_0 = 93.1 cc.	Vacuum = 16.4 inches
			0.520[a]	105[a]		Oxygen reacted with milk during storage[b] = 1.47 cc. = 0.011 N.T.P. cc. per gram
Gross	207.0	2.70[a]				
Tare	7.8				$V = \frac{r_1}{1-k}$ = 42.2 cc.	
Net	199.2	Package Vacuumized, Buret at 1 Atmosphere			CO_2 = 35.87 cc.	
					O_2 = 0.17 cc.	
Temperature, 75° F.		r_r = 51.0 cc.			N_2 = 6.16 cc.	
Barometer, 761 mm.		V_0 = 93.1 cc.				

[a] These values, high due to desorption of gas, omitted from averages.
[b] Assuming all nitrogen present is residue from air sealed in package.

method to food products packed in various sizes of cans and glass jars with metal or paperboard covers. The usual procedure with such packages is to weigh them and determine their gross volume by displacement of water, then to seal them to the apparatus and determine the gas space volume and gas content and composition, and finally to empty the contents and determine the tare weight and volume. The true density of the solid contents may be calculated from these data. The results obtained on a vacuum-packed can of peanuts are given in Table IV.

Examination of the data in Table IV indicates that the package was free from leaks, that there was little desorption of gas from the peanuts during examination, that the peanuts were relatively freshly roasted when packed, since they evolved some carbon dioxide after packing, that they were sealed at approximately 24.8-inch vacuum, and that during storage substantially all the oxygen of the residual air in the package reacted with the peanuts. The age of this package of peanuts was not known, but it was at least several months. The peanuts were crisp and dry, but very slightly stale and rancid, owing to the action of the oxygen absorbed.

The results obtained on a can of commercially gas-packed whole milk powder purchased on the open market are given in Table V.

The fact that the true density found here is lower than the 1.27 value reported by Muers and Anderson (*4*) is attributed to effectively sealed gas spaces inside the particles, and indicates 0.07 cc. of such contained gas per gram of powder, in agreement with the values which they reported for normal whole milk powders. When the milk from this package was reconstituted to normal whole milk concentration, it was found to be very slightly rancid. This would be expected from the indicated amount of oxygen in the package when sealed, which is slightly in excess of the maximum safe limit of 0.01 cc. per gram reported by Lea, Moran, and Smith (*3*).

Although the apparatus was primarily designed for examination of smaller packages, it has been applied satisfactorily to 1-pound cans of vacuum-packed coffee. Table VI presents a typical set of results on this type of package, examined 25 days after packing.

Here we have an example of a semirigid container which is swollen somewhat at the start of the test, because of an internal gas pressure greater than 1 atmosphere, and of a packaged product which progressively desorbs gas as the pressure is reduced, both conditions complicating interpretation of the data and making the results less certain. However, results on a number of similar packages on the same lot of coffee were in agreement within ±5% or better.

APPLICATION TO FOOD PRODUCTS IN FLEXIBLE VACUUM PACKAGES

The method has been applied to large numbers of flexible vacuum packages of dry food products, including coffee, whole milk powder, ice cream mix, dehydrated soups, and peanuts, generally obtaining agreement within ±5% or better on duplicate packages of the same lot.

To illustrate results on a flexible package with above 1 atmosphere internal gas pressure, the data in Table VII are for freshly roasted drip-grind coffee, of the same lot as that in Table VI, but vacuum-packed in a nonpermeable flexible package 1.5 hours after grinding, and examined 19 days after packing.

The figures for true density of this sample of drip-grind coffee are in close agreement when packed in the rigid and in the flexible package, as shown in Table VI and VII.

Application of the method to flexible vacuum packages with very little residual gas is illustrated in Table VIII, covering examination of a package of dry whole milk, sealed at 29.5-inch vacuum in a nonpermeable flexible package, and examined 6 weeks later.

The calculation of gas contained in the dry milk particles is based on the true density of 1.27 grams per cc. reported by Muers and Anderson (*3*) and the value of 1.14 found by gas displacement. This amounts to 9.4 cc. for the 105 grams of dry milk in that package, and offers an explanation of the source of the 6.0 cc. of air found in the package, as compared with less than 2 cc. that should have been left in the free gas space of the package when it was sealed at 29.5-inch vacuum. This package, and others of the same lot, showed a bell-jar vacuum of 29.5 inches immediately after sealing, dropped to 29 inches overnight, and reached substantial equilibrium at 27 inches in about a week. This is clear evidence that the increasing internal gas pressure was not due to leakage, but to gradual desorption of gas from the milk powder.

Apparently, air contained inside the walls of the dry milk particles was not entirely removed during vacuumizing and sealing of the package, but gradually diffused into the space between the particles after the package was sealed, until equilibrium was established.

Among the many studies of gas content of food products in flexible vacuum packages to which the method has been applied, an interesting example is that of the relationship between fineness of grind and time between grinding and packing of freshly roasted coffee and the amount and composition of gas evolved by the vacuum-packed coffee at equilibrium.

Table VI. Drip-Grind Coffee Vacuum-Packed in a Can

Weights, Grams	Gas Measurement	Gas Analysis	True Density
Gross 606.5 Tare 151.5 Net 455.0 Volumes, Cc. Gross 1010 Tare 20 Net 990 Temperature, 75° F. Barometer, 762 mm.	r k V_0 90.0 0.839 518[a] 75.5 0.841 526[a] 63.5 Package Vacuumized, Buret at 1 Atmosphere r_r = 17.0 cc. V_0 = 485 cc.[b] Probable V_0 = 510 cc.[c]	Sample 50.0 cc. CO_2 40.5 = 81.0% O_2 0.45 = 0.9% CO 3.30 = 6.6% N_2 5.75 = 11.5% $V = \frac{r}{1-k} = 550$ cc. CO_2 = 445 cc. CO = 36 cc. O_2 = 5 cc. N_2 = 63 cc.	$\frac{455}{990-510}$ = 0.95 gram per cc. $P_0 = V/V_0$ = 1.08 atmospheres Vacuum = −2.4 inches Oxygen reacted with coffee during storage = 12 cc. = 0.024 N.T.P. cc. per gram

[a] Values somewhat high, owing to progressive desorption of gas.
[b] Value low, because ends of can are now pushed in somewhat.
[c] Approximate value at start of test, probably ±5 to 10 cc.

Table VII. Drip-Grind Coffee Vacuum-Packed in a Flexible Package

Weights, Grams	Gas Measurement	Gas Content	Density
Gross 92.2 Tare 6.8 Net 85.4 Volumes, Cc. Gross 175[b] Tare 5 Net 170 Temperature, 75° F. Barometer, 758 mm.	r_1 = 53.5 cc. r_r = 55.5 cc. V_0 = 77.2 cc.[a] Gas Analysis Sample 50.0 cc. CO_2 44.1 = 88.2% O_2 0.15 = 0.3% CO 3.20 = 6.4% N_2 2.55 = 5.1%	$V = \frac{r_1(V_0 + 103)}{100}$ = 96.5 cc. CO_2 = 85.1 cc. CO = 6.2 cc. O_2 = 0.3 cc. N_2 = 4.9 cc. Oxygen reacted with coffee during storage = 1.0 cc. = 0.011 N.T.P. cc. per gram $P_0 = V/V_0$ = 1.25 atmosphere[c]	True = $\frac{85.4}{170-77.2}$ = 0.92 gram per cc. Bulk = 85.4/170 = 0.50 gram per cc.

[a] With package walls collapsed against contents.
[b] From measurement of package dimensions before evolution of gas caused it to swell.
[c] If package walls had not swelled.

Table VIII. Dry Whole Milk in a Flexible Vacuum Package

Weights, Grams	Gas Measurement	Gas Analysis	Density
Gross 112.0 Tare 7.0 Net 105.0 Volumes, Cc. Gross 155 Tare 5 Net 150 Bell-jar vacuum = 27 inches	r k V_0 3.75 0.374 56.7 1.40 r_r = 62.0 cc. V_0 = 58.3 cc. Av. V_0 = 57.5 cc.	Sample 5.00 cc. O_2 1.00 = 20.0% N_2 4.00 = 80.0% $V = \frac{r_1}{1-k} = 6.0$ cc. O_2 = 1.2 cc. N_2 = 4.8 cc. $P_0 = V/V_0$ = 0.103 atmosphere	True = $\frac{105}{150-57.5}$ = 1.14 grams per cc. Bulk = 105/150 = 0.70 gram per cc. Gas contained in dry milk particles = 1/1.14−1/1.27 = 0.09 cc. per gram Vacuum = 26.9 inches

A representative 15-pound sample of a regular commercial blend of Colombian and Costa Rican coffee was taken from a 450-pound lot immediately after roasting. Twenty minutes later, this sample was ground on a small power grinder, one third of it to "regular grind" size, one third to "drip-grind" size, and one third to "pulverized" size. These three grinds were then packed at 29.5-inch vacuum in lots of five packages of each grind, at four different time intervals after grinding. Bell-jar vacuum determinations were made on these packages at intervals for 40 days, by which time substantial pressure equilibrium had been reached. The packages were then examined for gas content. The bell-jar vacuum results are given in Table IX, each value representing the average for five packages.

The results of the examination of these packages for gas content and gas composition are summarized in Table X, each value representing the average for five packages. In general, results for individual packages did not deviate from the group averages by more than ±2 to ±5%.

Results such as those in Tables IX and X, for a particular blend and roast of coffee, permit selection of fineness of grind and time interval between grinding and packing required to prevent swelling of flexible vacuum packages due to gases evolved after sealing. They also show the amount of residual oxygen in the packages, which eventually reacts substantially completely with the coffee. Studies are planned to correlate the amount of absorbed oxygen with the staleness or rancidity of the coffee after various times and conditions of storage.

Approximate determinations of true density were made on freshly roasted and ground coffee by displacement of a light petroleum naphtha, but some error due to solubility of the coffee oil is introduced. The results vary for different grinds of the same coffee, increasing with the fineness of grind, indicating substantial residual entrapment of gases in the cellular structure. The author has found true density values for coffee varying from 0.90 gram per cc. for a lightly roasted regular grind to 1.30 grams per cc. for a heavily roasted pulverized coffee. These figures check those shown in Table X, obtained by a different method.

Table IX. Effect of Grind and Age on Gas Pressure Developed by Coffee

Average bell-jar vacuum readings for groups of five 3-ounce flexible vacuum packages of one lot of freshly roasted coffee, in three grinds, packed at four times after grinding

Days after Packing	Age When Packed, Hours											
	Regular Grind				Drip Grind				Pulverized Grind			
	0.6	1.3	3.5	4.1	0.6	1.3	3.5	4.1	0.6	1.3	3.5	4.1
	Inches				Inches				Inches			
1	6	10	14	15	7	11	15	16	26	26	26	26
2	2	6	11	12	4	8	12	13	25.5	25.5	25.5	25.5
4	−1	2	7	8	1	5	8	9	25	25	25	25
8	−2	0	4	5	0	3	6	7	24	24	24	24
14	−4	−2	1	2	−2	0	2	3	23	23	23	23
40	−5	−3	0	1	−3	−1	1	2	22	22	22	22

Negative values represent internal pressures above 1 atmosphere, and are only estimates of conditions that would have prevailed if package walls had not swelled.

APPLICATION TO GAS LEAKAGE OR PERMEATION INTO PACKAGES

Leakage or permeation of air into flexible vacuum packages made of various sheet materials can be determined by this method. Test packages are filled with the 50- to 70-mesh Ottawa sand previously described and sealed at 29.5-inch vacuum. These packages are then stored under any desired conditions and tested from time to time for residual vacuum by the bell-jar method. Representative packages are examined at suitable intervals for gas content and gas composition. Since the sand exhibits no significant sorption or desorption of gases, any change in gas content on storage is due to leakage through pinholes or faulty seals or to permeation through the sheet material itself.

In general, uniform decrease in residual vacuum for all similar packages made of a particular material is clear evidence of gas entry by permeation instead of leakage, since it is extremely improbable that any two packages would leak at exactly the same rate. When gas entry is by permeation only, determination and

Table X. Effect of Grind and Age When Packed on Gas Evolved in 40 Days by Coffee Vacuum-Packed in Impermeable Flexible Packages

	Regular Grind				Drip Grind				Pulverized Grind			
Av. true density, grams per cc.	0.95				1.00				1.30			
Av. bulk density, grams per cc.	0.50				0.52				0.60			
Age when packed, hours	0.6	1.3	3.5	4.1	0.6	1.3	3.5	4.1	0.6	1.3	3.5	4.1
Av. net weight, grams	78.0	76.8	81.6	80.2	81.0	79.2	80.6	80.8	77.0	77.0	81.0	86.8
Av. gas space, V_0, cc.[a]	74	73	77	76	75	73	75	75	70	69	73	78
Av. gas content, V, cc.[b]	135	115	90	80	115	90	80	75	19.5	19.0	19.5	20.5
Av. pressure, P_0, atm.[c]	1.82	1.58	1.17	1.05	1.54	1.23	1.07	1.00	0.278	0.275	0.267	0.263
Av. gas composition												
CO_2, cc.	125	105	80	70	106	81	71	66.2	12.5	12.0	12.0	12.6
CO, cc.	6.3	6.0	5.8	5.7	5.5	5.6	5.5	5.4	3.0	2.8	3.0	3.2
O_2, cc.	0.5	0.6	0.5	0.4	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2
N_2, cc.	3.2	3.4	3.7	3.9	3.1	3.1	3.2	3.2	3.8	4.0	4.3	4.5
Av. CO_2, N.T.P. cc. per gram	1.47	1.26	0.90	0.80	1.20	0.94	0.81	0.75	0.15	0.14	0.13	0.13

[a] Calculated from average true and bulk densities, independently determined.
[b] Calculated by formula $V = r_1 (V_0 + 103)/100$.
[c] From $P_0 = V/V_0$; values over 1.00 are those that would obtain if package walls were rigid.

Table XI. Sand Vacuum-Packed in Permeable Flexible Packages

Package No.	1	2	3	4	5	6	7	8	Av.
Net weight, grams	265	275	276	286	271	293	269	277	277
Gas space, V_0, cc.	63.6	66.0	66.3	68.6	65.0	70.4	64.6	66.5	66.5
Day examined, D	0	0	10	10	42	42	98	98	
O_2 pressure, P, atmosphere	0.002	0.002	0.063	0.064	0.163	0.152	0.201	0.202	
N_2 pressure, P, atmosphere	0.008	0.007	0.051	0.052	0.166	0.152	0.316	0.307	
O_2 permeability, R_0, N.T.P. cc. per sq. meter per day per atmosphere			71	74	71	66	64	68	69
N_2 permeability, R_N, N.T.P. cc. per sq. meter per day per atmosphere			12	12	11	10	10	10	11
Air permeability, R_A, N.T.P. cc. per sq. meter per per day per atmosphere, calculated from O_2 and N_2 permeabilities			24	25	24	22	21	22	23
Directly determined on sheet material									27

analysis of the gas in the package permit calculation of the permeability of the package material to the surrounding gas or gases during storage. In work thus far, the author has used only storage in air at 75° F., 50% relative humidity, ambient atmospheric pressure, which has permitted determination of the permeability of various packaging materials to oxygen and to nitrogen under these conditions. The method, however, should be equally useful for determining permeability to other gases under other temperature and humidity conditions by suitable alteration of the storage conditions.

For gas entering a package by permeation, with no sorption or desorption by the package contents, $dV = 1.087\ RA\ (P_x - P)dD$, where V is the volume of gas inside the package, if measured in cubic centimeters at 75° F., 1 atmosphere, R is the permeability of the package material in N.T.P. cc. per square meter per day for 1-atmosphere pressure difference, A is the area of the package material in square meters, P_x is the external gas pressure in atmospheres, P is the internal gas pressure in atmospheres, and D is time in days. But, since $V = PV_0$, where V_0 is the gas-space volume of the package in cubic centimeters, $dV = V_0 dP$; whence we have $\ln(P_x - P_1) - \ln\ (P_x - P_2) = 1.087\ RA\ (D_2 - D_1)/V_0$.

This relation, which holds for each gas independently of the other gases present, permits calculation of the permeability of the package material from data on the gas content of the package, obtained by the author's method a suitable number of days after packing. Conversely, when the permeability of the package material to oxygen and to nitrogen is known, it permits calculation of air permeation into the package and prediction of internal pressure at any future date.

Most test packages of sand for this work have been of one standard size, containing approximately 300 grams of sand, where A = 0.030 square meters and V_0 is approximately 72 cc. The actual value of V_0 for these packages is 0.24 times the net weight of sand, as shown above. When these packages are sealed at 29.5-inch vacuum, the residual air left in each package is approximately 1.4 cc., or 0.3 cc. of oxygen and 1.1 cc. of nitrogen, so that for oxygen P_1 = 0.004 and P_x = 0.21, while for nitrogen P_1 = 0.015 and P_x = 0.79.

In studying the properties of a given packaging material, a considerable number of test packages are filled with sand and sealed at 29.5-inch vacuum. All are checked for uniformity of residual vacuum by the bell-jar method, which incidentally serves to detect any that are leaking moderately. A few representative packages are examined for amount and composition of gas, to establish the P_1 of oxygen and nitrogen at time D_1. The remaining packages are checked for uniformity of decrease in residual vacuum at suitable intervals. When there has been a substantial drop in vacuum, say to 25 inches or so, one or more packages are examined for amount and composition of gas. This permits calculation of the permeability of the package material to oxygen and nitrogen and prediction of the amounts of each of these gases in the remaining packages as of any future date.

As an illustration of the application of this method data are given in Table XI on eight packages of sand packed at 29.8-inch vacuum in a cellulose acetate–Pliofilm lamination.

The values of air permeability hold only for the condition that the ratio of partial pressure of oxygen to partial pressure of nitrogen is the same on both sides of the sheet as their ratio in normal air. The calculated air permeability is given by $R_A = 0.21\ R_0 + 0.79\ R_N$, while the direct determination of air permeability was by a method developed by the author (*2*).

Similar determinations on various cellophane-Pliofilm laminations have shown oxygen permeabilities ranging from 6 to 30 and nitrogen permeabilities from 2 to 10 N.T.P. cc. per square meter per day per atmosphere. With the exception of one experimental transparent sheet material which, in a limited preliminary study, has shown an oxygen permeability of less than 1 N.T.P. cc. per square meter per day per atmosphere, these are the lowest permeabilities the author has found for flexible packaging materials containing no metal foil. On the other hand, a considerable number of materials containing 0.0005 inch or thinner aluminum foil in combination with other materials, including cellophane, Pliofilm, and various heat-sealing coatings, have shown no measurable gas permeability.

The maximum permissible gas permeability of sheet material used for flexible vacuum packaging depends, of course, on the product to be packaged and the shelf life required of the package If it is merely required that the package retain a substantially lower pressure than atmospheric for a few months, a material such as cellulose-acetate–Pliofilm lamination might serve. However, for many food products, protection against oxygen is of utmost importance and is the primary reason for resorting to vacuum packaging. In these cases, the package material must be substantially impermeable to oxygen and to water vapor in many instances.

Dry whole milk, for example, must not be permitted to absorb more than some 0.04 cc. of oxygen per gram (*4*) if it is to remain free from staleness or rancidity. Only about 10% of this amount remains in the package when it is vacuum-packed under the most favorable commercial conditions. A 4-ounce flexible vacuum package, with a total sheet material area of 0.03 square meter and an oxygen permeability of 1 N.T.P. cc. per square meter per day per atmosphere, would admit 0.007 cc. of oxygen per day, reaching the maximum permissible limit of 4 cc. in about 18 to 20 months, and might be considered to give commercially acceptable protection against oxygen. At the same time, dry whole milk should not be allowed to gain more than some 2% in moisture content during storage, indicating a maximum permissible water vapor permeability of 0.13 gram per square meter per day for the sheet material, under the conditions of storage, to give adequate protection for 18 to 20 months. Incidentally, in this case the rates of permeation of both oxygen and water vapor into the package would remain practically constant, not falling off logarithmically with time, because both would be absorbed substantially completely by the dry milk instead of building up any appreciable back pressure.

ACKNOWLEDGMENT

The author is indebted to the Flex-Vac Division of Standard Cap and Seal Corporation for permission to publish the data herein reported, to Cornelia T. Snell for her comments and criticism of the paper, and to T. Hirata for preparation of the drawings.

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Determination of Egg Yolk in Egg White

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A method for the quantitative determination of traces of egg yolk in white involves the extraction and estimation of the cholesterol carried into the whites by the contaminating yolks, and the correlation of this value with the yolk content. Data are presented establishing the constancy of this relationship.

IN THE production of bulk egg whites problems of variation in the finished product may arise to which there are no ready answers. The quality of a batch of egg whites has generally been estimated by functional bakery tests which include measurement of the whipping properties of the whites together with examination of a test cake. These tests serve to detect poor quality, but give no clue as to its cause. Possible causes may include unknown quality characteristics, conditions of storage, or the presence of yolk in the white. It is this last item with which this paper deals.

During the breaking and separating process it is possible for a small amount of yolk to escape into the white, and bakery tests have shown that only a trace of yolk is needed to reduce materially the quality and performance of the white. In fact, as little as 0.05% yolk in the white leads to a noticeable lowering in quality, while the presence of 0.10% yolk may result in a product which is below a satisfactory standard.

The quantitative determination of minute quantities of a material as complex in composition as egg yolk necessarily involves the use of procedures not generally encountered in routine analysis. The obvious attack is to select some constituent present in the yolk but not present in the white, and set up a procedure for its determination. To be of much value, this constituent must bear a close correlation to the actual amount of yolk present—i.e., it must occur in approximately the same percentage in all egg yolks.

Since egg white contains no fat, the first approach to the problem was an attempt to extract the fat present in yolk-contaminated whites, correlating this result with the percentage of fat in yolk. These efforts were unsuccessful because of the extremely small quantity of fat actually contributed by a trace of yolk and difficulty in extracting this small amount. Attention was then turned to the possibility of detecting the cholesterol carried into the whites by the contaminating yolks.

Cholesterol in trace quantities has been detected by colorimetric means for many years and much has appeared in the literature, especially in the field of blood chemistry. The problem at hand appeared to be that of quantitatively isolating the cholesterol from the contaminated white. Procedures of this type have been applied to other dairy products including ice cream, one such procedure being the Mojonnier modification of the Roese-Gottlieb method used by Lampert (*2*) in his work on ice cream mixtures. This procedure served as a basis for a beginning, but several important changes were necessary in order to obtain quantitative extraction, since the original method was intended for use on mixtures containing much higher percentages of yolk than those encountered here. Further modifications were necessary because egg white, in the presence of alcohol, one of the solvents used in the method, coagulates into a gelatinous mass which resists extraction.

The method used to develop the color was based on the Liebermann-Burchard reaction for cholesterol. Many references to this method appear in the literature and the results reported are numerous and varied. The procedure is essentially as follows:

Extracted cholesterol is dissolved in some anhydrous reagent such as chloroform. An aliquot is pipetted into a dry tube and a specific volume of a 10 to 1 mixture of acetic anhydride–sulfuric acid reagent is added. The color which develops is matched with that obtained with standards treated in the same manner, prepared from pure cholesterol dissolved in the same solvent.

The Coleman Universal Model 11 spectrophotometer with PC-4 filter was used throughout this work, and round cuvettes, 19 × 105 mm., were used for all readings. To establish ideal conditions it became necessary to study color development of this reaction.

EXPERIMENTAL

The first efforts were directed toward applying the Coleman spectrophotometer to reading the color developed by the Liebermann-Burchard reaction. Solutions containing pure cholesterol in chloroform were prepared and a procedure recommended by Reinhold (*3*) for color development was used. Five milliliters of a chloroform solution containing pure cholesterol were pipetted into a dry test tube, 2 ml. of a 10 to 1 mixture of freshly distilled acetic anhydride and sulfuric acid were added, and the solution was allowed to stand in the dark at 35° C. for 24 minutes. The green color which developed was read in the spectrophotometer against pure chloroform in the solvent cell. The transmittance was determined over the range 400 to 800 mμ using the appropriate filters. The spectral transmittance curve obtained appears in Figure 1. The point of maximum absorption, 640 mμ, was used for all measurements.

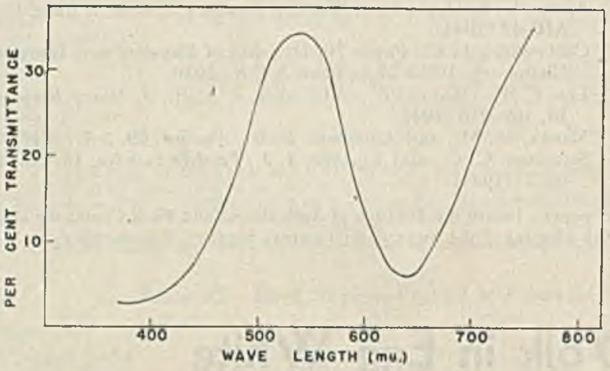

Figure 1. Spectral Transmittance Curve

Color developed with pure cholesterol in chloroform using acetic anhydride-sulfuric acid mix

The intensity of the color produced by the Liebermann-Burchard reaction is dependent not only upon the cholesterol content, but also upon the time of standing and the temperature. A study was made of these factors to establish the most suitable conditions. When color development was allowed to take place at 35° C., the color increased sharply in intensity during the first few minutes of reaction, after which it gradually faded to a much lighter shade.

Work by Ireland (*1*) indicated that use of lower temperatures during color development leads to much more favorable results. After trying several temperatures, it was found that color development at 18° C. in the dark gave the best results. A comparison of the rate of color formation at 35° and 18° C. appears in Figure 2.

While color development is slower at 18° C., it leads to conditions of higher stability near the point of maximum intensity; the change in transmittance between readings at the 20- and 30-minute intervals is 0.5%. This eliminates the need for making readings after an exact time has elapsed and permits an analyst to run a greater number of samples at one time. The curve in Figure 2 indicates that the color near the point of maximum intensity, when developed at 35° C., is unsatisfactory, as it remains at this intensity only momentarily and is in a gradual state of change thereafter. After standing for 25 minutes the rate of change is not so rapid, extensive fading having already occurred. Transmittance curves for known amounts of cholesterol subjected to the color development procedure at both temperatures are shown in Figure 3.

As indicated in the graph, the lower temperature is the more favorable. Standing time refers to standing in the lightproof cabinet until immediately before reading.

For ordinary work a suitable container can be made by wrapping several sheets of asbestos paper around a tin can. The lid is lined with asbestos with a small hole through the top just large enough to permit a thermometer to pass. The can may be placed on an asbestos pad. Water is poured into the cabinet and regulated to 18° ± 0.5° C. It will be found to change less than 0.5° C. in a half hour. The tubes containing the chloroform solution of cholesterol must remain in the bath at 18° C. until they come to temperature. The bath is regulated to maintain proper temperature control and the reagent is then delivered to each tube. The lid is replaced until the time for development has elapsed.

Some difficulty was encountered in extracting the cholesterol by the Mojonnier modification of the Roese-Gottlieb procedure, which calls for successive additions of alcohol, ether, and petroleum ether, with a shaking period after each addition. The alcohol coagulated the egg white to form a gelatinous mass which resisted extraction. After several unsuccessful modifications it was found that addition of 25 ml. of ammonia to the sample before introducing the solvents left it in a highly fluid state. Three extractions are made, but the ammonia need be added only once. This procedure is set up to determine all the cholesterol present in a 10-gram sample of egg white, but when analyzing yolk, a 1-gram sample is used and the extracted cholesterol is dissolved in chloroform. This is made to volume in a 250-ml. volumetric flask and a 5-ml. aliquot is used for analysis.

In order to establish the cholesterol content of egg yolk, numerous individual yolks were analyzed. Some of the values obtained appear in Table I.

These data confirm results reported in the literature and lie in a sufficiently close range to provide useful criteria for the amount of yolk present.

Eggs of varying histories were separated and the uncontaminated whites were analyzed (Table II) to determine the "blank" value which would be obtained when no yolk was present.

Table I. Cholesterol Content of Egg Yolk

Yolk No.	Cholesterol %	Cholesterol Contributed by Adding 0.05% Yolk to 10 Grams of White *Gram*
1	1.30	0.000065
2	1.20	0.000060
3	1.35	0.000067
4	1.35	0.000067
5	1.45	0.000072
6	1.20	0.000060
7	1.35	0.000067
8	1.25	0.000062
9	1.30	0.000065
10	1.40	0.000070
Av.	1.32	0.000065

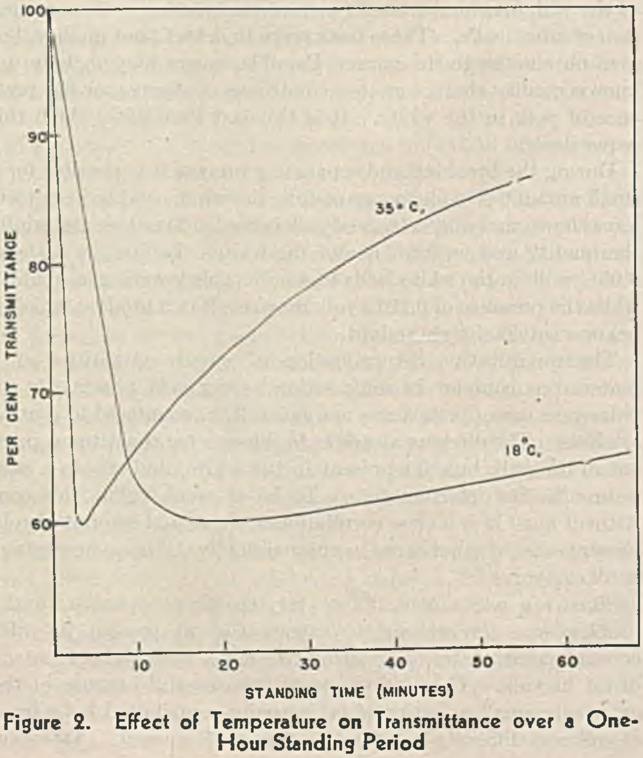

Figure 2. Effect of Temperature on Transmittance over a One-Hour Standing Period

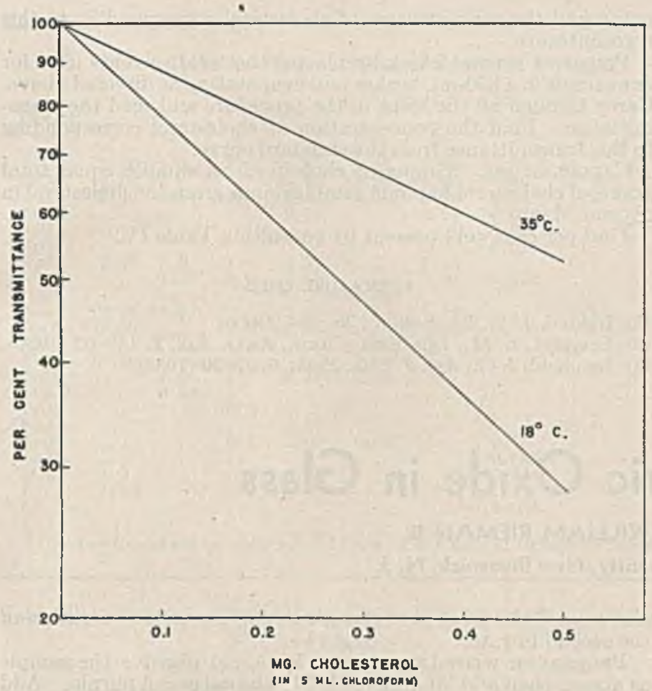

Figure 3. Comparison of Calibration Curves

At 35° and 18° C., 650 mμ

Table II. Blank Value of Pure Egg White

White	Cholesterol in 10 Grams of Sample *Gram*
Fresh white	0.00011
	0.00011
	0.00011
	0.00011
	0.00012
	0.00011
	0.00012
	0.00011
White from 6 months old cold storage egg	0.00012
	0.00012
Av.	0.000114

This blank value appears to be essentially the same for all egg whites. Analyses of a large number of samples of pure egg whites confirm the constancy of this figure.

Having established the cholesterol content of yolk and the blank obtained with pure white, mixtures of yolk in white in varying percentages were prepared and analyzed.

Table III indicates that the process accounts for all the cholesterol in the sample. Agreement between actual figures and theoretical values is extremely close. On the basis of these findings it is possible to set up a table relating the weight of cholesterol found to the per cent yolk responsible for its presence (Table IV).

A reagent blank determination should also be made by adding the total amount of solvents used for the analysis of one sample to a beaker and evaporating them on the steam bath. The residue should be carried through all the steps in the analysis and the value obtained subtracted from that found for the sample. Occasional contamination of solvents will lead to high results if a correction is not made.

METHOD

Reagents. Ammonium hydroxide (sp. gr. 0.90), A.C.S. specification.

Ethyl Alcohol (95%).

Ethyl ether, A.C.S. specification.

Petroleum ether, b.p. 35–38° C., A.C.S. specification.

Potassium hydroxide, A.C.S. specification.

Chloroform, A.C.S. specification.

Cholesterol, powdered, reagent quality.

Table III. Analysis of Egg Whites Containing Known Amounts of Added Yolk

Sample		Cholesterol in 10 Grams of Sample *Gram*	Cholesterol Theoretically Present in 10 Grams of Sample *Gram*
Pure white + 0.05% yolk		0.00018	0.00018
		0.00018	
		0.00018	
		0.00018	
	Av.	0.00018	
Pure white + 0.10% yolk		0.00024	0.00024
		0.00023	
		0.00024	
		0.00023	
		0.00024	
	Av.	0.00024	
Pure white + 0.20% yolk		0.00037	0.00037
		0.00035	
		0.00036	
		0.00037	
	Av.	0.00036	

Sulfuric acid (sp. gr. 1.84), A.C.S. specification.

Acetic anhydride, A.C.S. specification.

Solutions. Acetic anhydride–sulfuric acid mixture. Add 10 ml. of sulfuric acid (sp. gr. 1.84) slowly and with cooling to 100 ml. of freshly distilled acetic anhydride in a 200-ml. glass-stoppered Erlenmeyer flask. Reagent should be water-white.

Preparation of Standard Curve. Weigh accurately 50 ± 0.2 mg. of pure cholesterol into a clean dry 500-ml. volumetric flask. Add pure chloroform to dissolve and make to volume with chloroform. This solution contains 0.1 mg. of cholesterol per ml.

Pipet 1, 2, 3, 4, and 5 ml. of the cholesterol solution into five clean dry 15 × 150 mm. test tubes, and make total volume of each to 5 ml. with chloroform. Place in a lightproof constant-temperature bath at 18° C. for 5 minutes. Check temperature of bath at the end of 5-minute period and readjust to 18° C. if necessary.

Add 2 ml. of acetic anhydride–sulfuric acid mixture (18° C.) to each tube, mixing each thoroughly with a clean, dry, glass rod. Do this as quickly as possible, allowing a minimum of light to enter the cabinet. Replace cover on cabinet and allow to stand for 25 minutes.

Leave each tube in the cabinet until immediately before reading. Using an appropriate filter determine the transmittance in a spectrophotometer set at 640 mμ with a solvent cell of pure chloroform set at 100% transmittance. Plot transmittance against concentration of cholesterol using semilogarithmic paper. This is the standard curve.

Procedure. Weigh 10 ± 0.1 grams of liquid egg white into a 200-ml. glass-stoppered flask, add 25 ml. of ammonium hydroxide (sp. gr. 0.90), and swirl to mix. Add 10 ml. of 95% alcohol and shake for 1 minute. Add 25 ml. of ethyl ether and shake for 1 minute. Add 25 ml. of petroleum ether and shake for 1 minute. Allow to stand until the clear solvent layer separates at the top. If an emulsion forms, break it with 5 ml. of alcohol.

Decant the clear solvent layer into a clean, dry, 250-ml. beaker. Repeat the extractions on the residue in the flask twice, beginning with the addition of alcohol, but using 5 ml. of alcohol each time instead of 10, adding each final solvent layer to the 250-ml. beaker.

Place the beaker containing the extracts on a steam bath and evaporate until only a small amount of alcohol remains. Remove and cool. Add 15 ml. of alcohol, cover with a watch glass, and bring to a boil on a hot plate covered with a sheet of asbestos.

Table IV. Relationship between Cholesterol Content and Egg Yolk Present

Cholesterol Found in 10 Grams of White	Egg Yolk Present, %
0.00011	0.000
0.00015	0.025
0.00018	0.050
0.00021	0.075
0.00024	0.100
0.00027	0.125
0.00030	0.150
0.00033	0.175
0.00037	0.200

Add 1 ml. of 50% aqueous potassium hydroxide solution and boil gently for 10 minutes. Cool, wash down the sides of the beaker with 30 ml. of ethyl ether, and transfer to a clean 125-ml. separatory funnel. Wash out the beaker with two 25-ml. portions of distilled water, transferring each to the separatory funnel. Rotate the funnel, but do not shake. Break any emulsion with 5 ml. of alcohol. Withdraw the soap solution from the bottom. Wash the ether layer 3 times with 50-ml. portions of distilled water. If the last washings are not neutral to phenolphthalein, repeat until washings are neutral.

Pour the ether layer into a 50-ml. beaker and evaporate on a steam or water bath until all moisture is gone. Cool and pipet 5.0 ml. of chloroform into the beaker, swirling gently to ensure solution. Transfer the solution to a clean, dry 15 × 150 mm. test tube and place in a lightproof constant-temperature cabinet at 18° C. for 5 minutes. Proceed as directed above and determine the transmittance of each solution. From the standard curve find the concentration of cholesterol corresponding to this transmittance.

Prepare a reagent blank by placing the total solvents used for one sample in a 250-ml. beaker and evaporating as directed above. Carry through all the steps in the procedure and read the transmittance. Find the concentration of cholesterol corresponding to this transmittance from the standard curve.

CALCULATIONS. Grams of cholesterol in sample equal total grams of cholesterol found in sample minus grams of cholesterol in reagent blank.

Find per cent yolk present by consulting Table IV.

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Determination of Boric Oxide in Glass

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A method has been developed for the determination of boron in glass which is more accurate and more rapid than the methods commonly used. Data obtained on synthetic mixtures and actual glass samples show that this method yields results with a mean error, signs disregarded, of 0.04% B_2O_3 with glasses containing less than 15% B_2O_3.

THE essential differences among the various methods for the determination of boric oxide in glass lie in the method of separating the interfering substances, such as iron, aluminum, or silica, from the solution containing the boric acid, which is then titrated with sodium hydroxide in the presence of mannitol. Thus, Wherry and Chapin (*5*) dissolve the sodium carbonate fusion mixture in hydrochloric acid, and add calcium carbonate in moderate excess in order to neutralize the free hydrochloric acid and to precipitate the sesquioxides and most of the silica. In another procedure (*5*), they recommend separation of the boric acid from the solution by distillation of the methyl ester. Glaze and Finn (*1*), on the other hand, base their method on the partition of boric acid between water and ethyl ether in the presence of ethyl alcohol and a small amount of sulfuric acid.

The method described in this paper is more accurate and less time-consuming than procedures which have been in use heretofore.

EXPERIMENTAL

PROCEDURE WITH pH METER. Fuse a 500-mg. sample with 3 grams of sodium carbonate for 10 minutes. Dissolve the melt in 20 ml. of 6 *N* hydrochloric acid and adjust the pH of the solution to 5.0 to 5.5 by means of 6 *N* sodium hydroxide. Aluminum, iron, and similar elements, along with most of the silica, are precipitated at this point. Sweep out the carbon dioxide by bubbling air (purified by passing through concentrated sulfuric acid and Ascarite) through the solution at 60° ± 5° C. for 30 minutes. Filter the reaction mixture, and wash the precipitate with warm water until the volume of the filtrate is 250 ml. Cool the solution to room temperature, and adjust its pH to 6.30 by means of carbonate-free 0.05 *N* sodium hydroxide. Add 40 grams of mannitol to the solution. The pH is decreased markedly by the formation of mannitoboric acid. Now titrate to a pH of 6.30 again with 0.05 *N* sodium hydroxide. The alkali used in this titration is a measure of the boron in the sample.

In some cases, a double precipitation of the residue is necessary to recover the coprecipitated boric acid. In order to accomplish this, dissolve the precipitate in 10 ml. of 6 *N* hydrochloric acid, and repeat the same procedure, running a separate titration of the second filtrate.

PROCEDURE WITH INDICATOR. Fuse and dissolve the sample as above, then add 20 drops of 0.04% bromocresol purple. Add 6 *N* sodium hydroxide until the first distinct color change (yellow to dirty green) can be recognized. At this point, the pH of the solution is approximately 5.5. Then proceed as in the pH meter method. Adjust the pH to 6.30 by comparing the color of the solution with that of a phosphate comparison buffer.

TITRATION CORRECTIONS. The regular titration of boric acid with sodium hydroxide in the presence of mannitol, following the

Table I. Titration Corrections

$HBO_2.H_2O$ Found, Milliequivalents	Corrections, Milliequivalent	$HBO_2.H_2O$ Found, Milliequivalents	Corrections, Milliequivalent
0.0	0.000	1.2	0.024
0.1	0.005	1.4	0.026
0.2	0.008	1.6	0.029
0.4	0.013	1.8	0.031
0.6	0.016	2.0	0.033
0.8	0.019	2.4	0.036
1.0	0.022	2.8	0.040

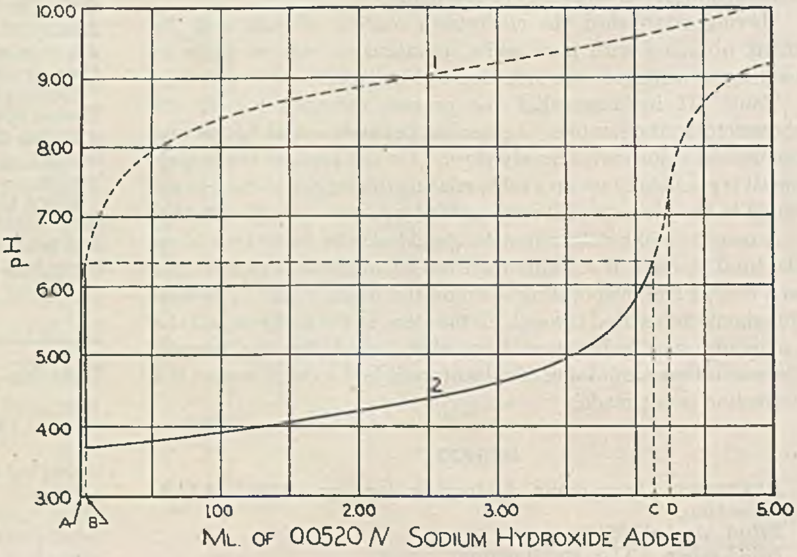

Figure 1. Potentiometric Titration Curves for Boric Acid

1. Without mannitol
2. With mannitol

Table II. Compositions of Synthetic Mixtures

Constituent	Mixture Number										
	1	2	3	4	5	6	7[a]	8	9	10	11
B_2O_3	1.47	2.0	3.0	4.13	6.15	7.22	12.76	18.3	41.0	42.8	71.8
SiO_2	40.16	67.3	..	66.80	37.04	66.90	80.60	52.40	..	..	..
Al_2O_3	2.90	2.5	10.0	2.54	3.70	6.38	1.94	1.9	..	5.0	22.4
Fe_2O_3	...	...	..	0.17	...	0.22	0.076	...	..	..	..
TiO_2	...	...	..	...	...	...	0.027	...	..	..	..
ZrO_2	...	...	..	...	...	...	0.013	...	..	..	..
CaO	7.21	7.0	..	1.73	...	7.94	....	0.3	..	..	..
MgO	...	0.17	4.0	2.60	...	0.61	0.026	...	..	..	..
BaO	...	...	..	...	42.04	...	....	...	..	..	..
Na_2O	12.06	14.0	..	7.40	...	1.25	4.16	2.3	..	..	..
K_2O	2.00	...	12.0	1.75	...	2.40	0.16	4.3	..	..	..
Li_2O	...	...	..	...	...	...	....	...	..	..	5.8
PbO	25.50	...	..	...	1.26	...	....	...	..	52.0	..
ZnO	...	7.0	..	9.75	9.25	...	....	...	59.0	..	..
Mn_2O_3	...	0.28	..	...	...	...	....	...	..	..	..
P_2O_5	...	...	70.5	...	...	...	....	...	..	..	..
Sb_2O_3	...	...	..	1.29	...	...	....	20.4	..	..	..
As_2O_3	...	...	0.5	2.05	0.56	...	0.14	0.1	..	..	..
As_2O_5	...	...	..	...	...	...	0.085	...	..	..	..
SO_3	1.0	...	..	...	...	...	0.009	...	..	..	..
F	7.10	...	..	...	...	...	....	...	..	..	..
Cl	...	...	..	...	...	...	0.036	...	..	..	..

[a] Composition given on certificate of glass 93 of National Bureau of Standards.

Table III. Determination of Boric Oxide in Synthetic Mixtures by pH Meter

Mixture No.	No. of Determinations	Average Error, %	Mean Deviation, %
1	1	−0.03	...
2	3	+0.03	0.03
3	3	−0.03[a]	0.03
4	4	+0.06	0.03
5	6	+0.03	0.03
6	1	−0.03	...
7	4	−0.04	0.03
8	1	−0.10	...
9	2	−0.20	0.07
10	3	−0.03	0.03
11	4	−0.36	0.10

[a] Results obtained by modified method designed to remove phosphate.

Table IV. Determination of Boric Oxide in Glasses

Glass	B_2O_3 Reported, %	B_2O_3 Found, %	Difference, %	Mean Deviation, %	No. of Precipitations	Method
Bureau of Standards 128	1.52	1.52[a]	0.00	0.00	One	pH meter
Bureau of Standards 93	12.76	12.51[b]	0.25	0.01	Two	pH meter
Corning, 1	0.61	0.59	0.02	0.01	One	pH meter
Corning, 3	ca. 14.7	14.71	0.0	0.0	Two	pH meter
Armstrong 224*abc*	9.80[c]	9.91	0.11	.01	Two	pH meter
Armstrong 427*abc*	9.75[c]	9.66	0.09	0.02	Two	pH meter
Bureau of Standards, 92	0.70	0.65	0.05	0.01	One	Indicator
Bureau of Standards, 128	1.52	1.50	0.02	0.01	One	Indicator

[a] Corrected for change in loss on ignition.
[b] Dried at 500°.
[c] By method of Glaze and Finn.

directions of Hollander and Rieman (*2*), cannot be employed because of the interference of varying amounts of carbon dioxide and colloidal silica which remain in the solution. Therefore, the method of titration illustrated by the solid parts of the curves in Figure 1 is used. The first adjustment of the pH to 6.30 results in the neutralization of a small fraction of the boric acid along curve 1, for which correction *AB* must be applied. Upon the addition of mannitol, the boric acid is converted to the stronger mannitoboric acid; consequently, the pH of the solution is depressed markedly. This is illustrated by the solid vertical line connecting the two curves. The second adjustment of the pH to 6.30 follows the path of curve 2. The pH of 6.30 is reached before the equivalence point (steepest part of curve 2). Therefore, another correction corresponding to volume *CD* must be applied.

The total corrections, $AB + CD$, for various amounts of boric acid are given in Table I. These data were obtained by potentiometric titrations of the indicated quantities of boric acid and of mannitoboric acid under the recommended conditions and subsequent interpretation of the graphs as explained above. The correction is to be added in all cases.

The recommended conditions for the titration—i.e., an initial and final pH of 6.30 and the addition of 40 grams of mannitol—were chosen because they give minimum corrections. The recommended initial volume of 250 ml. is the smallest that can be used without evaporation if the precipitate is to be washed thoroughly.

Small amounts of carbonic acid and silica may be present in the solution during the titration without interfering because the pH is the same at the end as at the beginning. Large amounts of these substances interfere, however, by giving small slopes to the graph in the vicinity of pH = 6.30, thus making it impossible to measure accurately the sodium hydroxide required for the titration. The recommended procedure leaves only small amounts of these substances in the solution.

RESULTS

Several synthetic mixtures, similar to some glass compositions given by Morey (*3*), were analyzed by this method (Tables II and III). Several glasses were also analyzed (Table IV).

DISCUSSION

Table III shows that the boric oxide content of glasses with less than 15% B_2O_3 can be determined by the pH meter method with a mean error of ±0.04% B_2O_3 without interference from Al_2O_3, Fe_2O_3, CaO, BaO, MgO, K_2O, Li_2O, PbO, ZnO, Mn_2O_3, Sb_2O_3, As_2O_3 (As_2O_5), TiO_2, ZrO_2, SO_3, and F.

Phosphate causes high results unless the melt is dissolved in 6 *N* nitric acid and the phosphate removed by the addition of a slight excess of silver nitrate at pH 5.5. This interference was also mentioned by Ruehle and Shock (*4*). It is caused by the activation of the phosphoric acid by mannitol.

The authors' method yielded results with a mean error of −0.04% B_2O_3 on a synthetic mixture (No. 7) identical in composition with the certified value of glass 93 of the National Bureau of Standards. The authors believe, therefore, that the true boric oxide content of this glass is not 12.76%, but nearer 12.51%.

The indicator method gives satisfactory results for glasses with low boric oxide contents. High-boron glasses will buffer the solution too much to yield distinct color changes by which the end point can be recognized.

This method is probably applicable to many samples other than glasses.

ACKNOWLEDGMENT

The authors are indebted to the Armstrong Cork Company and the Rutgers Research Council for financial assistance in this work, and to the Armstrong Cork Company and the Corning Glass Works for their analyzed glass samples.

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Presented before the Division of Analytical and Micro Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J.

The pH of Wines

Examination of Glass and Quinhydrone Electrode Values

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Values obtained for the pH of wines by means of the glass and quinhydrone electrodes sometimes agree, but often differ by more than 0.1 pH unit. The effects of several constituents of wine on these electrode systems have been examined and it is concluded that, whereas the glass electrode values are essentially correct, the quinhydrone electrode, when used in wines, is subject to at least two sources of error. Alcohol causes the quinhydrone electrode to register low values, while reducing substances, such as sulfites and tannin, lead to high values. The correct and near-correct values obtained with the quinhydrone electrode in some wines are due to a compensation of such errors. Neither the hydro-quinhydrone nor the quino-quinhydrone electrodes give more reliable results in wines than the regular quinhydrone electrode.

THE significance of pH values in relation to the physical, chemical, and biological changes which occur in wine has been pointed out by many investigators, notably Ventre (*17*), Genevois and Ribéreau-Gayon (*11*), Brémond (*3*), and Ribéreau-Gayon (*14*, *15*). The present writer (*10*) has indicated the importance of pH in relation to bacterial spoilage of wines.

Of the various methods available for determining the pH value of wine, the quinhydrone electrode system has been one of the most widely used. Chief among the advantages claimed for this system are that it is easily and quickly assembled, simple to operate, reaches a stable potential rapidly, and can be used in wines which contain small to moderate amounts of sulfites. Because of these features it has been widely recommended for determining the pH values of wines (*3*, *6*, *11*, *16*). Within recent years, however, improvements in the design and construction of glass electrodes and vacuum tube potentiometers have resulted in the introduction of the glass electrode system into industrial laboratories and an increasing number of glass electrode pH meters are now being used in wineries.

From time to time, discrepancies have been noticed between the results obtained by means of the glass electrode and the quinhydrone electrode for the pH values of wines. Thus Ribéreau-Gayon (*16*) found that the pH values of wines determined by means of the glass electrode were slightly (up to 0.06) higher than those registered by the quinhydrone electrode. Using tartrate buffers containing different amounts of alcohol, he obtained evidence that the deviation was due to alcohol, but did not indicate which electrode system gave the more correct values. Hooper (*12*) recorded differences between glass electrode and quinhydrone electrode values for several Australian fortified wines, which varied from 0.05 to 0.18 pH unit. Liebmann and Rosenblatt (*13*) determined the pH values of different whiskies by means of the glass and the quinhydrone electrodes and found the quinhydrone electrode values lower than the glass electrode values by about 0.37 pH unit. They calculated, from experimental data obtained by Dole (*8*), that the theoretical deviation of the glass electrode values in 45% alcohol was only about 0.03 pH unit and they therefore concluded that the glass electrode values for whisky were essentially correct and the quinhydrone electrode values in error by about −0.37 pH unit.

In view of the foregoing, it seemed desirable to make a more detailed examination of the values obtained with the glass and quinhydrone electrode systems for the pH of wines.

APPARATUS AND REAGENTS

ELECTRODE SYSTEMS. *Glass Electrode System.* The glass electrode was a Kerridge pattern recessed bulb type, having the bulb blown of Corning 015 special electrode glass. This was used with an internal quinhydrone–0.1 *N* hydrochloric acid half-cell and a saturated calomel half-cell as a reference half-cell. Between determinations the outside of the bulb of the glass electrode was rinsed with distilled water, dried lightly with filter paper, and then rinsed with a portion of the next test solution. When not in use, the glass electrode was kept filled with, and immersed in, distilled water.

Leads from the electrodes to the potentiometer were of insulated copper wire, kept as short as possible, and the electrode clamps were supported in blocks of polystyrene.

Quinhydrone Electrode System. The electrodes were made of pieces of 10 × 7 mm. platinum foil, each welded to a length of platinum wire and sealed into a glass tube. Electrical connections were made by means of binding screws at the top of the wire. The electrodes were heated to redness in an alcohol flame for a few seconds before use and at frequent intervals during each batch of determinations.

Quinhydrone freshly prepared from hydroquinone and ferric ammonium alum according to the method of Biilmann, described by Britton (*4*), was washed four times with iced distilled water and dried between filter paper at room temperature. Since the presence of traces of iron in quinhydrone prepared by Biilmann's method may be a source of error, a batch of quinhydrone prepared by mixing alcoholic solutions of quinone and hydroquinone according to the method of Valeur (described by Britton, *4*), was also used for comparison. This latter product was in a coarser state of division and was rather slower in giving stable potentials than that prepared by Biilmann's method, but otherwise no significant differences were noticed between the results obtained with the two preparations.

Bubbling Hydrogen Electrode System. The platinum electrodes were of similar construction to those described above. They were cleaned by heating in dilute (1 + 1) aqua regia and lightly platinized, so that only thin brown coatings of platinum black were obtained. Before each determination, these electrodes were connected to the negative pole of a 4-volt storage battery, electrolyzed for half a minute in 0.1 *N* sulfuric acid, then carefully washed with distilled water before being placed in the test solution. All determinations were made in duplicate, using two electrodes and electrode vessels, and when discrepancies occurred, the electrodes were cleaned and replatinized.

The electrode vessels were a modification (*2*) of the bubbling hydrogen electrode vessel described by Best (*1*).

REFERENCE HALF-CELL. A saturated calomel half-cell was used in conjunction with each of the above electrode systems.

LIQUID JUNCTIONS. Liquid junctions between the calomel cell and the test solutions were formed by means of a side tube which was kept filled with a saturated solution of potassium chloride from a reservoir, and which was closed with a ground-glass cap. Before each determination the lower end of the tube was washed with distilled water and dried with filter paper. The junction was then renewed by loosening the cap momentarily to allow a few drops of the potassium chloride solution to escape and the outside of the cap was lightly wiped with filter paper.

POTENTIOMETER. pH measurements were made with a vacuum tube potentiometer calibrated to give readings directly in pH units, and connected to a 12-volt storage battery as a source of current. The calibration of the instrument was checked by using it with a quinhydrone electrode, to measure the pH values of the buffers listed below, and comparing these values with those obtained for the same buffers and with the same electrode, by means of a Cambridge portable potentiometer. The values obtained with the two instruments did not differ by more than 0.02 pH unit in any of these solutions.

BUFFER SOLUTIONS. The reagents used in the preparation of buffer solutions were all of analytical reagent grade.

For standardizing and checking the electrode systems the following solutions were used:

0.05 *M* potassium hydrogen phthalate	pH 4.01 (3.97)
Sorensen's phosphate buffer	pH 6.26 (6.24)
McIlvaine's citrate-phosphate buffer	pH 4.63 (4.6)

The pH values in parentheses are those given by Clark (*5*) for these solutions, but in these investigations the value of 4.01 for

Table I. pH Values of Wines

Type	No.	Alcohol % by Volume	pH Values		
			Glass electrode	Quinhydrone electrode	Deviation of quinhydrone from glass
Sweet red	1	20	3.74	3.50	−0.24
	2	20	3.72	3.52	−0.20
	3	20	3.71	3.56	−0.15
	4	20	3.84	3.69	−0.15
	5	20	3.66	3.52	−0.14
	6	20	3.45	3.29	−0.16
	7	20	3.69	3.56	−0.13
	8	20	3.73	3.62	−0.11
	9	19	3.64	3.52	−0.12
	10	19	3.64	3.52	−0.12
Sweet white (spoiled)	11	19	4.29	4.16	−0.13
Muscat	12	20	3.94	3.81	−0.13
Dry white	13	14	3.21	3.18	−0.03
Dry white (carrying sherry flor)	14	13	3.32	3.30	−0.02
	15	15	3.31	3.24	−0.07
Dry white (sherry)	16	17.5	3.40	3.30	−0.10
Dry white	17	14.5	3.32	3.26	−0.06
	18	15	3.59	3.56	−0.03
	19	13.5	3.73	3.70	−0.03
	20	14.0	3.80	3.77	−0.03
	21	11.5	2.95	2.93	−0.02
	22	10.0	3.22	3.22	0.00
Dry red	23	11.5	3.48	3.58	+0.10
	24	11.5	3.53	3.65	+0.12
White grape juice (pasteurized)	25	..	3.33	3.34	+0.01
	26	..	3.42	3.41	−0.01

the pH of 0.05 *M* phthalate was adopted as the primary standard in accordance with the recommendation of Dole (*7*). The pH values of the Sorensen and McIlvaine buffers were then found to be 6.26 and 4.63, respectively, by means of the glass electrode.

The effect of ethyl alcohol on pH determinations was studied with phthalate, tartrate, and citrate buffers, the last two being used instead of the phosphate buffers previously mentioned, as it was considered that they would provide conditions more comparable with those in wine. These solutions were made up in the following concentrations:

0.1 *M* potassium hydrogen phthalate
0.1 *M* tartrate solution. 15.0 grams of tartaric acid and 80 ml. of 1.0 *N* sodium hydroxide per liter
0.066 *M* citrate solution. 14.0 grams of citric acid and 68 ml. of 1.0 *N* sodium hydroxide per liter

Hundred-milliliter quantities of these solutions were diluted with 100-ml. quantities of appropriate alcohol-water mixtures before use, so that the final concentrations were 0.05 *M* phthalate, 0.05 *M* tartrate, and 0.033 *M* citrate and the pH values of the diluted aqueous solutions were found by means of the glass electrode to be 4.01, 3.33, and 3.87, respectively.

EXPERIMENTAL

All determinations were carried out at room temperature, which was 15° ± 2° C. during the course of the investigations, but the variation never exceeded 0.5° C. during any one batch of determinations.

Standardizing and Checking Electrode Systems and Potentiometer. Before each batch of determinations with the glass or quinhydrone electrodes, the potentiometer was adjusted to give a reading of 4.01 for the pH of the 0.05 *M* phthalate buffer. The electrode system and potentiometer were then further checked against the phosphate and the citrate-phosphate buffers before other measurements were made. The check against these three buffers was repeated at the end of each batch of determinations and if the pH values recorded in the second check differed from those first obtained by more than ±0.02, the whole batch of determinations was repeated with fresh samples. With electrode systems other than the glass and quinhydrone, the potentiometer was standardized as indicated in Tables II and V.

The pH values obtained for the phosphate and citrate-phosphate buffers on different days provide an indication of the reproducibility of results. The standard deviations calculated from these results did not exceed ±0.02 for either the glass or the quinhydrone electrode. The standard deviations of the values obtained for wines were not determined statistically, but all determinations were made in duplicate and the mean values taken. When, as rarely happened, the values obtained for duplicate samples differed by more than 0.02, the determination was repeated with fresh samples. This procedure could not be followed with the quinhydrone values recorded in Table IV, however, for in those samples which showed appreciable drift in potential, agreement between duplicates was usually unsatisfactory. Except in this special case, however, it is considered that under the experimental conditions differences exceeding ±0.03 pH unit are significant.

Determination of pH Values of Wines by Means of Glass and Quinhydrone Electrodes. The pH values of several wines as determined by the glass and the quinhydrone electrodes are shown in Table I. As can be seen, the glass electrode values are nearly all higher than the quinhydrone electrode values, but the differences between them vary considerably from one wine to another.

Effect of Ethyl Alcohol on Glass and Quinhydrone Electrodes. In view of the results obtained by Ribéreau-Gayon (*16*) and by Liebmann and Rosenblatt (*13*) concerning the effects of ethyl alcohol, it seemed desirable to determine the extent to which differences such as those recorded in Table I were due to the alcohol present in the wine. Accordingly, the pH values of phthalate, tartrate, and citrate buffers containing different concentrations of ethyl alcohol were determined by means of the glass and the quinhydrone electrodes (Table II).

Duboux and Tsamados (*9*) have shown that the dissociation of organic acids is depressed by the presence of ethyl alcohol and so, as would be expected, the pH values found for the buffer solutions in Table II increased with increasing alcohol content. Although it seemed likely from the data of Liebmann and Rosenblatt (*13*) that the glass electrode values would be correct, it was considered desirable to check these values with the bubbling hydrogen electrode as a standard. The hydrogen electrode values for the tartrate and citrate solutions are shown in column 3 of Table II, and as can be seen, they agree well with the glass electrode values.

A comparison of the results presented in Tables I and II indicates that the deviations of the quinhydrone from the glass electrode values in wines are often smaller than would be expected from a consideration of the amounts of alcohol present. It seems likely, therefore, that in some wines the error in quinhydrone electrode values due to alcohol is in part offset by some other factors which cause an apparent increase in pH values. In order to obtain more information on this point several wines were treated as follows: 200 ml. of wine were evaporated to about 40 ml. under reduced pressure at 60° C. to remove alcohol. Half of each de-

Table II. pH Values of Buffers Containing Ethyl Alcohol

Buffer	Alcohol Content % by Volume	pH Values				
		Hydrogen electrode	Glass electrode	Deviation of glass from hydrogen	Quinhydrone electrode	Deviation of quinhydrone from glass
0.05 *M* phthalate	None	...	4.01[a]	....	4.01[a]	....
	10	...	4.21	....	4.14	−0.07
	20	...	4.44	....	4.30	−0.14
Tartrate	None	3.33[a]	3.33[a]	....	3.33[a]	....
	5	3.40	3.40	0.00	3.36	−0.04
	10	3.47	3.47	0.00	3.40	−0.07
	15	3.55	3.54	−0.01	3.43	−0.11
	20	3.64	3.63	−0.01	3.48	−0.15
	25	3.75	3.73	−0.02	3.52	−0.21
Citrate	None	3.87[a]	3.87[a]	....	3.87[a]	....
	5	3.94	3.94	0.00	3.91	−0.03
	10	4.01	4.01	0.00	3.95	−0.06
	15	4.08	4.08	0.00	3.99	−0.09
	20	4.16	4.15	−0.01	4.03	−0.12

[a] In each case potentiometer and electrode system was standardized to give correct value for aqueous buffer solution.

Table III. Effect of Alcohol on pH Values of Wines as Measured by Glass and Quinhydrone Electrodes

Wine No.	7	9	11	12	13	14
Original wines						
Alcohol content, volume %	20	20	19	20	14	13
pH by glass electrode	3.69	3.64	4.29	3.94	3.21	3.32
pH by quinhydrone	3.56	3.52	4.16	3.81	3.18	3.30
Quinhydrone deviation	−0.13	−0.12	−0.13	−0.13	−0.03	−0.02
Dealcoholized wines						
pH by glass electrode	3.37	3.36	4.09	3.62	3.07	3.17
pH by quinhydrone	3.40	3.41	4.07	3.64	3.15	3.23
Quinhydrone deviation	+0.03	+0.05	−0.02	+0.02	+0.08	+0.06
Reconstituted wines						
pH by glass electrode	3.67	3.65	4.36	3.93	3.23	3.32
pH by quinhydrone	3.57	3.56	4.18	3.80	3.21	3.29
Quinhydrone deviation	−0.10	−0.09	−0.18	−0.13	−0.02	−0.03

alcoholized wine was then made up to 100 ml. with distilled water, while the other half was made up to 100 ml. with distilled water and ethyl alcohol, so that the final alcohol content of the treated wine was the same as that of the original wine. The pH values of the treated wines were determined by the glass and the quinhydrone electrodes. These values together with those of the original wines and the quinhydrone electrode deviation in each case are shown in Table III.

These results show that:

> The pH values and the quinhydrone electrode deviations for the reconstituted wines agree reasonably well with those found for the original wines except for wine 11. This wine had undergone bacterial spoilage and had a high volatile acidity. The loss of a portion of the volatile acid during evaporation probably accounts for the higher pH value of the reconstituted wine.
>
> The quinhydrone electrode values of several of the dealcoholized wines are slightly higher than the glass electrode values. This is particularly noticeable in wines 13 and 14, the quinhydrone electrode values of which were only slightly below the glass electrode values before treatment. Removal of the alcohol from these wines thus reveals the presence of factors which cause a positive error in the quinhydrone electrode values, an error which in the untreated wine partially or wholly offsets the negative error caused by alcohol.

It is well known that the quinhydrone electrode is subject to errors in the presence of oxidizing or reducing substances which are sufficiently active to change the ratio of quinone to hydroquinone in solution. It seemed likely, therefore, that the high quinhydrone electrode values obtained in some of the dealcoholized wines were due to reduction of quinone to hydroquinone by some constituents of the wines.

EFFECT OF TANNIN, SULFITE, AND ACETALDEHYDE ON GLASS AND QUINHYDRONE ELECTRODES. In order to study the influence on the quinhydrone electrode of some of the reducing substances which occur in wine, tannin, sulfite, and acetaldehyde were added to the aqueous tartrate solution and to a dry white wine in amounts which are comparable with those occurring in wines. The tannin used was Merck's analytical reagent tannic acid, the sulfite was added as potassium metabisulfite, and the acetaldehyde was added as a 10% solution of acetaldehyde. The pH values of the treated wines and buffer solutions were determined with the glass and the quinhydrone electrodes and the results are shown in Table IV.

None of the additions had any significant effect on the glass electrode values, but the tannin and the sulfite affected the quinhydrone electrode values, appreciably both in the tartrate buffer and in the wine, although the effects were less marked in the wine. Moreover, the sulfite caused the quinhydrone electrode potential to drift both in the tartrate buffer and in the wine, while the tannin caused a drift in the tartrate buffer but not in the wine. As can be seen from the table, the drift due to sulfite was different from that due to tannin. The addition of acetaldehyde did not affect the quinhydrone electrode values appreciably either in the tartrate buffer or in the wine.

THE HYDRO-QUINHYDRONE AND QUINO-QUINHYDRONE ELECTRODES. According to Clark (*5*) the effects of side reactions in disturbing the ratio of quinone to hydroquinone in the quinhydrone electrode system can sometimes be eliminated by saturating the test solution with quinone and quinhydrone or with hydroquinone and quinhydrone. It was thought that such systems might give better results in wines than the ordinary quinhydrone electrode system. Values obtained in wines, however, were not found more reliable than those obtained with the regular quinhydrone system.

The figures presented in Table V show the results obtained in the presence of varying amounts of alcohol in the tartrate buffer with the glass, quinhydrone, quino-quinhydrone, and hydro-quinhydrone electrodes. The results obtained with the glass, quinhydrone, and quino-quinhydrone electrodes in several wines are also shown. In order to simplify comparisons, the results obtained with the quinhydrone, quino-quinhydrone, and hydro-quinhydrone electrodes are shown as deviations from the glass electrode values.

Table IV. Effect of Tannin, Sulfite, and Acetaldehyde on pH Values

		pH Values			
		Glass electrode	Quinhydrone Electrode		
Solution	Additions		0.5 min.	5 min.	30 min.
Tartrate buffer (0% alcohol)	None	3.33	3.33	3.33	3.33
	Tannin 1 gram per liter	3.32	3.35	..	3.37
	Tannin 2 grams per liter	3.32	3.36	..	3.40
	$K_2S_2O_5$ 100 p.p.m.	3.33	3.43	3.46	3.40
	$K_2S_2O_5$ 200 p.p.m.	3.32	3.48	3.52	3.46
	$K_2S_2O_5$ 400 p.p.m.	3.32	3.73	3.97	3.61
	CH_3CHO 200 p.p.m.	3.33	3.35	..	3.34
	CH_3CHO 400 p.p.m.	3.33	3.35	..	3.34
Dry white wine (14.5% alcohol)	None	3.32	3.26	..	3.26
	Tannin 2 grams per liter	3.32	3.31	..	3.31
	$K_2S_2O_5$ 200 p.p.m.	3.32	3.27	3.30	3.28
	$K_2S_2O_5$ 400 p.p.m.	3.32	3.51	3.57	3.36
	CH_3CHO 400 p.p.m.	3.32	3.26	..	3.25

As can be seen from the table the error due to alcohol was even greater with the hydro-quinhydrone than with the regular quinhydrone system. On the other hand, the quino-quinhydrone system, although giving pH values showing reasonably good agreement with those obtained by means of the glass electrode in buffers containing alcohol, appeared to be greatly affected by those constituents of wine which cause the quinhydrone electrode to give high values. Thus in wines 12 and 16 for which the quinhydrone electrode values were considerably lower than the glass electrode values, the quino-quinhydrone electrode values agreed well with those of the glass electrode. In wines 13, 14, and 18, for which the quinhydrone electrode values were only slightly lower than the glass electrode values, however, the quino-quinhydrone electrode gave values appreciably higher than those obtained with the glass electrode.

DISCUSSION

The pH values of wines as determined by means of the glass electrode are essentially correct, for the glass electrode is not affected by the concentrations of ethyl alcohol that occur in wines nor by oxidation-reduction systems. On the other hand the quinhydrone electrode, when used in wines, is subject to at least two sources of error.

Table V. Comparison of pH Values

Solution	Alcohol Content % by Vol.	pH, Glass Electrode	pH Values with Different Electrodes Expressed as Deviations from Glass Electrode Values: Quinhydrone	Hydro-quinhydrone	Quino-quinhydrone
Tartrate buffer	None	3.33	0.00[a]	0.00[a]	0.00[a]
	5	3.40	−0.04	−0.10	+0.02
	10	3.47	−0.07	−0.12	+0.02
	15	3.54	−0.11	−0.17	+0.03
	20	3.63	−0.15	−0.17	+0.02
	25	3.73	−0.21	−0.19	0.00
Wine					
11	19	4.29	−0.13	.....	+0.06
12	20	3.94	−0.13	.....	−0.02
13	14	3.21	−0.03	.....	+0.07
14	13	3.32	−0.02	.....	+0.06
15	15	3.31	−0.07	.....	+0.02
16	17.5	3.40	−0.10	.....	+0.01
17	14.5	3.32	−0.06	.....	+0.01
18	15	3.59	−0.03	.....	+0.20

[a] Potentiometer set to give value of pH 3.33 for aqueous tartrate buffer with each electrode system.

Alcohol causes the quinhydrone electrode to register pH values which are too low, possibly because of the greater increase in the solubility of quinone in comparison with that of hydroquinone as the solvent is changed from water to alcohol. Within the range of alcohol concentrations studied in buffer solutions, the deviation of the quinhydrone electrode values from those obtained with the glass electrode appears to bear a linear relationship to the alcohol content of the solution.

Reducing substances such as tannin, sulfites, and probably the coloring matter of red wines cause the quinhydrone electrode to register pH values which are too high, presumably because of the reduction of quinone to hydroquinone.

Because these two sources of error operate in opposite directions, the quinhydrone electrode values for many wines, particularly those of low to moderate alcohol content, are reasonably good approximations of the glass electrode values. In other wines, however, particularly fortified wines, the quinhydrone electrode may give values which are more than 0.15 pH unit too low without showing any appreciable drift in potential. In some light wines, particularly those with a high tannin content and those which have been heavily sulfited, the quinhydrone electrode values may actually be too high. In such wines, however, the drift in potential would probably warn the operator that something was wrong.

Liebmann and Rosenblatt (*13*) concluded that since the only appreciable error to which the quinhydrone electrode was subject in whisky was that due to alcohol, the pH of whisky could be determined equally accurately by either the glass or the quinhydrone electrode, provided that a correction was applied to the quinhydrone electrode values to compensate for the alcohol error. No such simple correction can be applied to the quinhydrone electrode values for wines, however, for in wines the errors are not caused by a single factor and are not constant in amount. For this reason the glass electrode system appears to provide the most satisfactory means of determining the pH values of wines accurately.

SUMMARY

The pH values of wines and buffer solutions containing alcohol have been determined by the glass, quinhydrone, quino-quinhydrone, and hydro-quinhydrone electrodes and the alcohol-containing buffer solutions have been checked with the bubbling hydrogen electrode. Values obtained by the glass electrode were found to be essentially correct.

The effects of the presence of tannin, sulfites, acetaldehyde, and alcohol at various concentrations on the readings of the glass and the quinhydrone electrodes were examined. None of these influenced the glass electrode significantly, but the presence of alcohol causes the quinhydrone electrode to register values which are too low, while tannin and sulfites cause errors in the opposite direction.

In wines the pH values recorded by the quinhydrone electrode are usually lower than the glass electrode values. It was concluded that both types of errors occur in wines, a positive error being caused by the presence of tannin and sulfites and a negative one by alcohol. In a number of samples, correct and near-correct values given by the quinhydrone electrode were shown to be due to a compensation of errors.

Neither the quino-quinhydrone nor the hydro-quinhydrone electrodes give more reliable results in wines than the regular quinhydrone electrode.

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Corrections

In the article on "Iodometric Method for the Assay of Penicillin Preparations" [Alicino, J. F., IND. ENG. CHEM., ANAL. ED., 18, 619 (1946)] errors were made in stating units.

Page 619, second paragraph under Assay of Unknowns, the first line should read: 800 to 1000 units per mg.

Page 620, Table I, the headings of the second and third columns should read: Units per mg. Table II, the heading over the last four columns should be: Units per cc. The second line under Example, below the tables, should read: bioassay 800 units per mg.

In the article on "Determination of Cuprous Chloride" [IND. ENG. CHEM., ANAL. ED., 18, 136 (1946)] under the heading Recommendations on page 137, the second sentence under Ceric Ammonium Sulfate should read: Add 250 ml. of water and 1 drop of ferrous-phenanthroline indicator solution and titrate with 0.1 *N* ceric ammonium sulfate solution (made up in 0.5 *M* sulfuric acid solution).

LEWIS F. HATCH

An omission was made in the article on "Improved Apparatus for Karl Fischer Water Determination" [IND. ENG. CHEM., ANAL. ED., 18, 726 (1946)], in failing to give credit for use of the cathode ray magic eye tube in a titrimeter. The fundamental principles involved in this application were first described by G. F. Smith and V. R. Sullivan in "Electron Beam Sectrometer", G. Frederick Smith Chemical Co., in 1936.

RICHARD KIESELBACH

In the article on "Viscosities of Pure Hydrocarbons" [IND. ENG. CHEM., ANAL. ED., 18, 611 (1946)] an error occurs in Table I. The density of *n*-octane at 20° C. is 0.702 gram per cc.

J. M. GEIST

Iodometric Microtitration for Mustard Gas

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Mustard gas in amounts varying from less than 0.5 to 200 micrograms may be determined accurately by iodometric titration from the reaction of dichloramine T and mustard in organic solvents. Under the conditions outlined this reaction differentiates mustard from derivatives of mustard and is unaffected by substances which can be extracted, with the solvents used, from the biological materials tested (blood and cornea). A modification of this method, utilizing the quantitative catalyzing action of the sulfide on the reduction of dichloramine T in the presence of cyclohexanol, increases the sensitivity twentyfold in the range of 0.2 to 5 micrograms.

THE available methods for determining mustard gas (β,β'-dichloroethyl sulfide) are chiefly nephelometric and have so many other limitations that it has not been possible heretofore to do quantitative work, particularly on residual mustard in biological material. For this purpose, a simple quantitative analytical method has been developed.

The reaction described takes place in organic solvents, thereby eliminating competing hydrolysis which occurs in aqueous solution. It has a high degree of specificity for mustard compared with many mustard derivatives tested, especially when these are extracted from aqueous solutions. The test appears to be sufficiently sensitive to estimate less than 0.5 microgram of mustard with reasonable accuracy.

THE REACTION

The method is based on an oxidation, advantage being taken of the well-known reaction of dichloramine T with mustard. The amount of chlorine available from dichloramine T after a part is used in chlorinating the mustard is determined by adding potassium iodide and acetic acid and titrating the amount of iodine liberated with sodium thiosulfate. The end point is sufficiently sharp to make starch unnecessary. The difference between the amount of sodium thiosulfate required with and without mustard gives a measure of the amount of mustard in the sample. The equation for this reaction cannot be given, since the extent of the reaction of mustard varies with the concentration of dichloramine T and the solvent used to dissolve the mustard. Under the conditions in which the reaction is carried out it would appear that about 10 equivalents of chlorine are utilized per molecule of mustard.

THE SOLVENTS

In order to avoid extra blanks and possible inaccuracies resulting from side reactions of the dichloramine T with the solvents used as carriers for the mustard and the dichloramine T, the stability of dichloramine T in various solvents was determined by iodometrically measuring the amount of chlorine available at various intervals after preparation of the solutions (Table I). The solutions were kept at room temperature and not exposed to direct sunlight.

Table I. Stability of Dichloramine T

Solvent	0.01 *M* $Na_2S_2O_3$ per Ml. of 0.2% DCT Solution Titrated Immediately *Ml.*	0.25 hour *Ml.*	1 hour *Ml.*	4 hours *Ml.*
Purified kerosene (commonly known as insecticide solvent)	3.34	3.33	3.33	3.33
CCl_4, technical	3.34	3.31	3.31	3.32
Cyclohexane (practical Eastman)	3.39	3.38	3.38	3.37
Benzene, c.p.	3.32	3.30	3.28	3.27
$CHCl_3$, U.S.P.	3.33	3.33	3.34	3.33
Xylene, c.p.	3.05	3.01	2.80	2.21
Benzine, c.p.	3.34	3.21	3.18	3.05

Table II. Efficiency of Solvents

(Ml. of 0.01 *M* sodium thiosulfate for 100 micrograms of mustard)

Mustard Solvent	Dichloramine T Solvents Purified kerosene	CCl₄	Benzene	Cyclohexane
Purified kerosene	0.58	0.73	...	0.94
CCl_4	0.80	0.59	...	1.00
Benzene	...	0.58	0.55	0.68
Cyclohexane Practical Eastman Kodak Co.	1.05	1.03	0.69	1.00
Xylene	...	0.46	...	...

From the table it may be seen that an appreciable loss of chlorinating power occurs only in xylene and benzine. Accordingly, dichloramine T was dissolved (0.2%) in carbon tetrachloride, and mustard in concentrations of 50 and 150 micrograms per ml. was dissolved in purified kerosene or in cyclohexane; 1 ml. of the chlorinating solution was added to 1 ml. of the mustard solution, and samples were withdrawn periodically over a 30-minute period for titration. Figure 1 shows that the reaction is essentially complete after 20 minutes. As a result of these experiments the reaction between dichloramine T and mustard was allowed to continue for 20 minutes in all experiments reported below.

Since the amount of mustard is represented by a difference in the amount of sodium thiosulfate required to reduce the iodine liberated by the dichloramine T in the blank and in the sample, it is obviously desirable to keep the amount of dichloramine T present to a minimum. To establish this minimum quantity, the concentration of dichloramine T was next varied from 0.10 to 0.20% and the amount of sodium thiosulfate required per microgram of mustard was determined. It was found that the

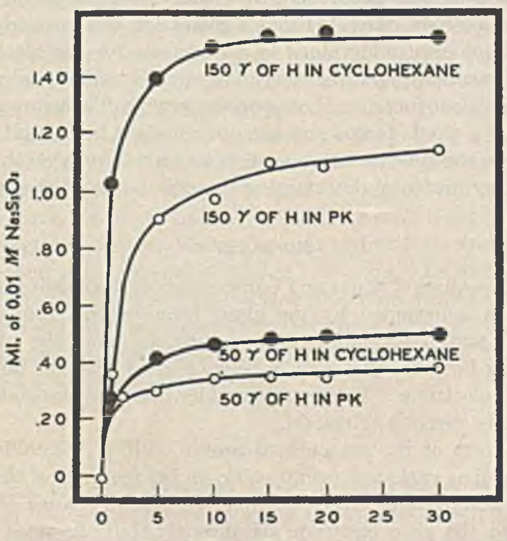

Figure 1. Rate of Reduction of Dichloramine T in Cyclohexane or Purified Kerosene Solution

H, mustard gas. PK, purified kerosene

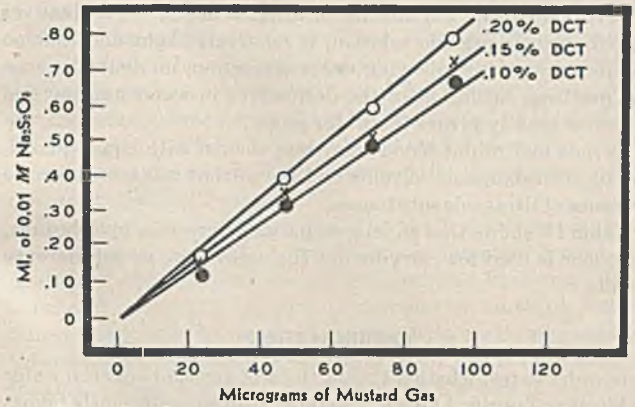

Figure 2. Reaction of Mustard Gas with Dichloramine T

DCT, dichloramine T

degree of chlorination of the mustard increased slightly over this range of concentration of dichloramine T. The results of these experiments are shown in Figure 2.

In order to find which solvent gives the best results—i.e., in which the greatest reaction occurs between the mustard and the dichloramine T—mustard (100 micrograms per ml.) and dichloramine (0.2%) were separately dissolved in different solvents and allowed to react. Table II shows the number of milliliters of 0.01 M sodium thiosulfate equivalent to 100 micrograms of mustard in each combination of solvents used.

The extent of the reaction is seen to be dependent upon the nature of the solvents employed. In every case the presence of cyclohexane appeared to accentuate the reaction. Because of solubility properties, carbon tetrachloride was selected as the best solvent for the dichloramine T and the mustard was dissolved in either cyclohexane or purified kerosene, for comparative purposes.

Analyses made using another lot of cyclohexane (practical, Eastman) gave somewhat different results from those shown in Table II. This suggests the advisability of running standard titration curves on each new lot of solvents or using C.P. grade cyclohexane; the latter gave a reproducible equivalent of 0.67 ml. of 0.01 M sodium thiosulfate per 100 micrograms of mustard and in addition had a negligible temperature coefficient.

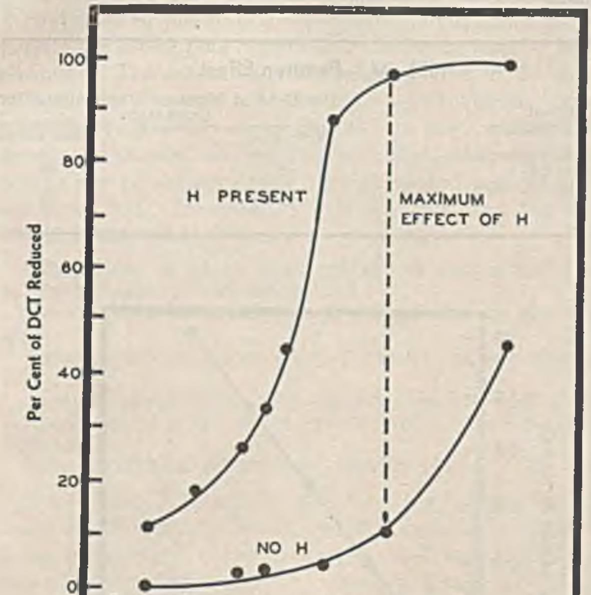

Figure 3. Proportion of Dichloramine T Reduced in 20 Minutes at 26° C. in Cyclohexane or Purified Kerosene Solutions of Varying Content of Cyclohexanol

Alone and with 6.3 micrograms of bis-β-chloroethyl sulfide, H, per ml. present

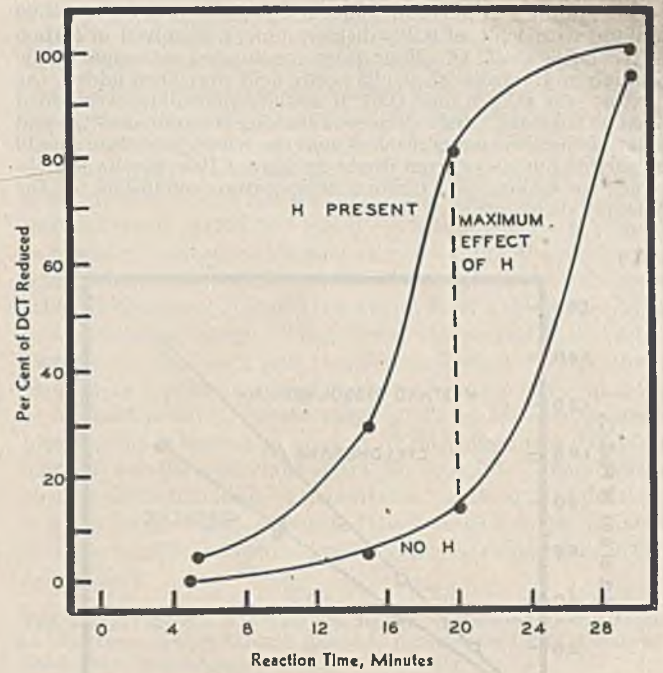

Figure 4. Proportion of Dichloramine T Reduced with Varying Time of Reaction in 1.67% Cyclohexanol Solution at 27° C.

With and without 3.33 micrograms of bis-β-chloroethyl sulfide, H, per ml. present

As a result of a search for an impurity in practical cyclohexane which presumably was responsible for the difference in sensitivity, it was found that the presence of cyclohexanol could produce a manifold increase in the sensitivity of the test. While the amount of the oxidizing agent reduced per unit of the sulfide could be increased about twentyfold, the effect was found to be present only over an extremely narrow concentration range of cyclohexanol in pure cyclohexane or purified kerosene.

The relationship of the extent of reduction of dichloramine T in the presence of mustard to the concentration of cyclohexanol and the time of reaction was investigated. The amount of unreduced dichloramine T in the reaction mixtures was measured by iodometric titration. The proportion of a 0.1% solution of dichloramine T reduced in 20 minutes at 26° by 6.3 micrograms of mustard per ml. with varying concentrations of cyclohexanol present is shown in the upper curve of Figure 3. The lower curve shows the amount of dichloramine T reduced when no mustard is present. It is obvious that for the concentrations of cyclohexanol shown, the presence of mustard increases the reaction. The greatest difference between the amount of dichloramine T used by the blank and the amount used for the given amount of mustard is seen to occur at approximately 1.67% cyclohexanol in the reaction mixture.

The time of reaction of dichloramine T with mustard and cyclohexanol appears to be as critical as the concentration. Figure 4 shows that for 1.67% cyclohexanol the difference between the mustard-sensitized reduction of a 0.067% solution of dichloramine T (upper curve) and the reduction of a control solution without mustard is a maximum at 20 minutes.

PROCEDURE I

Analyses of known quantities of mustard in cyclohexane or purified kerosene were next carried out using the following technique:

One milliliter of mustard solution was allowed to react for 20 minutes with 1 ml. of 0.2% dichloramine T dissolved in carbon tetrachloride at 27° C. Four drops of saturated potassium iodide solution and 4 drops of glacial acetic acid were then added, the mixture was shaken, and 0.01 *M* sodium thiosulfate was added until no color persisted. Vigorous shaking is required as the end point of the titration is reached, and the whole procedure should be carried out away from direct sunlight. Best results are obtained by maintaining uniform temperature conditions for the mustard–dichloramine T reaction.

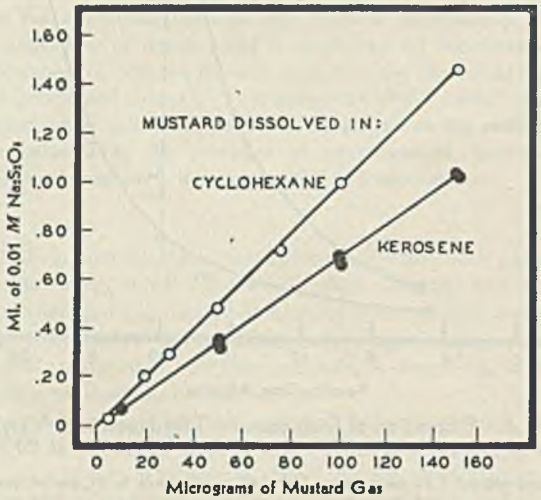

Figure 5. Results of Analyses of Mustard Gas

Concentration 0 to 160 micrograms

Figure 5 shows the results of mustard analyses performed over a range of 0 to 160 micrograms. The top and bottom lines of the figure refer to the results obtained when the mustard was dissolved in cyclohexane or purified kerosene, respectively. All the analyses in which the mustard was dissolved in purified kerosene were run separately by three different people.

Figure 6 shows the analytical results in the range of 0.5 to 4.5 micrograms. The latter quantities of mustard were contained in 0.1 ml. of purified kerosene.

For these analyses the following quantities of reagents were employed: 1 ml. of 0.2% of dichloramine T in carbon tetrachloride, 1 drop of potassium iodide, and 1 drop of glacial acetic acid. The titration was carried out with 0.02 *M* sodium thiosulfate which was contained in a micropipet.

It is clear that the usefulness of an analytical method for determining mustard in the presence of biological materials depends to a large extent upon whether derivatives of mustard or substances extracted from the biological specimens interfere with the test. Accordingly, a series of compounds closely related to mustard was prepared and dissolved in purified kerosene either to saturation, or 1000 micrograms per ml. Analyses were then made of these solutions using the technique previously outlined for determining mustard; the equivalent amount of sodium thiosulfate required is shown in Table III in comparison with that for 150 micrograms of mustard.

Table III. Interference of Derivatives

Derivatives Tested	Concentration Used in Purified Kerosene, γ/ml.	Ml. of 0.01 *M* $Na_2S_2O_3$ per Ml. of Solution	
		Original solution	After extraction with H_2O
$(ClCH_2CH_2)_2S$	150	1.03	1.02
$(ClCH_2CH_2)_2SO$	Saturated solution	0.35	Blank
$(ClCH_2CH_2)_2SO_2$	1000	Blank	Blank
$(HOCH_2CH_2)_2S$	Saturated solution	0.15	Blank
$(HOCH_2CH_2)_2SO$	Saturated solution	0.35	Blank
$(HOCH_2CH_2)_2SO_2$	1000	Blank	Blank

It is evident that the amount of interference of the derivatives tested, even in organic solution, is relatively slight and that no interference occurs following water extraction, no doubt because the partition coefficient of the derivatives in water and purified kerosene greatly favors the water phase.

Cornea and rabbit blood were next shaken with equal quantities of several organic solvents and the solvent was tested for the presence of titratable substances.

Table IV shows that so long as purified kerosene, cyclohexane, or xylene is used for carrying out the extraction, no interference results.

PARTITION EFFECT

In order to test whether the partition of mustard between water or blood and purified kerosene and cyclohexane sufficiently favors the organic solvent to function properly as an extractant, equal quantities of these solvents containing mustard were shaken with water and blood for 15 seconds and the loss of mustard was measured.

From Table V it may be seen that most of the mustard remains with the purified kerosene or cyclohexane when water is used to extract the mustard. When blood is used to make the extraction, cyclohexane retains most of the mustard.

From these studies of possible interfering substances and partition coefficients it is concluded that the method described may be used for making mustard analyses in biological materials.

This test carried out in the manner prescribed determines β,β'-dichloroethyl sulfide and not the first hydrolysis product of mustard, β-hydroxyethyl-β'-chloroethyl sulfide. The latter,

Table IV. Biological Material Blanks

Solvent Used	Material Extracted	Ml. of 0.01 *M* $Na_2S_2O_3$ per Ml. of Solution
Purified kerosene	Cornea	Blank
Purified kerosene	Blood	Blank
Cyclohexane	Blood	Blank
Xylene	Blood	Blank
Benzene	Blood	0.08
CCl_4	Blood	0.03

Table V. Partition Effect

Original Mustard Solution	Per Cent of Mustard Remaining after Extraction	
	With H_2O	With blood
In purified kerosene, 200 γ per ml.	98	88
In cyclohexane, 125 γ per ml.	99	97

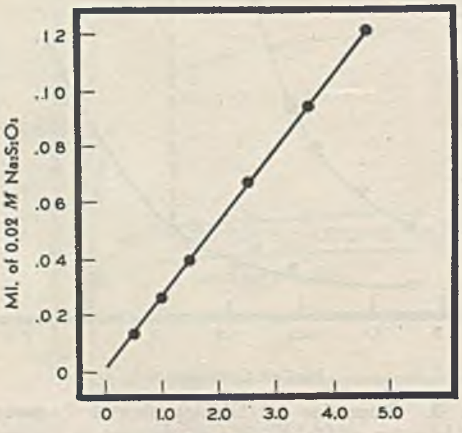

Figure 6. Results of Analyses of Mustard Gas

Concentration 0 to 5 micrograms

it was ascertained from the pure compound, is highly water-soluble and remains in the water phase when purified kerosene is used to extract the mustard; and only a trace of the hydrolysis product is extracted by cyclohexane. Sulfonium salts similarly remain in the water phase and are not determined by this method. (The isolation of β-hydroxyethyl-β'-chloroethyl sulfide and its subsequent synthesis will be described in the *Journal of the American Chemical Society.*)

The reagent with the most desirable physical and solvent properties for performing the extractions was found to consist of a mixture of 80% cyclohexane and 20% purified kerosene. Maximum and essentially complete extraction of mustard was obtained from water by vigorous shaking with an equal volume of this mixture for 20 seconds, and from rabbit blood by 2 minutes' shaking. Application of this method to a study of hydrolysis rates of mustard in water, salt solutions, and blood will be discussed in a subsequent publication in the *Journal of Biological Chemistry.*

PROCEDURE II

For applications necessitating the greatest sensitivity in the range of 0.2 to 5 micrograms of mustard gas the following procedure, which takes advantage of the sensitizing action of cyclohexanol, may be utilized: One milliliter of cyclohexane (Eastman Kodak Co., pure) containing 0 to 5 micrograms of mustard is added to 1 ml. of a 5.00% solution (by volume) of cyclohexanol in purified kerosene (Insecti-Sol insecticide solvent) or pure cyclohexane. The mixture, in a test tube, is placed in a thermostatic water bath. The temperature coefficient of the sensitized reaction was found to be large enough to require careful control of the temperature at which the reaction with dichloramine T takes place. This is best accomplished by means of a thermostatic bath controlled to within at least 0.1° C., preferably in the range of 25° to 28° C. One milliliter of 0.1% dichloramine T in carbon tetrachloride is added and exactly 20 minutes later 4 drops of saturated potassium iodide solution and 4 drops of glacial acetic acid are added with shaking. The iodine liberated by the unreacted dichloramine T is titrated with 0.01 M sodium thiosulfate to a colorless end point. The difference in amount of thiosulfate required by the blank and that required when various known amounts of mustard are present gives a measure of the quantity of mustard present. In the range of 0.2 to 5.0 micrograms of mustard the difference in amount of thiosulfate was 0.2 ml. of 0.01 M solution per microgram of mustard. There was a straight-line relationship of thiosulfate to mustard. In the range of 0.2 to 1.0 microgram of mustard the average absolute deviation from the mean for ten individual titrations was equivalent to 0.03 microgram.

THE work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Harvard University.

A Source of Error in the Gutzeit Method for Arsenic

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By using a constant-area zinc pellet for the generation of gases, slightly modifying the method of sensitizing the absorption strips, and yet maintaining the simplicity of the Gutzeit procedure, the error is reduced.

IN THE microdetermination of arsenic the Gutzeit method continues to maintain its popularity over other procedures despite the rather poor opinion of its accuracy held by analytical chemists. The reason for this popularity lies in the simplicity of both the procedure and the apparatus required. Investigators (*10*, *21*) generally concluded that the requirements of microchemical accuracy are wanting and that relatively consistent results can be achieved only after considerable experience with the procedure. In attempts to reduce the error the principal modifications proposed were:

Substitution of paper disks (*19*, *22*) or cotton threads (*3*, *4*, *15*, *16*) for paper absorption strips.
Use of activators or zinc alloys (*12*, *15*) for the generation of gases.
Temperature control on whole or part of the generator (*11*, *14*, *15*).
Applications of the molybdenum blue reaction (*9*, *17*, *20*, *24*).
Absorption of arsine into a liquid followed by a titration procedure (*8*).
Spot-filtration of arsine under vacuum (*22*).

None of these variations has achieved general acceptance, because they require the use of special apparatus or the procedure is too complicated. The method of Cassil and Wichmann produces a satisfactory degree of accuracy and shortens the time required for an analysis, but special apparatus and a supplementary iodine titration are necessary. The molybdenum blue procedures and the spot-filtration modification are subject to similar limitations, and How in his searching investigation prescribed a set of carefully standardized conditions in addition to special apparatus which might be acceptable to a laboratory where arsenic analysis is a day by day routine, but would not be adopted readily by the analyst who makes an occasional arsenic determination. Furthermore, the evaluation of these variations by collaborative effort (*6*, *7*, *18*, *23*) has not been completed and hence the official method (*1*) still enjoys considerable vogue.

Since the Gutzeit method is empirical, consistent results depend on close adherence to uniformity in reagents, apparatus, and procedure, rigid specifications for which are prescribed by the official method in all particulars save one—the zinc used for generation of gases. Where stick zinc is used the analyst is instructed to sort out the overactive or underactive pieces on the basis of visual observation of the rate of gas evolution during activation, and to equalize the surface area exposed as far as possible. Cassil (*5*) has shown that the principal factors influencing the length and intensity of the stain are the rate of evolution of hydrogen and the method of impregnating the strips. He found that a definite rate of evolution could not be maintained by the use of granular zinc, though the most satisfactory stains were produced with 20-mesh spherical granular zinc. Gross (*13*) obtained a substantially greater recovery of arsenic with stick zinc than with 30-mesh granular zinc under identical conditions.

The present investigation was pursued on the theory that if a zinc pellet could be devised which exposed a constant surface area to the surrounding liquid, a uniform rate of evolution could be maintained and a more constant reproducibility in length and intensity of stain would result. The author devised such a pellet by molding zinc in the form of cylindrical rod of definite cross-sectional area and rendering the cylindrical surface inactive by a coating of wax, leaving the two plane circular ends as generating surfaces.

EXPERIMENTAL

PREPARATION OF PELLETS. For molding zinc cylindrical rods 15 × 125 mm. Pyrex test tubes were employed. Since these vary somewhat, a number having identical inside diameters were selected, and tested with a pair of inside calipers. A tube is clamped on a stand in a vertical position and carefully preheated with a Bunsen burner while a sufficient quantity of arsenic-free zinc is being melted in a Pyrex beaker, then filled with the molten zinc. The tube is tapped to eliminate air pockets and the zinc is to solidify gradually, the flame being played on the upper so that this portion remains in the liquid state longest. This precaution prevents the formation of a hollow core due to contraction as the metal solidifies and results in a solid, uniform cylinder. The zinc is allowed to cool and the cylinder removed by breaking the test tube. With a hack saw the rod is cut into suitable lengths (slightly less than the inside diameter of the generating bottle used), the ends are smoothed on an emery wheel, and the pellet is ready for wax coating.

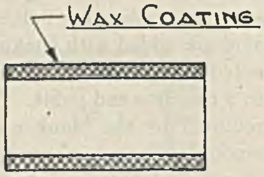

Figure 1. Constant Surface-Area Pellet

A mixture of three parts of paraffin to one of Acrowax C (Glyco Products Company, Brooklyn, N. Y.) was found most satisfactory for coating. Some white pigment such as magnesium carbonate is rubbed into gum arabic paste, and the plane ends of the pellet are coated with this paste, and allowed to dry. One end of the pellet is dipped into a beaker of molten wax, withdrawn, and allowed to harden; then the operation is repeated on the other end, the entire surface being covered with a layer about 0.16 cm. (1/16 inch) thick. A second dipping may be necessary. The plane ends are scraped free of wax and soaked in water to remove the coating of paste. The pellet is activated with stannous chloride solution as directed in the official method and stored under water to which a drop of hydrochloric acid has been added. For greater uniformity the author preferred to activate with stannous chloride–hydrochloric acid (1 + 7) solution rather than that of the official method, since this concentration prevails in the actual arsenic determination. It is advisable to scrape away with a knife the protruding collar of wax exposed by solution of zinc. A pellet 3.75 cm. (1.5 inches) long serves for about 15 determinations before becoming too short for further use (Figure 1).

Sensitization of Paper Strips. The author has adopted a slight variation in the manner of sensitizing the Hanford-Pratt paper strips.

Instead of sensitizing them each time a determination is to be made, a sheet of 32 strips is cut into 9-cm. lengths and kept permanently suspended in the alcoholic mercuric bromide solution stored in a 10-cc. glass-stoppered graduate cylinder in the dark. Strips are withdrawn as required from this reservoir, pressed immediately between sheets of filter paper, and air-dried for 0.5 hour before using. Length of storage time had no influence on results even after several months of storage. In this manner freshly prepared strips are available whenever required. As a matter of economy determinations were made using strips 3 cm. in length, and to accommodate this variation a constriction was blown into the upper absorption tube, and the strip was dropped into the tube to rest on the constriction. Shorter strips have less tendency to curl, thus producing a more uniform stain (Figure 2).

REAGENTS

Standard Arsenic Solution. Dissolve 1 gram of arsenic trioxide in 25 cc. of 20% sodium hydroxide, saturate the solution with carbon dioxide, and dilute to 1 liter with recently boiled water. Dilute 40 cc. of this solution to 1 liter. Make 50 cc. of the diluted solution to 1 liter; 1 cc. contains 0.002 mg. of arsenic trioxide.

Stock Arsenic Solution 1. To 75 cc. of standard arsenic solution add 150 cc. of hydrochloric acid (specific gravity 1.19), cool, and make to volume of 1050 cc.; 35 cc. of this solution contain 0.005 mg. of arsenic trioxide and 5 cc. of hydrochloric acid.

Stock Arsenic Solution 2. To 150 cc. of standard arsenic solution add 150 cc. of hydrochloric acid (specific gravity 1.19), cool, and make to volume of 1050 cc.; 35 cc. of this solution contain 0.010 mg. of arsenic trioxide and 5 cc. of hydrochloric acid.

Stock Solution of Digested Oysters. Digest a quantity of raw shucked oysters with nitric and sulfuric acids, and treat with ammonium oxalate in the usual manner. Dilute to 500 cc. Determine the acid concentration on an aliquot, then add the exact amount of hydrochloric acid necessary, so that on dilution to 1050 cc. a 35-cc. aliquot contains 5 cc. of acid.

Alcoholic Mercuric Bromide Solution. Dissolve 4 grams of mercuric bromide in 95% alcohol, filter, and add alcohol to make 100 cc.

Potassium Iodide Solution. Dissolve 15 grams of potassium iodide in water and dilute to 100 cc.

Stannous Chloride Solution. Dissolve 40 grams of arsenic-free stannous chloride dehydrate in hydrochloric acid and make up to 100 cc. with acid of the same strength.

For the absorption tower use cleaned sand moistened with 10% lead acetate solution.

PROCEDURE

A series of determinations was made on each stock solution in replicates of six, each set of replicates being run on different dates. Using the same pipet for all determinations 35-cc. aliquots were transferred to generating bottles, 5 cc. of potassium iodide solution and 4 drops of stannous chloride solution were added to each, and the mixtures were allowed to stand for 0.5 hour at 25° C. To ensure uniformity in the amount of stannous chloride solution added, a small pipet was set aside and used solely for this purpose. After introduction of activated zinc pellets, which must lie flat to expose the generating surfaces freely, the absorption tubes were connected, the generators were immersed to within 2.5 cm. (1 inch) of the top in a constant-temperature water bath at 25° C., and the evolution was allowed to proceed for 1.5 hours. The paper strips were then removed and stain lengths measured in the usual manner—by drawing sharp pencil lines across the termination of the stain and averaging both sides of the strip. Readings were made to 0.25 mm.

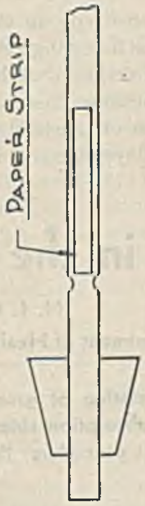

Figure 2. Absorption Tube

DISCUSSION

In the published investigations of the accuracy of the Gutzeit method, Barnes and Murray (*2*), using 30-mesh granulated zinc, reported a probable error ranging from 7 to 100%, covering a concentration range from 40 micrograms of arsenic trioxide down, and Neller, with stick zinc, calculated a probable error of 10% for single determinations. How, using a zinc alloy in stick form, but substituting cotton threads for paper strips and maintaining a very carefully controlled set of conditions, was able to reduce the probable error to 3% for single determinations. The statistical analysis given in Table I presents figures arrived at

Table I. Microdetermination of Arsenic

Trial No.	Length of Stain, Mm. Pellet 1	2	3	4	5	6
			10 Micrograms of As_2O_3			
1	7.0	7.5	7.3	7.8	6.5	7.4
2	7.5	7.6	7.8	8.0	7.4	7.9
3	6.5	7.1	7.1	7.1	7.3	7.1
4	7.4	7.5	7.4	7.6	7.1	7.5
5	7.1	7.4	7.1	7.5	7.6	7.3
Mean = 7.3 Standard deviation = 0.35 Coefficient of variation = 4.7 with standard error of 0.61						
			5 Micrograms of As_2O_3			
1	4.5	4.5	5.0	4.5	5.3	5.6
2	4.6	4.9	5.0	5.1	5.2	4.9
3	5.5	5.2	4.9	5.5	5.1	5.2
4	5.4	5.5	6.0	6.0	5.0	5.0
5	5.0	4.9	4.5	5.9	5.0	5.0
6	4.4	4.5	4.8	4.9	5.0	5.0
Mean = 5.1 Standard deviation = 0.42 Coefficient of variation = 8.2 with standard error of 0.97						
			Digested Oyster Solution			
1	11.3	12.3	11.5	11.4	11.5	10.5
2	10.3	10.8	12.8	10.1	10.5	11.1
3	9.9	10.6	11.4	9.6	9.8	10.1
4	11.0	9.8	11.8	11.8	10.8	10.3
Mean = 10.9 Standard deviation = 0.84 Coefficient of variation = 7.7 with standard error of 1.12						
			Replicates on Diluted Oyster Solution			
5	5.6	4.8	5.4	5.1	5.3	5.5

by employing the more modern concepts prevailing today and is expressed in terms somewhat different from those given above; hence comparison cannot be made at a glance. However, the same statistical method applied to How's results with 10 micrograms of arsenic gives figures which fail to show any significant difference in accuracy compared to those in Table I for the same concentration. Heretofore no attempt has been made at accurate control of either the area of metal exposed to the reaction liquid or the uniformity of activation of the surface. That both these factors have an important influence on the accuracy of the method has been recognized but no means of controlling them has been suggested. The official method directs the analyst to vary the amount of zinc according to the activity of the particular batch used and recommends equalization in so far as possible of the surface area exposed. Left to the judgment of the operator merely on the basis of visual observation, these variables may result in error.

During the course of a determination there is a progressive plating out of metallic tin on the zinc surface, most of which forms a gas-filled sponge which eventually breaks away and floats to the surface of the liquid. The zinc surface retains a thin black coating of amorphous tin uniform in appearance, which does not wash away when a stream of water is played upon it, nor when the pellet is stored under water until again required. The uniformity of this tin plating is an important factor influencing the rate of gas evolution. Measurements showed that the evolution proceeds at a uniform rate and there is no necessity of sorting pellets according to apparent activity. Furthermore, the pellets wear down evenly without pitting or variation in form of the plane surfaces. In the experimental work the six pellets were identified by number, each vertical column of results in Table I having been obtained using the same pellet. No difference in activity of the pellets is discernible. The reduction in error shown in the tabulated results may fairly be ascribed to a control of these variables. It seems likely that a combination of the uniform area pellet and the use of sensitized cotton threads instead of paper strips in the manner described by Cahill and Walters would produce more accurate results in the lower range of 1 microgram of arsenic trioxide. Until a more satisfactory method is developed and generally accepted, approximating the Gutzeit procedure in simplicity, the latter need not be relegated to the limbo of outworn and discarded analytical methods.

SUMMARY

More accurate control of the surface and activation of the zinc pellet in the Gutzeit determination bring about a reduction in error. An improved pellet has been devised which exposes a constant surface area to the surrounding liquid, assuring a more uniform rate of evolution of gases. The pellet serves for a considerable number of successive determinations, and is economical. A more convenient and accurate way of sensitizing and using the paper absorption strips is proposed. These improvements are accomplished without sacrificing the simplicity of the Gutzeit method.

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Volumetric Determination of Water in Paints and Varnishes

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Water can be determined quantitatively in paints and varnishes by a volumetric method with greater accuracy, with small samples, and in less time than by the usual methods.

STANDARD methods of determining water in paints are known to be limited in accuracy and results are reproducible to 0.1% only with difficulty even if 100 grams of sample are used. Whether the determination is made by distillation or by refluxing over Dean and Stark tubes, the water collected is estimated in graduated tubes and suitable apparatus must be erected to test each sample. Time consumed will exceed an hour per sample tested and the amount of water collected is merely estimated. Toluene, xylene, or tetrachloroethylene used for separation of the water prevent wetting of the glass condenser, so that an unestimated quantity of water is always retained and not collected in the graduated part of the apparatus.

The water content of paints and varnishes can be determined accurately and quickly by a simple and efficient technique, employing a specific titrimetric method that involves the use of Karl Fischer reagent (*4*). Results are reproducible to 0.01%.

Karl Fischer reagent for rapid direct determination of water has been successfully applied to oils (*6*), fats (*8*), and waxes (*11*); hydrated salts (*9*); glue, plasticizers, and alcohols (*2*); pulp, paper, cotton, and cellulose (*7*); dry foods (*5*); and liquid petroleum fractions (*1*). With several modifications it can be applied to water analysis of paints and varnishes. The titration assembly is similar to that described by Almy, Griffin, and Wilcox (*2*).

ANALYTICAL PROCEDURE

All apparatus used must be carefully dried. From 10 to 20 grams of paint or varnish are weighed into a 250-ml. glass-stoppered flask. Anhydrous pyridine is added from a buret, the amount varying according to viscosity of sample; 10 ml. may suffice for thinned samples and up to 25 ml. for unthinned samples. The mixture is then swirled thoroughly and 25 to 50 ml. of Karl Fischer reagent are added without delay. The flask is stoppered and placed in an anhydrous glycol bath at 50° C. for 45 minutes. The stopper is loosened once to release pressure, then replaced tightly, and the flask is swirled at 10-minute intervals throughout the warming period. The flask is allowed to cool and contents are titrated electrically by adding pyridine containing 0.1% water.

The titration apparatus consists of a plastic plug equipped with stirrer and tungsten-platinum electrode connected to a Beckman pH meter (model G). Standardization of reagents will complete the operation.

Pyridine (0.1% water), used in back-titrating the unreacted Karl Fischer reagent, may also be used in place of anhydrous pyridine for diluting purposes, and its water content deducted in the calculations. Although anhydrous pyridine is recommended, its possible contamination with water must be checked by the reagent. Anhydrous C.P. pyridine was obtained from J. T. Baker Company, Phillipsburg, N. J., and Karl Fischer reagent was obtained, ready for mixing, from Eimer & Amend, New York.

ACCURACY OF METHOD

Recovery of known quantities of water added to anhydrous paints and varnishes was used to check accuracy. Varnishes and paints found to have no water content or very low known water content were used as a basis and a weighed quantity of 1% solution of water in pyridine was added. Uniformity of solution was obtained by warming at 50° C. for 45 minutes and allowing to cool. Water was then determined on the mixture.

Paint (Anhydrous)	Pyridine (1.16% Water)	Mixture Taken	Water Present	Water Recovered
Grams	*Grams*	*Grams*	%	%
46.1329	10.4001	6.9320	0.2133	0.216
37.9891	13.3605	8.014	0.2419	0.2401
56.4309	30.6477	12.4703	0.509	0.511

A similar procedure was used to compare the method with the present azeotropic distillation method (*3*). An anhydrous alkyd resin of medium oil length was used, 1% water-in-pyridine was added, and aliquot portions were used for each analysis.

Sample Weight				
Distillation Method	Volumetric Method	Water Present	Water Distillation	Recovered Volumetric
Grams	*Grams*	%	%	%
89.7960	7.4141	1.6477	1.448	1.651
114.3766	4.8950	0.8175	0.699	0.822
97.4304	6.0911	0.4394	0.308	0.435

APPLICABILITY AND INTERFERING SUBSTANCES

Many paint specifications do not specify water tolerances. The volumetric method described has been applied to many types of paints, enamels, and resins, including a number for which water analysis is not required. Resins which in isolated form are known to be insoluble in pyridine are completely compatible when previously dissolved in other solvents. Viscosity of the samples tested varied widely. Dry powdered pigments were checked for interference. Zinc oxide was the only constituent of enamels found to interfere. The presence of zinc oxide did not have to be predetermined, however, since its interference was shown by the behavior of the electrical titration apparatus, in that no state of balance could be obtained and the addition of either Karl Fischer reagent or standard water solution had an unexpected effect on the indicating needle. Thus its presence can be detected by one experienced in handling the titration. However, no paint specifications requiring water analysis have been encountered which also specify zinc oxide pigments, with the exception of Specification T-1715A (*10*), Type I. In the presence of zinc oxide, the A.S.T.M. method for determining water in petroleum products may be used.

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NOTES ON ANALYTICAL PROCEDURES

Precise Low-Pressure Measurements with a Thermocouple Gage

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PRESSURE gages which depend on thermal conductivity (Pirani and thermocouple gages) have been used chiefly for leak-hunting and other rough measurements in the range 0.001 to 0.1 mm. Usually they are operated at either constant current or constant voltage, and in these cases the upper limit of the sensitive range is due not to the thermal conductivity's becoming constant, but rather to the temperature gradient's becoming too small to be measured. The range can be extended considerably by operating at constant temperature (constant resistance on the Pirani gage, constant output on the thermocouple gage). By this means and by using very small dimensions (1-mm. radius), Rittner (*3*) was able to make a Pirani gage sensitive up to 15 mm.

There seems to be no reason, in principle, why these gages should not be used for precise as well as rough measurements. This would be desirable, especially for measurements on condensable vapors where the McLeod gage cannot be used, and also whenever the presence of mercury is undesirable. With the usual setup, the precision is limited by the electrical instruments used. The author has found that when a commercial thermocouple gage is used with sufficiently accurate electrical instruments, and with the addition of a constant-temperature jacket, the precision in the sensitive range is limited only by the pressure measurements used for calibration.

The gage used was a General Electric Type J-1 vacuum gage. It is intended to be used with a constant heater current of 30 ma. and a low-resistance microammeter. Under these conditions, the pressure can be read, at best, to ±4% (at 0.015 mm.); and at 0.1 mm. the sensitivity practically disappears. In these experiments, both the thermal e.m.f. and the heater current were read with a Leeds & Northrup Type 8662 portable potentiometer, the heater current being determined from the voltage drop across a 0.1-ohm precision resistor. In order to permit rapid alternate checks of both quantities, the cold-junction compensating slidewire of the Type 8662 was used as an auxiliary (fixed) potentiometer to compare with the thermal e.m.f. The heater current was adjusted to give a constant thermal e.m.f. of 3.050 mv, (this value is checked occasionally with the main potentiometer. the compensating slidewire being used only as a source of constant e.m.f.); the necessary heater current, which is the measure of pressure, varies from 27 ma. (below 0.001 mm.) to 150 ma. (above 20 mm.). The power supply was a single lead storage cell, with a rheostat consisting of a 100-ohm and a 500-ohm variable resistor in parallel, to give coarse and fine control over a wide range.

To determine the sensitivity, measurements were made on dry air against a McLeod gage and a U-tube mercury manometer which was read with a cathetometer to ±0.01 mm. The sensitivity may be expressed as the change in heater current for a 1% change in pressure. This was determined by graphical differentiation. When the sensitivity is plotted against the logarithm of the pressure, it falls off symmetrically from a maximum of 0.31 ma. at 0.2 mm., reaching 0.10 ma. at 0.02 and 2 mm., and 0.01 ma. at 0.002 and 20 mm.

In any one run the current could be determined to ±0.01 ma. This means that the gage is sensitive to a 1% change in pressure from 0.002 to 20 mm., while from 0.02 to 2 mm. it is sensitive to 0.1% or less. From one run to another, however, readings varied by as much as 3 ma. This was attributed to external temperature changes. By attaching a thermocouple to the outside of the gage, it was found that a change of 1° C. in its surface temperature changed the reading about 1 ma. The gage was therefore enclosed in a metal jacket, through which was circulated constant-temperature water. Although the surface temperature was slightly dependent on pressure, it was constant within 0.01° C. at any one pressure.

The major objection to any thermal pressure gage is the curved characteristic which necessitates extensive calibration against some standard. The McLeod gage is not accurate enough to utilize the full sensitivity of the thermocouple gage. Since it appears that a principal use of the gage as a precise instrument would be in measuring the pressure of water vapor above hydrates, a convenient standard is the vapor pressure of ice, which is known (*2*) to ±0.2%. Although a complete calibration curve has not been made, enough points have been measured to show that this is feasible.

The ice was contained in a tube lagged by an oil jacket and immersed in an alcohol bath whose temperature was controlled by a resistance-thermometer type of regulator, operating a pump which circulated alcohol from a dry-ice bath. The temperature in the tube, measured by a three-junction copper-constantan thermopile, was thus kept constant to ±0.02° C., which determines the pressure within 0.2%, the precision of the published data. As much as 1 hour may be required to reach equilibrium. The fluctuations in the gage reading are slightly larger than with air, about 0.02 ma. This may be due to thermal fluctuations, which might be expected to amount to as much as 0.06 ma. in the most sensitive region, but are largely smoothed out by the slow response.

The following readings, made in succession, show the reproducibility of the results whether equilibrium is approached from above or below:

Temperature, ° C.	Pressure, Mm.	Current, Ma.
−45.73	0.0497	60.98 ± 0.01
−36.69	0.1399	86.42 ± 0.02
−23.94	0.529	115.11 ± 0.02
−36.69	0.1399	86.42 ± 0.02

There seems to be no reason why a Pirani gage operated at constant temperature and with sufficiently accurate electrical instruments should not be as precise as the thermocouple gage. However, a metal filament should be used. The author has found that carbon filament bulbs, recommended by De Vries (*1*), are excessively difficult to outgas. Although such a gage is sensitive to ±0.1% in the range 0.1 to 0.5 mm., duplicate runs on water vapor agreed only to 1%, no doubt because of residual air.

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Determination of Gold with Ascorbic Acid

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ASCORBIC acid or vitamin C was isolated by Szent-Gyorgyi (*4*) and its synthesis was later effected by Reichstein (*2*) and Haworth and co-workers (*1*). Haworth and Hirst assigned the accepted structural formula which includes the endiol group. The reducing property of this group is shown in the reduction of gold chloride as represented by the following equation:

$$2AuCl_3 + 3C_6H_8O_6 \longrightarrow 2Au + 3C_6H_6O_6 + 6HCl$$

The detailed investigation of this reaction in the authors' laboratory (*3*) proved that ascorbic acid could be used for the quantitative determination of gold. The present report describes the procedure recommended.

REAGENTS USED. Hydrochloric acid, density 1.19. Ascorbic acid, strength, 4 grams per 100 ml. of solution. Gold solutions, prepared from pure gold as determined by sulfur dioxide method.

PROCEDURE. Dissolve 0.3 gram or less of gold in aqua regia and remove the nitric acid, nitrites, etc., by three evaporations with hydrochloric acid. Dissolve the residue in 3 to 5 ml. of concentrated hydrochloric acid and dilute to 20 ml. with water. Heat the solution to 80° to 90° C., add 10 ml. of the freshly prepared ascorbic acid reagent, and continue the heating for 5 minutes. After cooling to room temperature, filter the precipitate by a porcelain filter crucible, wash with hydrochloric acid solution, 1 to 99, and ignite.

The results are included in Table I. The influence of copper was investigated and the results in Table I prove that there is no interference.

Table I. Determination of Gold

Gold Added *Gram*	Copper Added *Gram*	Gold Found *Gram*	Method
0.2060	...	0.2061	Gravimetric
0.1585	...	0.1586	
0.0969	...	0.0968	
0.0152	...	0.0152	
0.2030	0.1080	0.2032	
0.1215	0.1208	0.1217	
0.0949	0.1930	0.0948	
0.0578	0.0281	0.0580	
0.1403	...	0.1401	Volumetric
0.1051	...	0.1050	
0.0947	...	0.0949	
0.0653	...	0.0653	

VOLUMETRIC DETERMINATION

Gold may be determined volumetrically with ascorbic acid by adding excess reagent to the cold solution of gold and subsequently titrating the excess with iodine. The reaction of ascorbic acid and iodine is described by the following equation:

$$C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2HI$$

PROCEDURE. Free the gold solution from oxidizing reagents, add 2 to 5 ml. of hydrochloric acid reagent, and dilute with water to 20 ml. Add 10 ml. of ascorbic acid solution with constant stirring for 5 minutes, then 2 ml. of starch solution, and titrate with 0.1 *N* iodine solution. Blank determinations are required. Some of the results obtained are recorded in Table I.

CONCLUSION

Gold may be determined with excellent accuracy by reduction of gold chloride with ascorbic acid. Copper does not interfere. Gold can also be determined volumetrically with ascorbic acid.

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Preparation of Standard Powders for Reference in Particle-Size Measurement

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IN TESTING new methods and techniques of particle-size measurement and in checking the performance of individual units of apparatus for such measurement, it is often desirable to have one or more standard powders as reference samples. The ideal standard must be composed of particles that possess such a degree of uniformity of size and regularity of shape as to facilitate calibration by microscopic measurement.

The difficulty of obtaining such samples economically and in generous quantity has been a handicap; usually each laboratory has had to make its own. Apparatus and procedures for making microscopic spheres of glass have been described, for example, by Sklarew (*2*), Sollner (*3*), and Bloomquist and Clark (*1*). The steps involved constitute a complete manufacturing process, from massive glass starting material (such as bottles or other macroscopic objects) to finished and classified particles.

It has been found in this laboratory that two types of uniform-particle powders can be prepared from inexpensive commercially available materials, by a small amount of processing with common laboratory equipment.

The first type is spherical, and the coarser of the two. The glass beads used first for coating projection screens, and later also in place of sand for hour glasses, contain a considerable percentage of material, easily separated by sieves, that is close to 100 microns in diameter. A sample investigated (obtained from Seed Filter Co., 47 East Merrick Road, Freeport, N. Y.) was almost entirely (99 to 100%) between the 210- and 74-micron sieves by dry test. The fraction between the 125- and 105-micron sieves (U. S. Nos. 120 and 140, respectively) constituted approximately 13% of the original sample. Most of the particles are accurately spherical, as shown by microscopic examination on a slide coated with grease to prevent rolling and selective orientation.

The few nonspherical particles—irregular fragments, dumbbell forms made by spherical twins, etc.—are removable by either of two treatments. In one method, similar to that used by Sullivan and Hertel (*4*), the spheres are rolled down a vibrating plane inclined slightly to the horizontal, the nonspherical particles being sorted out through their tendency to stall on the slope. More than one traversal of the plane may be necessary. A quicker method, and one that is thorough enough for the purpose, is to pass the spheres through a slightly oversize sieve with little or no agitation of the sieve. In this way a satisfactory refinement of the U. S. Nos. 120-140 fraction was effected with the No. 100 screen.

The second type of powder is rod-shaped, and finer than the first. It is made by pulverizing glass wool. A popular grade of laboratory wool is highly uniform, with a cross-section diameter around 8 microns. This wool can be ground in a laboratory hammer mill, if the skeins are first chopped into short pieces with shears or a print trimmer. A single run through the mill is likely to give insufficient grinding, but quick microscopic inspections, one after each run, will show when to stop grinding. Pebble-mill grinding was tried also, but without success; the wool was always either too little affected or broken into too short fragments. The hammer-mill process, on the other hand, gave a satisfactory range of particle lengths, mainly between 30 and 500 microns.

The range of lengths need not be very narrow, for two reasons: (1) In calculation of the average diameter, either of a single particle or of a collection of particles, if the highly important and much used surface mean is the average that is sought, the average is less affected by variation in the length than by variation in either of the other dimensions of the needle. (With uniform cross-section diameter and variable length, the surface-mean diameter is always between 1 and $1^1/_2$ times the cross-section diameter.) (2) Whatever type of average is desired, it is only in the cross-section diameter that a high degree of uniformity is really necessary, for the length is the dimension most easily and accurately measurable with the microscope.

The hammer-mill product is likely to be discolored somewhat if the interior parts of the mill are of the usual iron alloys, but the color, if objectionable, may be removed by washing with dilute hydrochloric acid.

Final calibration of the sample, in either type of powder, is done with a microscope. In the examples given, the acicular powder will have a surface mean particle diameter around 11 microns; the spherical powder about ten times this value, or 110 microns. The former value is a suitable magnitude for direct reading in air-permeation instruments commonly used for testing of subsieve powders. The coarser powder can be used in the same instruments if provision exists for loading several times the normal amount of sample into the regular sample cell, in order to bring the resistance of the powder column within the range normally encountered with subsieve materials.

The material costs are approximately the following: For the spherical powder, $1 per pound of original beads; if only the cited fraction is utilized, $8 per pound of finished standard powder. For the acicular powder, $3 per pound. It is estimated that a laboratory technician could prepare a pound of either finished powder in 1 to 2 days.

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BOOK REVIEW

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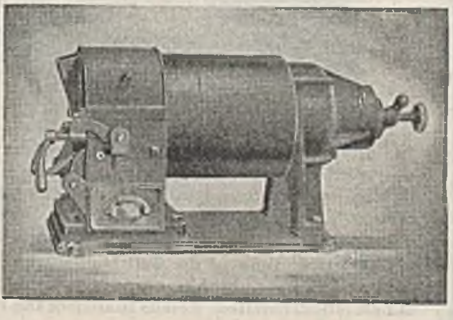

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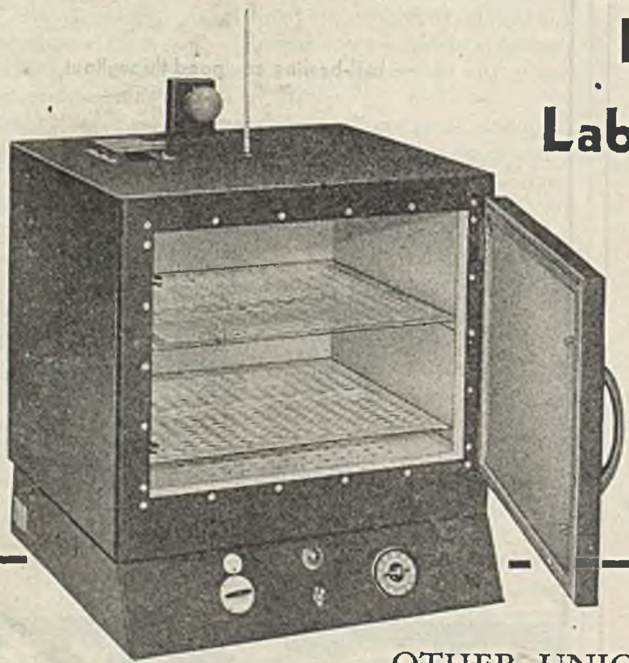

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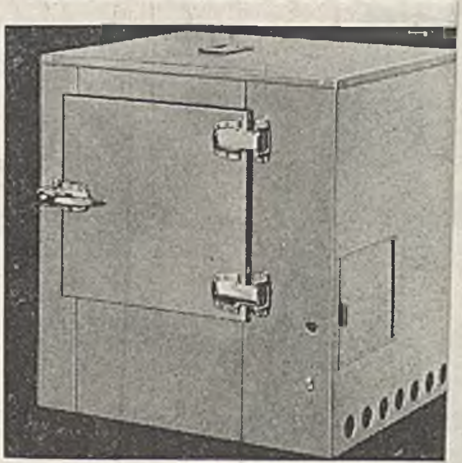

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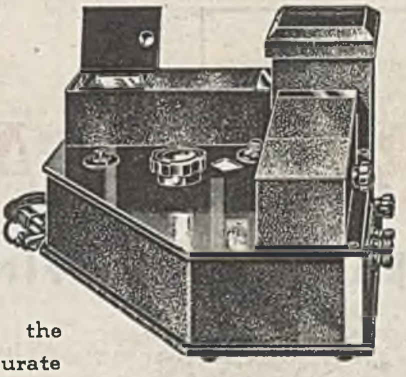

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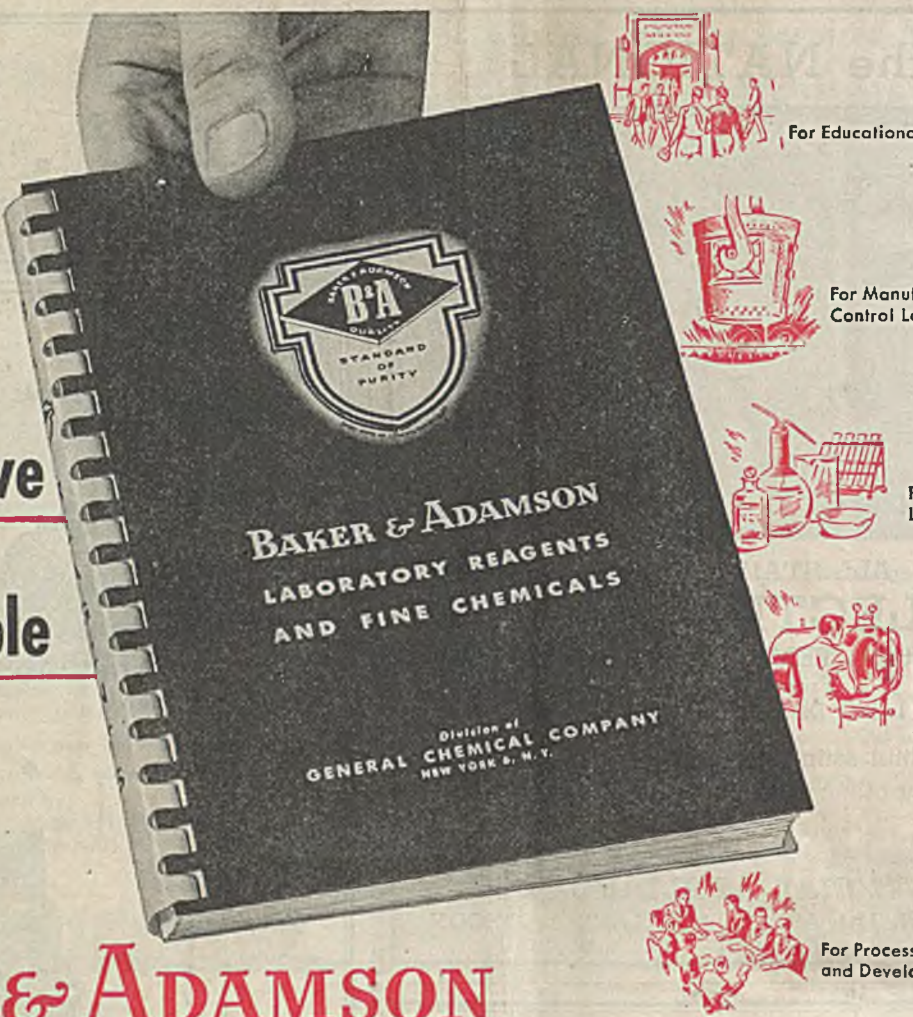

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